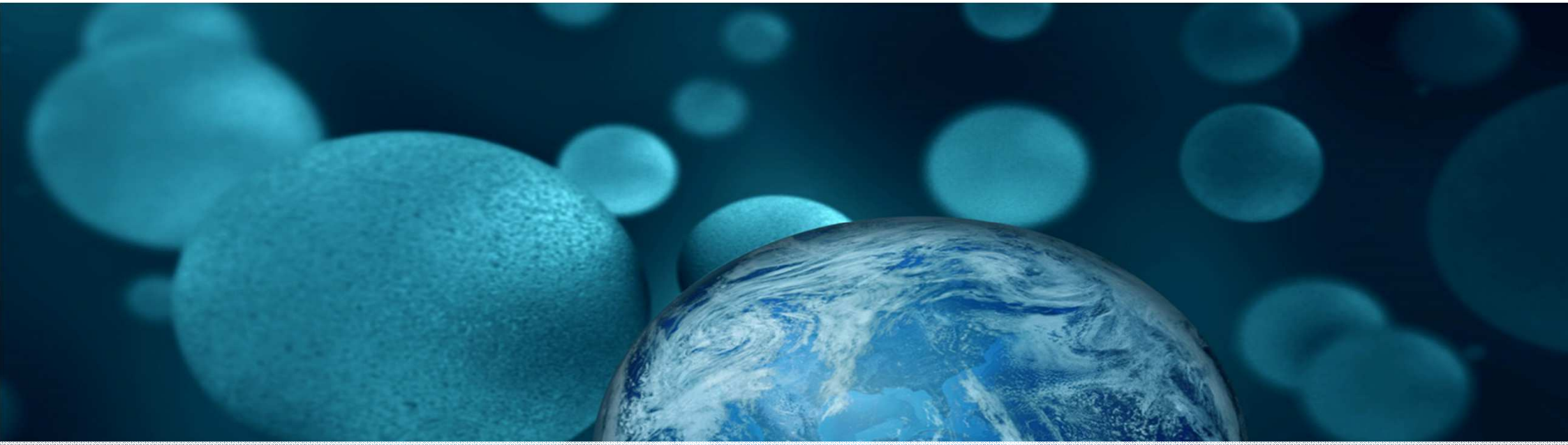

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XPS at Thermo Fisher Scientific, an Introduction

Richard White
Sales & Marketing Director

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The Widest Range of Analytical Methods to Drive Deeper Materials Insights

Electron Microscopy	XPS	EDS	Raman	FTIR	XRF	XRD	Rheometry	UV-Vis
Multi-scale imaging & analysis of various materials	Surface analysis quantitative chemical state	Elemental imaging at high spatial resolution	Chemical compound identification Identification of both organic and inorganic materials	Chemical compound identification Identification of organic materials in bulk state	Bulk state elemental composition	Structural crystallinity and composition	Characterization of fluid properties and other complex materials	Quantitative measurement of reflection or transmission properties of a material

We deliver a full spectrum of analytical tools that enable customers to accelerate innovation and enhance productivity

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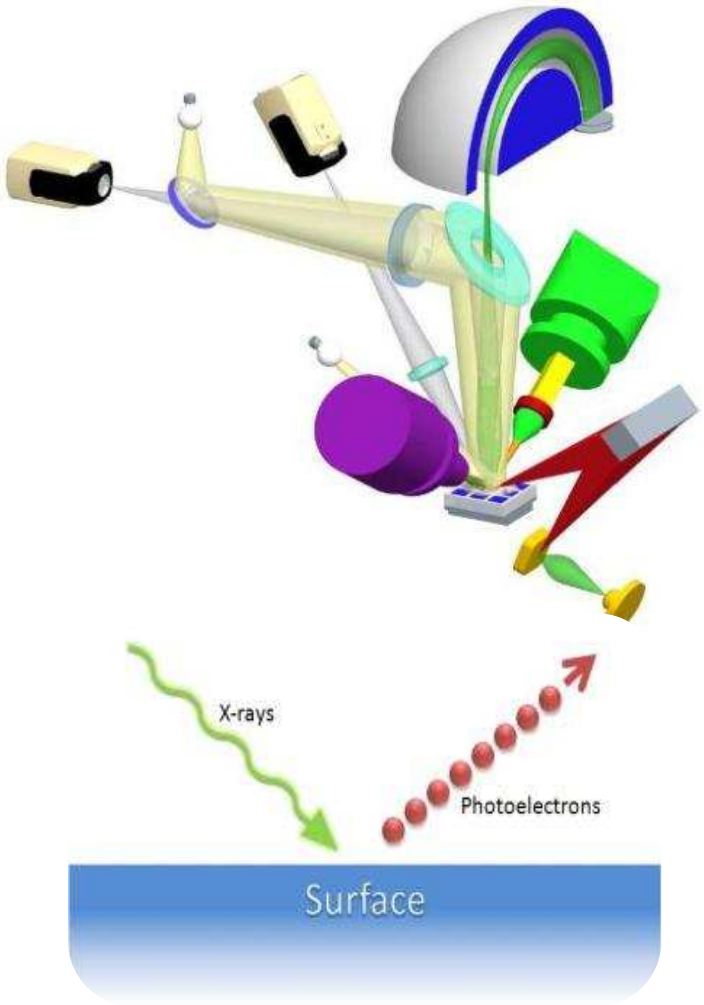
Agenda



- Who uses XPS
- What do we call “The Surface”
- The basic theory
- What’s in the spectrometer
- What type of information does it create
- What’s it good at, and what’s it not good at!
- Typical Applications
- The other complimentary techniques
- XPS & Raman for 2D materials

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XPS The basic facts

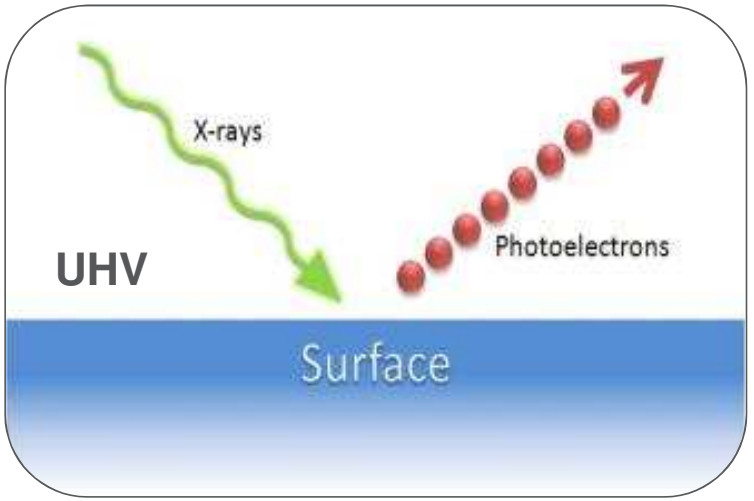
- **Sampling depth 5-10 nm from the top surface.**
- **Elemental quantification for Li and above.**
- **Quantitative chemical information.**
- **Detection limits ~ 0.1 At.%.**

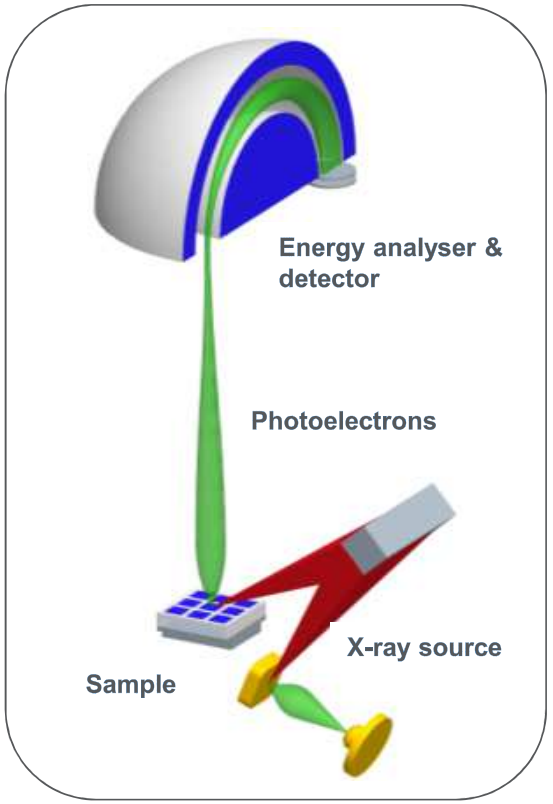
The sample is illuminated with X-rays causing the emission of photoelectrons from the surface atoms.

The photoelectron kinetic energy depends on the element, and chemical state of the atom

X-ray photoelectron spectra reveal what is in the top ~10 nm of the sample, and how much of each component is there.

Thicker layers can be analysed by removing material with an ion beam and analysing the remaining surface.





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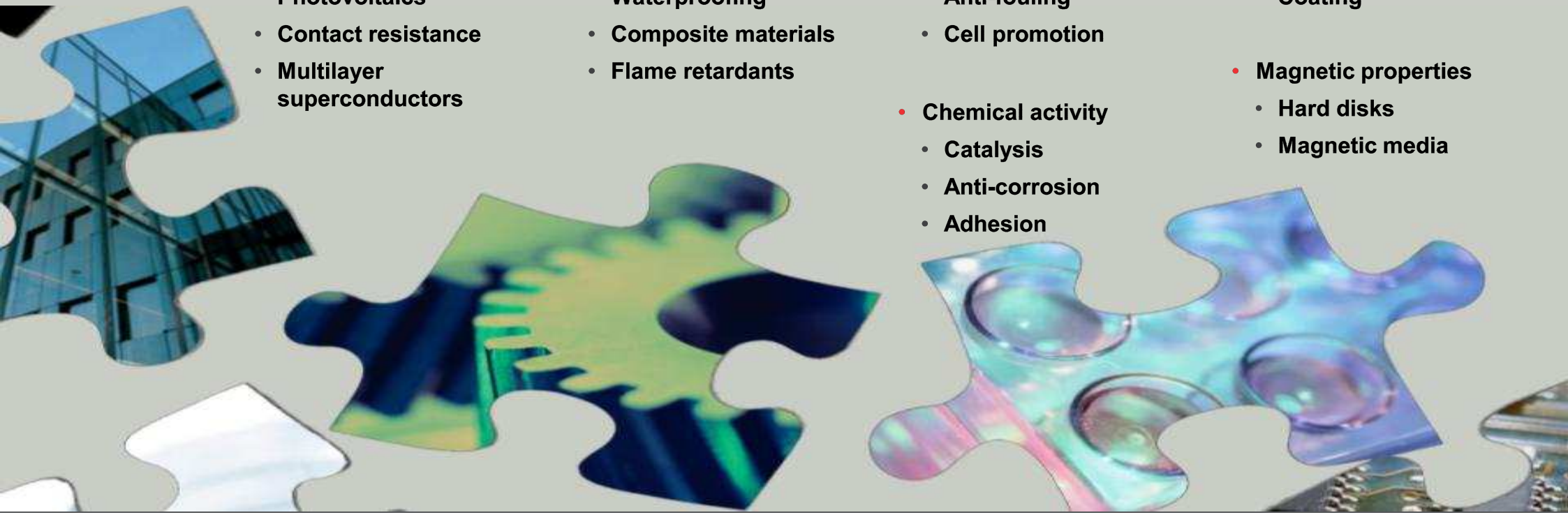
Why are we interested in the surface?

- **The surface of a solid is the point where it interacts with its environment.**
- **Electronic, chemical and physical properties can all depend on the first few atomic layers of the material.**

- **Electrical properties**
  - Transistor gates
  - Memory
  - Photovoltaics
  - Contact resistance
  - Multilayer superconductors
- **Physical interactions**
  - Non-stick
  - Scratch resistance
  - Waterproofing
  - Composite materials
  - Flame retardants
- **Biological**
  - Implant acceptance
  - Anti-bacterial
  - Anti-fouling
  - Cell promotion
- **Chemical activity**
  - Catalysis
  - Anti-corrosion
  - Adhesion
- **Appearance**
  - Light transmittance
  - Painting
  - Coating
- **Magnetic properties**
  - Hard disks
  - Magnetic media



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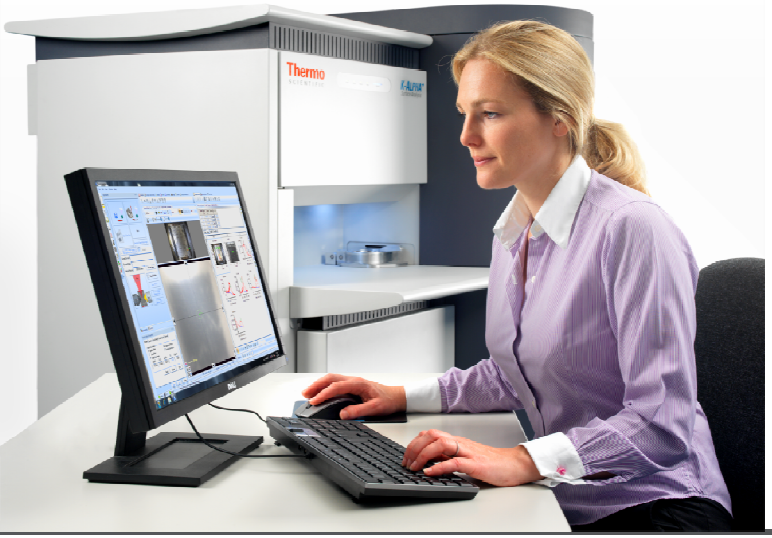
XPS: Chemical identification of solid materials

Metals | Oxides | Powders | Glass | Plastics | Polymers

Carbon | Ceramics | Bio-materials | Fibres | Nano-materials

New Material Development → Product development → Quality Control → Production support



- Quantitative chemical composition
- Characterisation of unknown materials
- Contaminant identification
- Classification of defects and stains
- Coatings: thickness and conformity
- Optimization of material treatments
- Depth composition for layered materials
- Understanding interface chemistry

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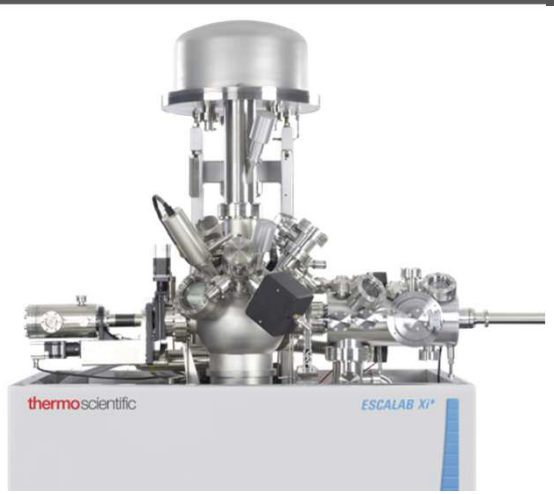
Thermo Scientific Surface Analysis product family

K-Alpha

- Entry-level system
- Routine XPS
- Large-scale imaging
- Depth profiling

Nexsa

- Performance XPS
- Multi-technique
- SnapMap Imaging
- Depth profiling
- Cluster ion source
- Raman integration



ESCALAB Xi+

- High resolution XPS
- Sample preparation
- Design flexibility
- Imaging
- Depth profiling
- Cluster ion source

The biggest selling range of XPS instruments on the market

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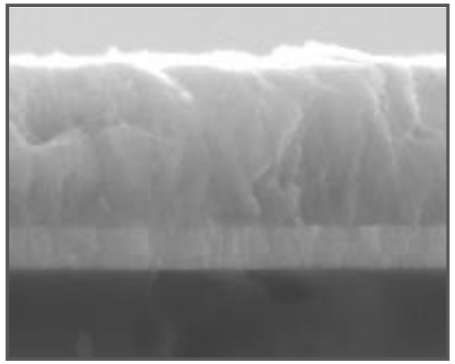
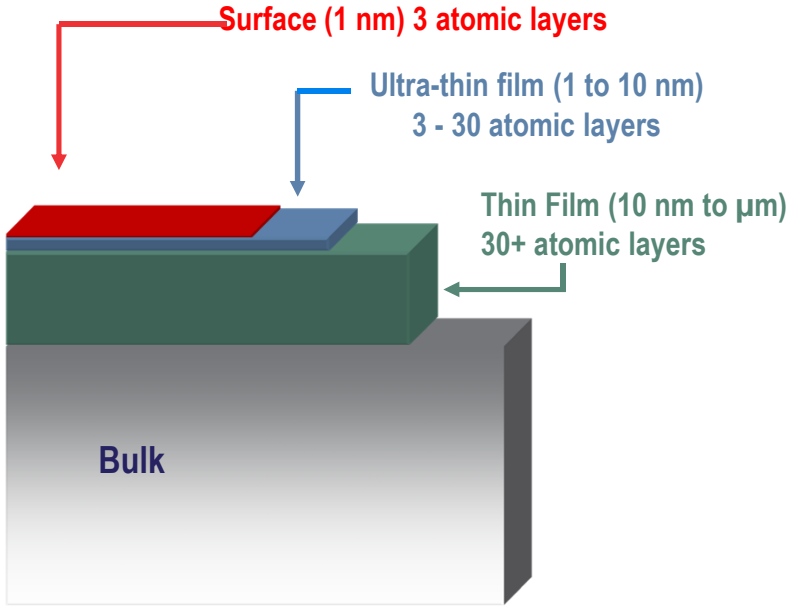
Definition of a surface



- XPS surface analysis
  - What is a surface?
    - XPS measures
      - Surfaces using XPS and angle resolved XPS
      - Ultra-thin films using XPS and angle resolved XPS (ARXPS)
      - Thin films using XPS in combination with sputter profiling

The modified layer is often far too thin to be characterized with most techniques.

The extreme surface sensitivity of XPS ensures that only the top few nanometers of the sample are analyzed.



Note: Approximate layer thickness only. Actual values depend upon materials

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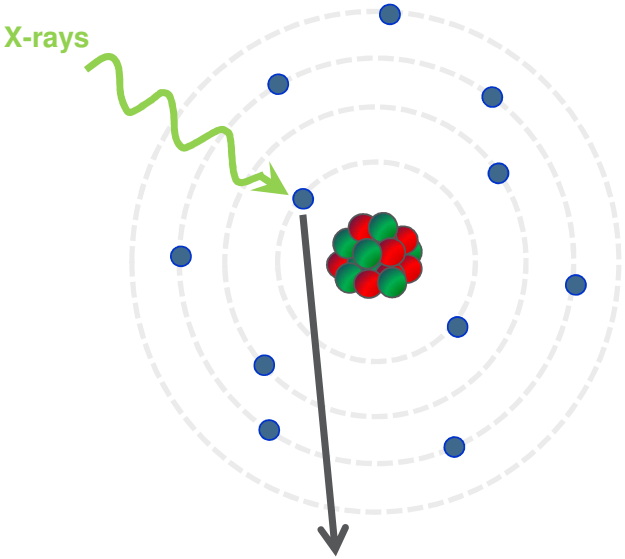
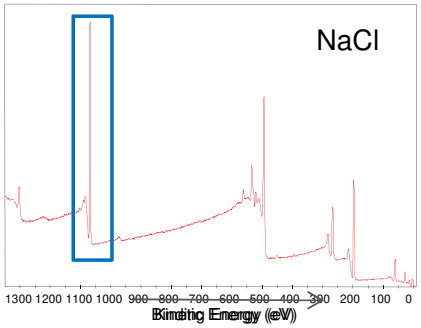
Basic XPS theory





- Surface is composed of atoms
- Electrons surround the nucleus of an atom, occupying orbitals at different energies
- Surface is irradiated with X-rays from a photon source
- X-rays cause electrons to be ejected (photoelectrons)
- Kinetic energy, KE, of photoelectrons is measured by an analyser
- The binding energy, BE, of the electrons is deduced from the kinetic energy and photon energy

$$BE = h\nu - KE$$

- Binding energy depends upon
  - Element
  - Orbital from which electron was ejected
  - Chemical state of the element

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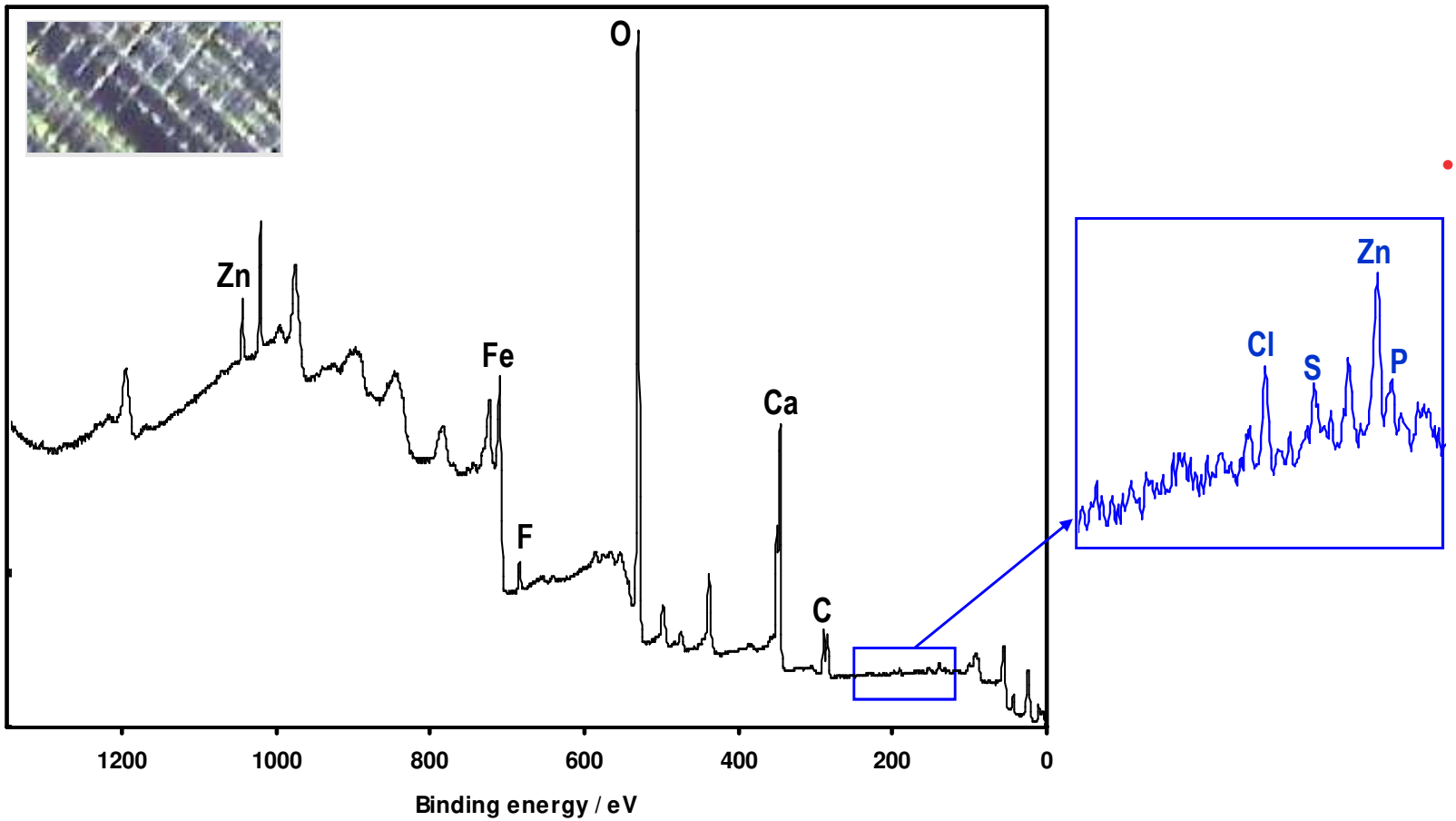
Surface analysis and XPS



Elemental identification of tribology sample

- Elemental identification
  - Which elements are present?
  - Can detect all elements except for H
- Elemental quantification
  - How much of an element is present?
  - Detection limit ~0.05% for most elements
  - Allows determination of stoichiometry

Element	At%
P	0.29
S	0.29
Cl	0.22
C	15.96
Ca	14.12
O	57.73
F	1.50
Fe	6.74
Zn	3.03
Mg	0.12

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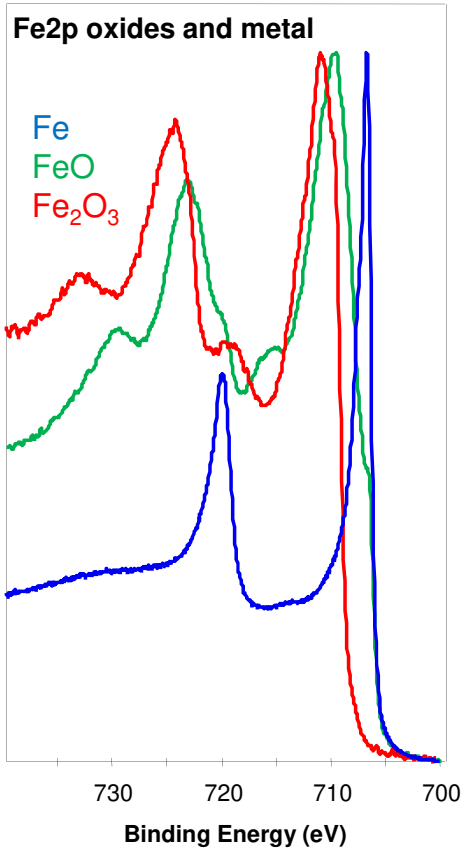
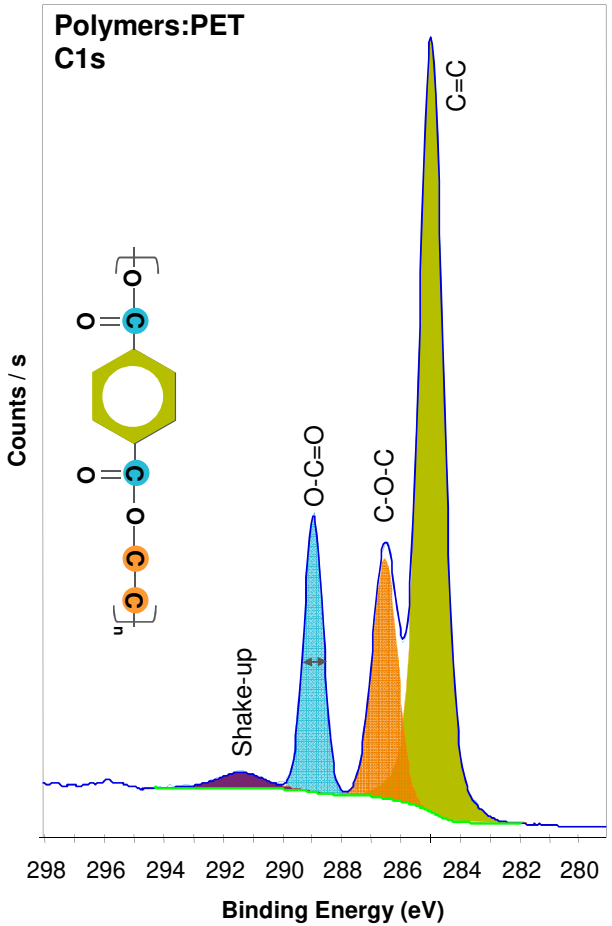
Surface analysis and XPS

- Chemical state identification and quantification
  - Bonding states for each element
  - Chemical structure





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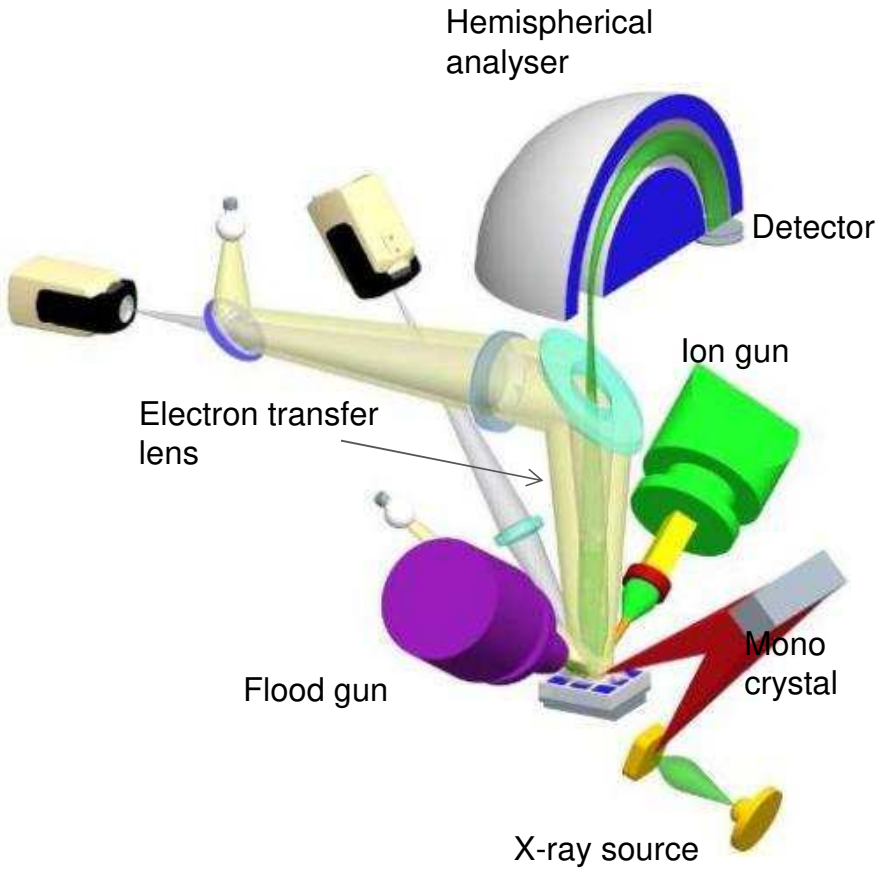
XPS instrumentation

- **UHV System**
  - Allows longer photoelectron path length
  - Ultra-high vacuum keeps surfaces clean
- **Electron analyser**
  - Lens system to collect photoelectrons
  - Analyser to filter electron energies
  - Detector to count electrons
- **X-ray source**
  - Typically Al Kα radiation
  - Monochromated using quartz crystal
- **Low-energy electron flood gun**
  - Analysis of insulating samples
- **Ion gun**
  - Sample cleaning
  - Depth profiling
  - For polymers, cluster ion sources may be required



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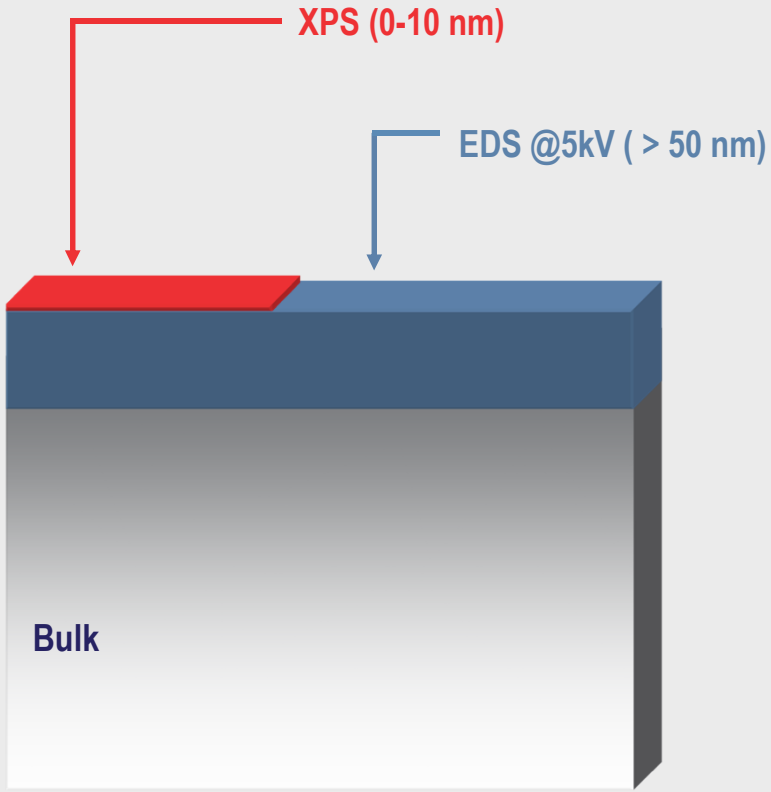
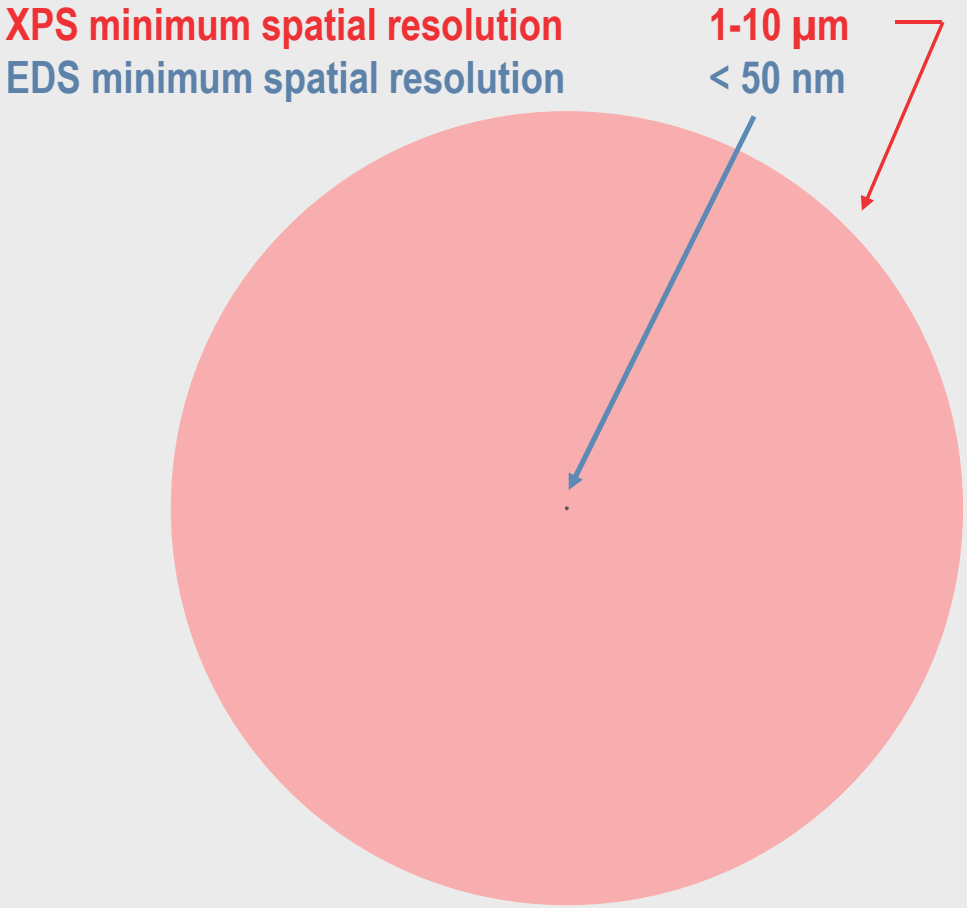
XPS is large area analysis, with nano-scale depth resolution

Depth resolution



X-Y spatial resolution



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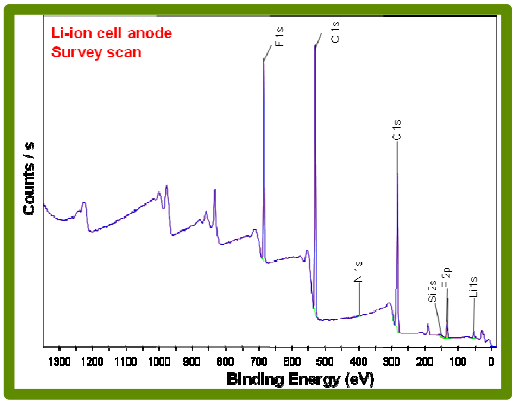
What information do we provide?

XPS

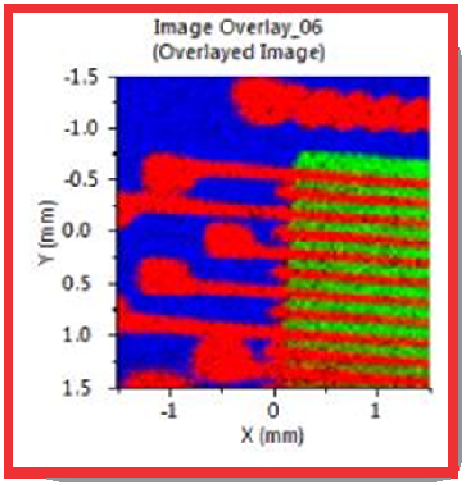
- Understand the surface chemistry



Name	Atomic %
C	76.0
O	16.8
Ag	4.9
Si	1.3
Zn	0.5
Ni	0.4

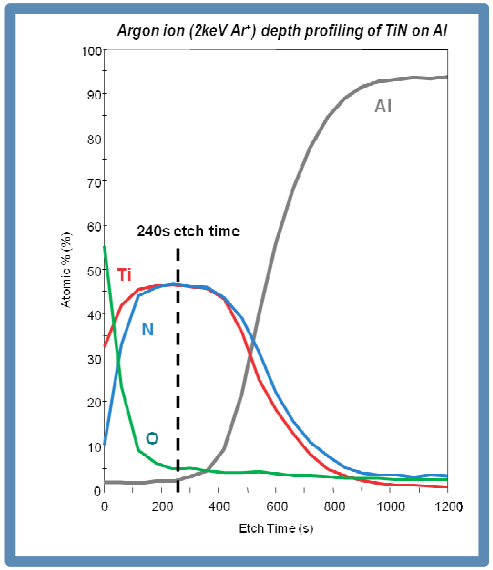
Imaging XPS

- Locate it on the surface



Depth Profiling

- Understand variation from surface to bulk



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What's XPS good for!

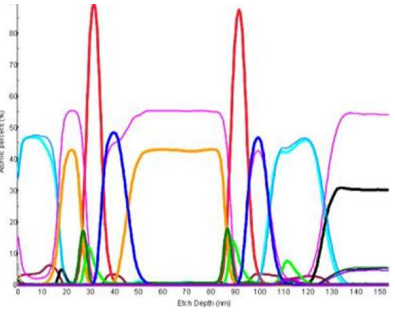
- Whenever someone says, "What's that?" -> Quantification of both elements and their chemical states
- Surfaces (10 nm), Thin films (few µms) and interfaces (2 nm)
- Stains, contamination, oxidation, corrosion, surface modification, defects, interfaces, delamination, thickness
- Metals, oxides, ceramics, powders, fibres, polymers, glasses, plastics, fabrics, nanomaterials….

What's XPS not good at!

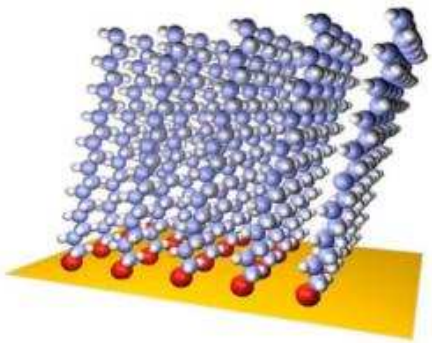
- PPM/PPB not possible. Detection limits typically ~ 0.1 at%
- An XPS spectrometer is not a microscope! Smallest analytical area is 5-10 µm for spectroscopy
- Limited specific organic information, vibrational techniques provide richer information
- Sample compatibility with UHV environment

Key Applications: Materials Science customers

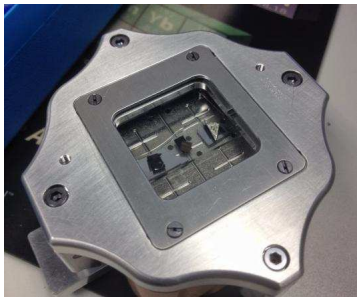
Application	Problem	Solution
Glass, Automotive/ Architectural	Checking thickness stoichiometry of layers (<10nm) and interfaces. IP protection, reverse engineering	Depth profiling through conductive and insulating layers
Coatings, wear-corrosion resistance, antibacterial	Defects and conformity of coating. Delamination failure analysis. Coverage of single monolayer coatings	Point and shoot for defects, rapid mapping for conformity. Depth profiling for interface control
Li-ion battery components	Characterisation of development SEI with cycle lifetime. Needs Vacuum transfer module to minimise air contamination.	Depth profiling of Anodes/Cathodes/Separators
Catalysts	Optimisation of precious metal content at the surface. Following metal oxidation state during processing and reprocessing of spent catalysts	Powder and particle analysis. Integrated gas reaction cell for following reaction dynamics
Graphene and C nanomaterials	Structure and chemical functionality of CNTs/Graphene. Contamination control	Use of combined XPS and Raman to ID correct regions of interest.



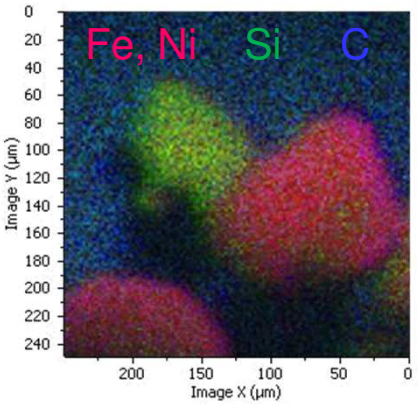
Low-E Glass



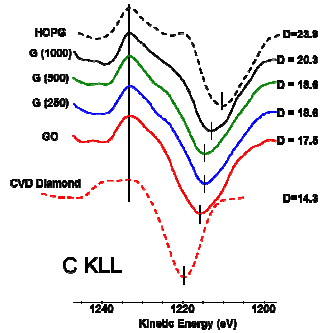
Self-assembled Monolayer coatings



Li-Battery Electrodes



Catalysts



Graphene and Carbon Nanomaterials

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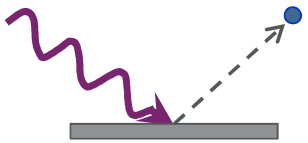
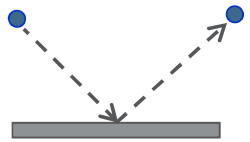
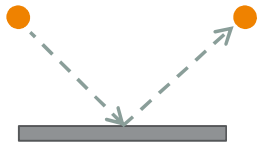
Related Surface Analysis Techniques



- **UV Photoelectron Spectroscopy (UPS)**
  Band structures and work function
  - Photons in, electrons out



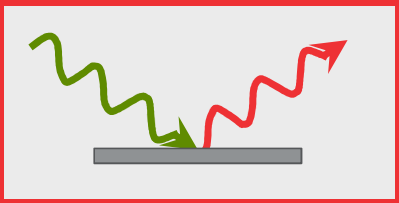
- **Reflected Electron Energy Loss Spectroscopy (REELS)**
  Hydrogen and band gap
  - Electrons in, electrons out



- **Ion Scattering Spectroscopy (ISS or LEIS)**
  Ultra thin film composition and coverage
  - Ions in, ions out

These techniques can be added to XPS instruments to provide complimentary information).

We can now add Raman spectroscopy too



- **Photons in, photons out**

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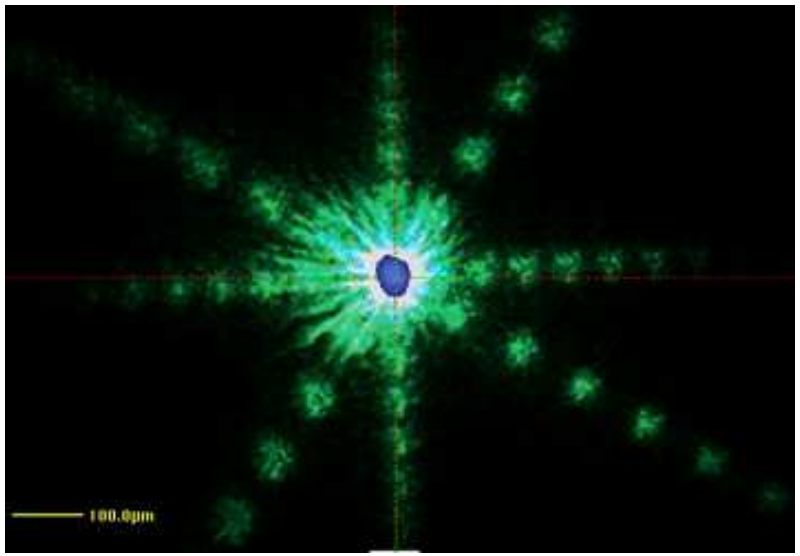
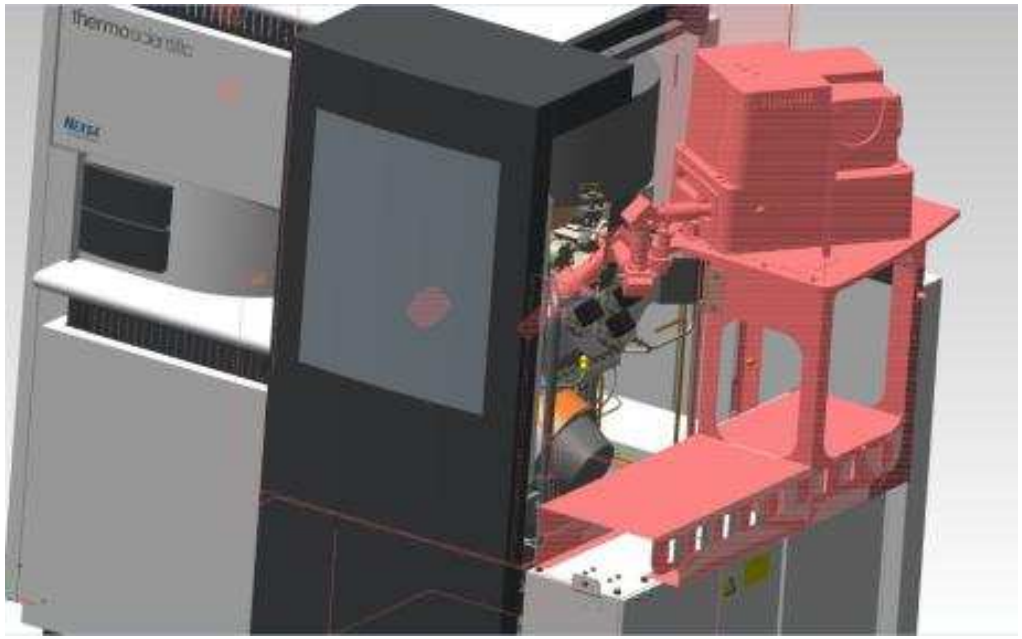
Coincident Raman & XPS

XPS
SnapMap
Depth Profiling
MAGCIS
UPS
ISS
REELS
Raman
Avantage

- Laser light (green here) is exactly aligned with the X-ray spot (blue)
- Spectrometer is mounted in temperature controlled section to protect during bakeout.
- Controlled via Avantage and Omnic software





NB Laser light intensity saturates camera making spot look bigger and flare

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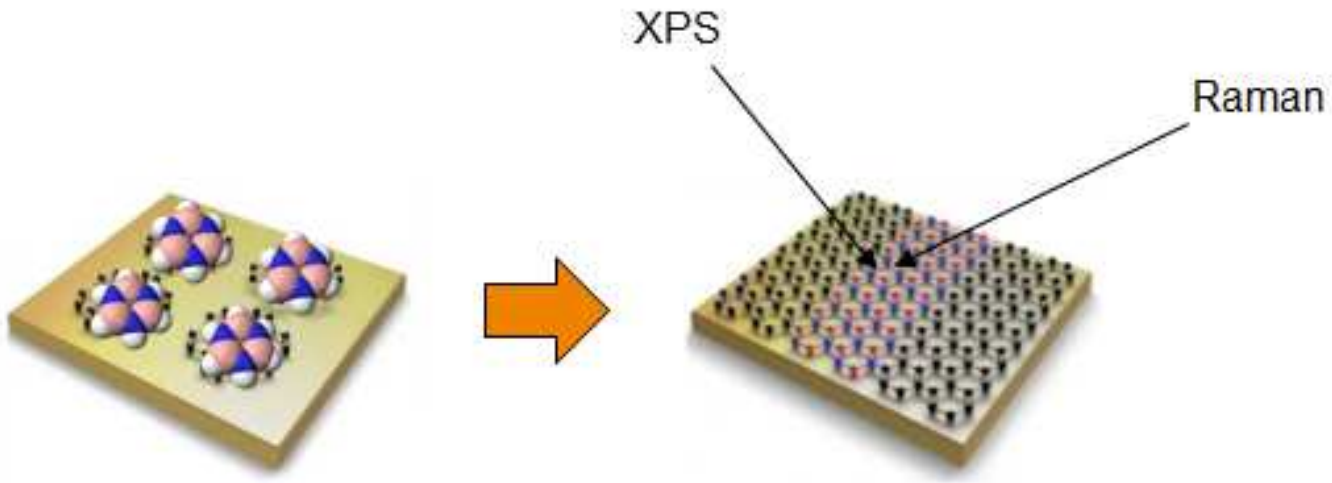
Fully characterise 2D materials: XPS-Raman analysis of BN

XPS
SnapMap
Depth Profiling
MAGCIS
UPS
ISS
REELS
Raman
Avantage

- **Hexagonal boron nitride (h-BN)**
  - h-BN composed of nanosheets of sp2-bonded boron and nitrogen
  - Electrical insulator (band gap ~5.9eV) but high thermal conductivity
  - Doping or functionalization can affect band gap
  - Excellent proton conductor which has potential use in fuel cells



Coincident XPS and Raman characterisation of boron nitride film

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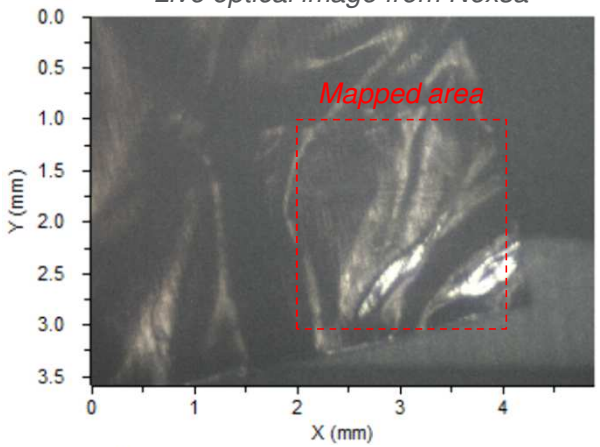
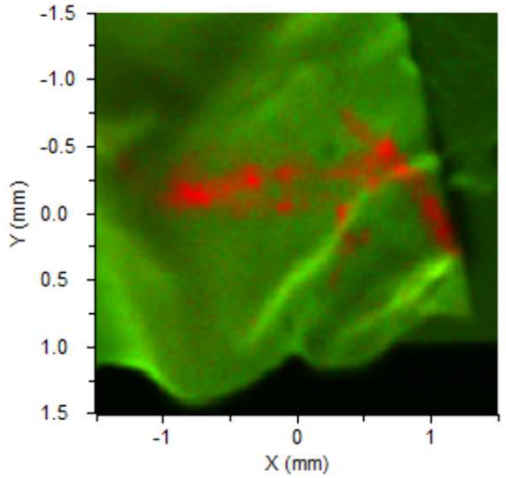
Fully characterise 2D materials: XPS-Raman analysis of BN

XPS
SnapMap
Depth Profiling
MAGCIS
UPS
ISS
REELS
Raman
Avantage

Live optical image from Nexsa

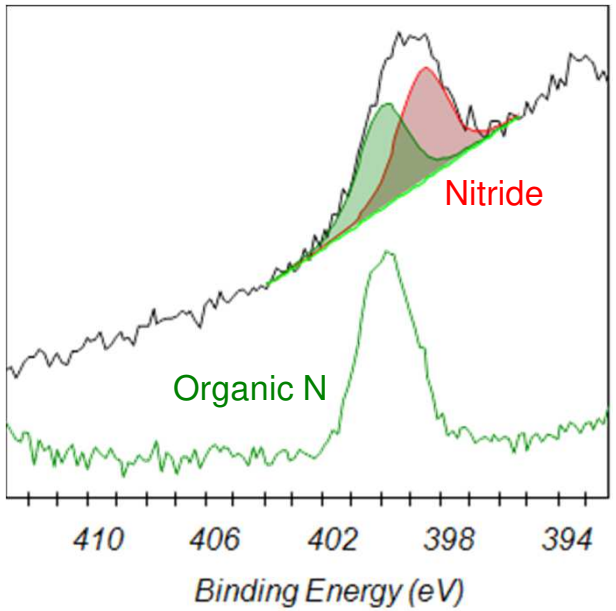




N1s nitride SnapMap image of sample

- A 30 µm X-ray spot was used to generate an N1s SnapMap image with 100 x 100 pixels
- The SnapMap image can be used to define the best position for Raman and XPS analysis

N1s spectra from green & red areas from SnapMap



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Fully characterise 2D materials: XPS-Raman analysis of BN

XPS
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REELS
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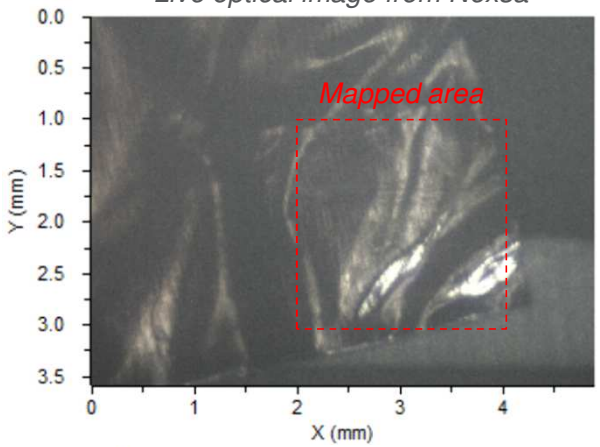
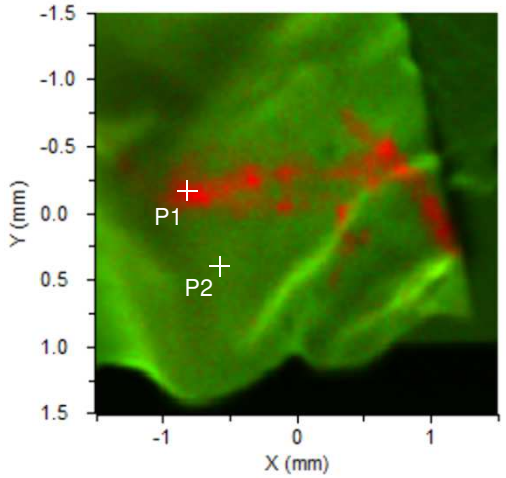
Avantage

Live optical image from Nexsa

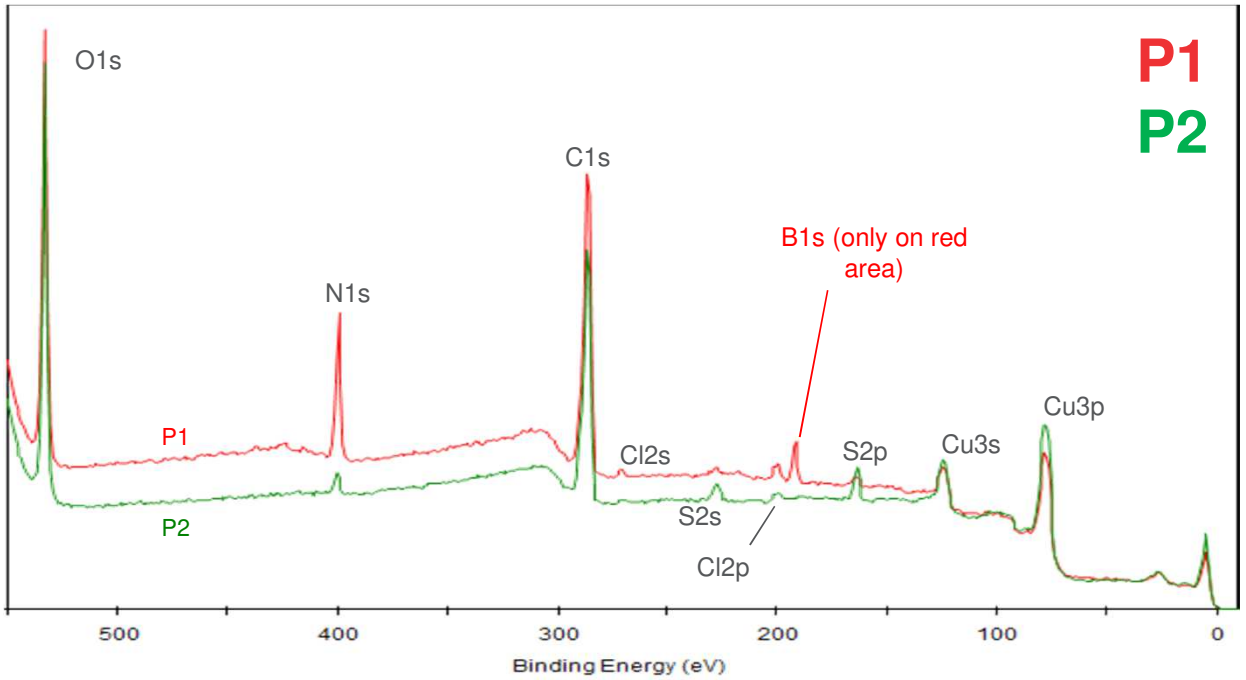




N1s nitride SnapMap image of sample

- A 30 µm X-ray spot was used to generate an N1s SnapMap image with 100 x 100 pixels
- The SnapMap image can be used to define the best position for Raman and XPS analysis

XPS survey spectra on/off high nitrogen area (defined using SnapMap)



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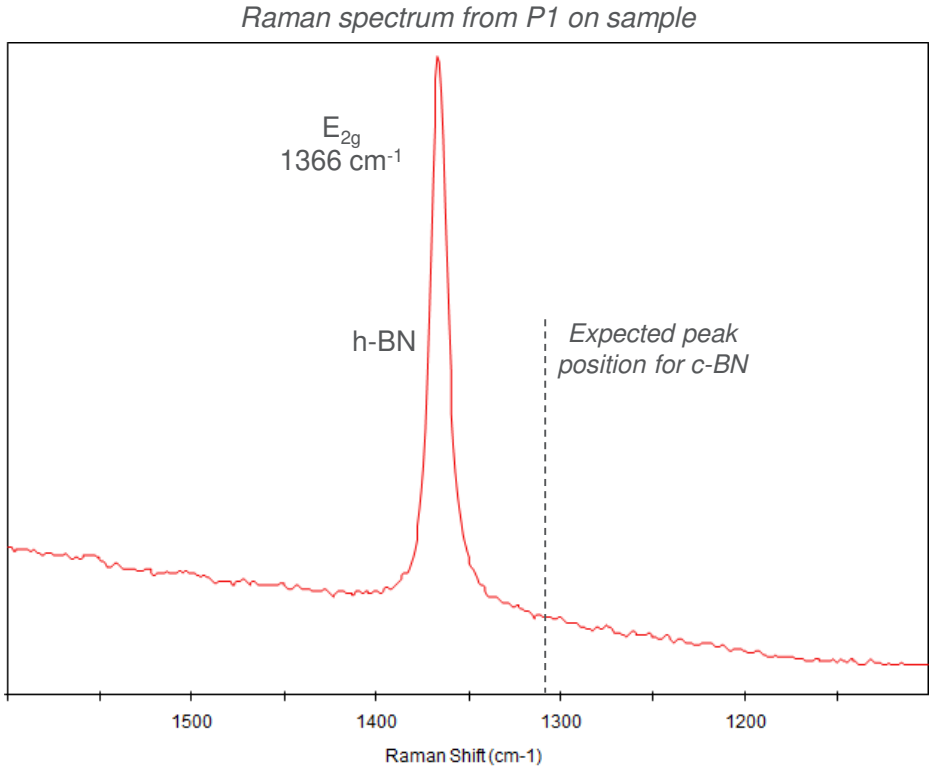
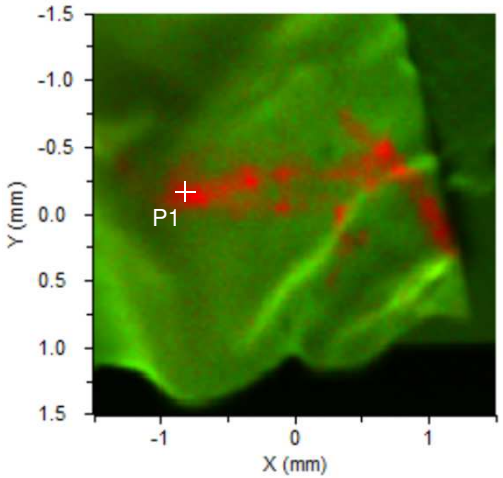
Fully characterise 2D materials: XPS-Raman analysis of BN

XPS
SnapMap
Depth Profiling
MAGCIS
UPS
ISS
REELS
Raman
Avantage





N1s nitride SnapMap image of sample

- Boron nitride can exist in different crystalline forms, e.g. c-BN or h-BN
- Raman spectrum of boron nitride on sample is consistent with hexagonal boron nitride (h-BN)

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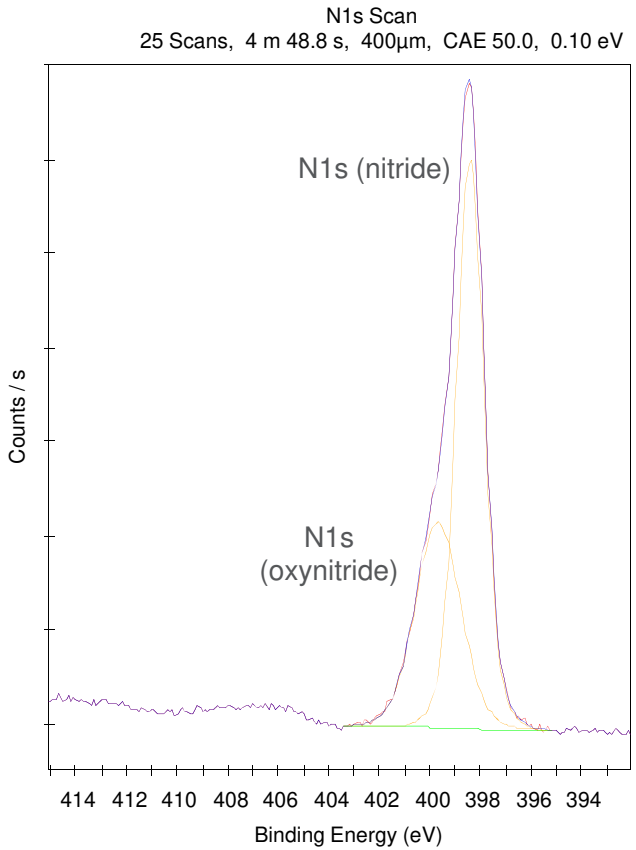

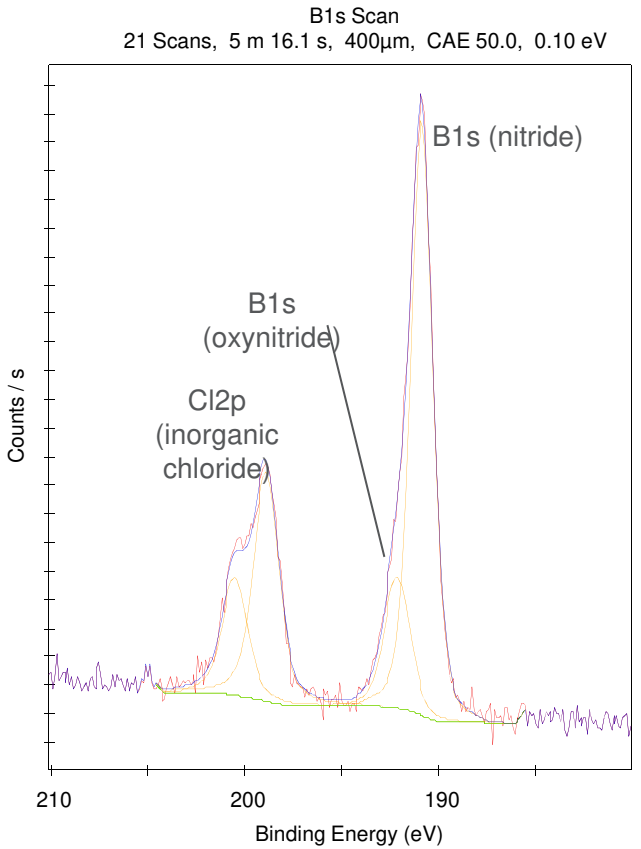

$[B_{total}]/[N_{total}]=1.14$

- High resolution XPS analysis shows the presence of boron oxynitride as well as boron nitride

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Fully characterise 2D materials: XPS-Raman analysis of BN

XPS

SnapMap

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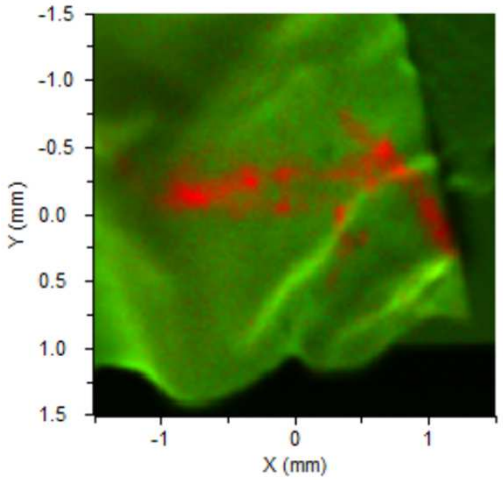
Avantage



- XPS SnapMap chemical imaging enables the boron nitride areas to be identified on the sample surface
- Co-incident Raman spectroscopy and XPS determined:
  - Presence of BN
  - BN only in hexagonal form
  - Some oxidation of the material to boron oxynitride

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