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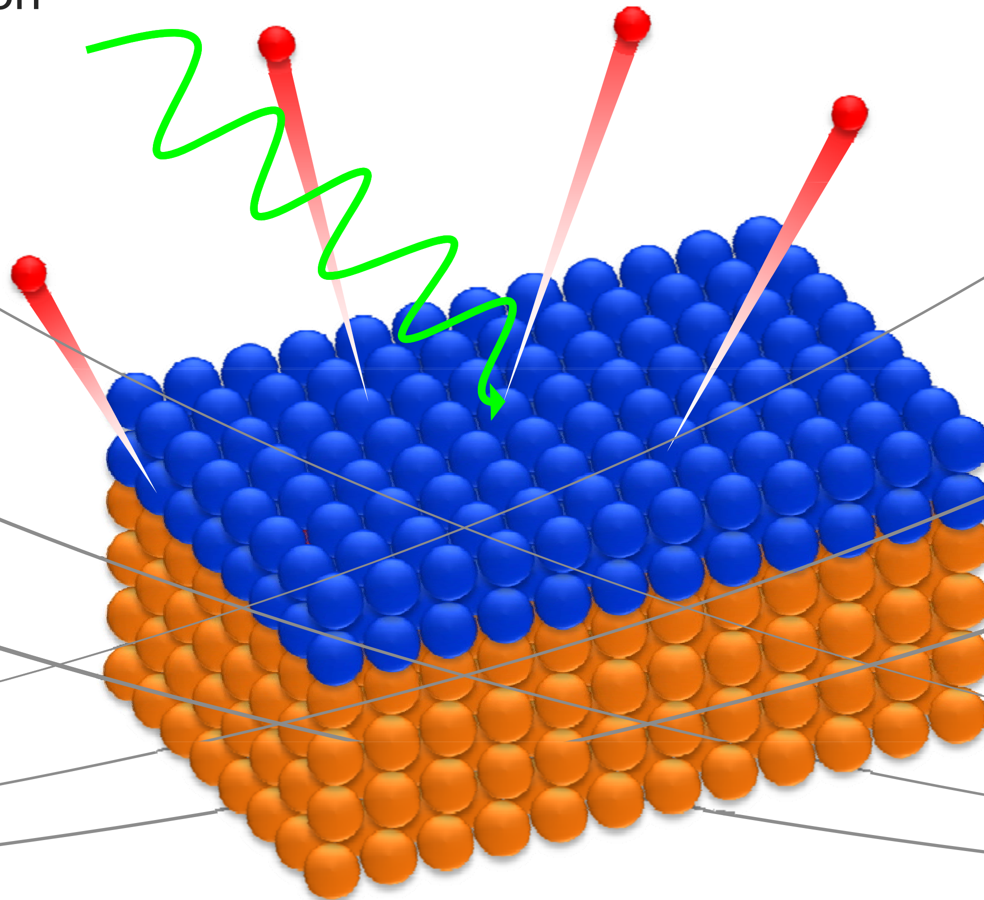
XPS in context: An Introduction to Materials & Surface Analysis

S. J. Hutton



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Kratos Analytical Ltd

Kratos Analytical headquarters in Manchester, UK

Manchester United!

- Sister company of Shimadzu Corporation, Kyoto, Japan
- All Kratos products are designed, assembled and supported from our HQ in Manchester
- 220 employees across two business groups (Surface and MALDI mass spectrometry).
- Business accredited with ISO9001 and ISO13485 standards
- Instruments assembled in clean-room environment

Materials Analysis

Bulk Vs. Surface

- Surface Composition
- Surface Roughness
- Homogeneity
- Surface charge
- Adhesion

- Cohesion
- Density
- Morphologies
- Homogeneity
- Young's Modulus
- Hardness
- Composition

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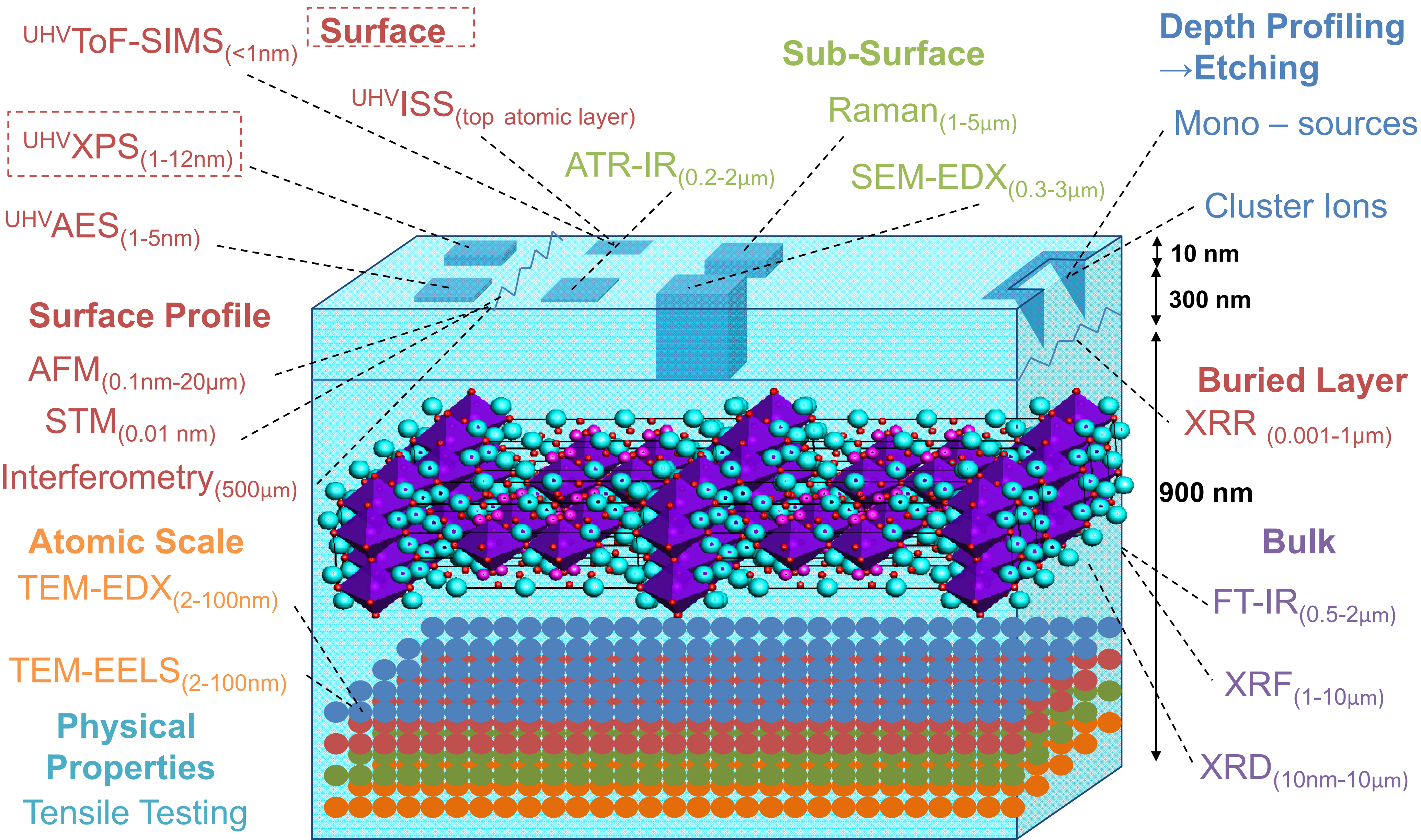
Bulk Vs. Surface: Techniques



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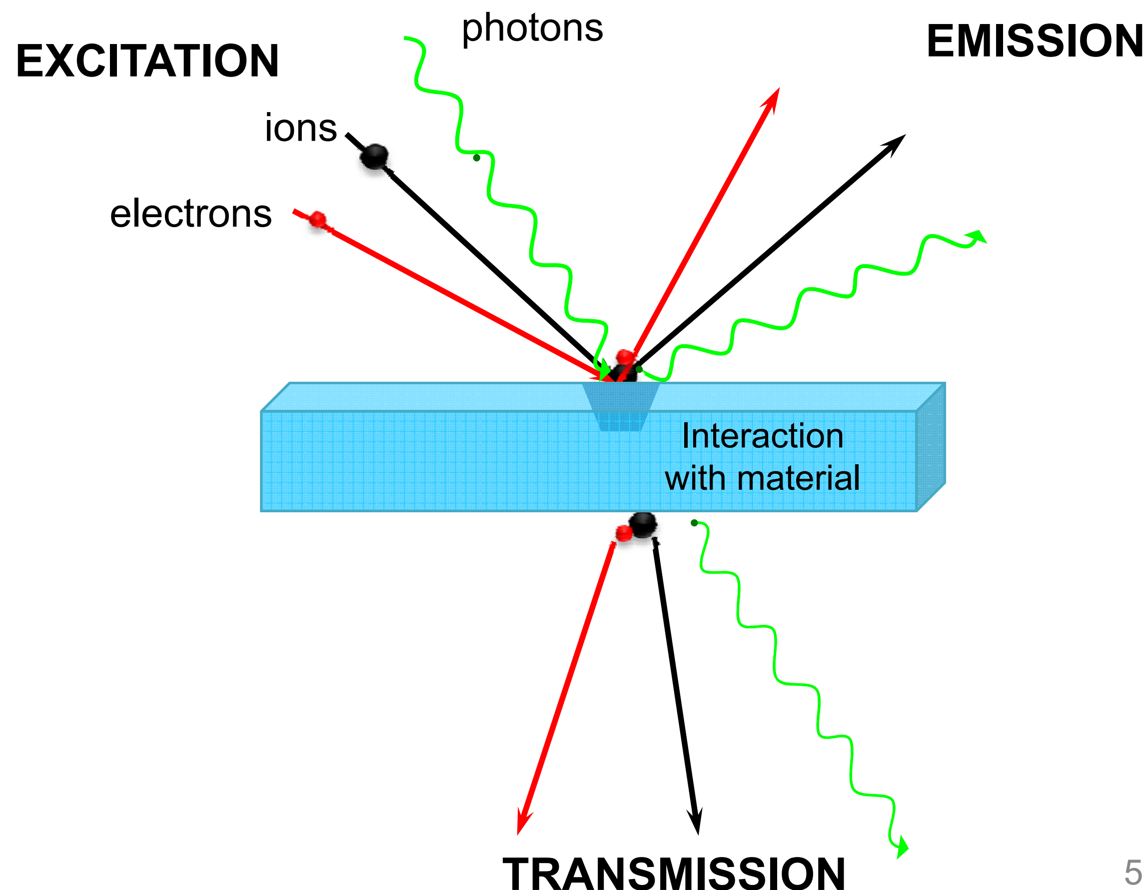
Surface Analysis Toolbox

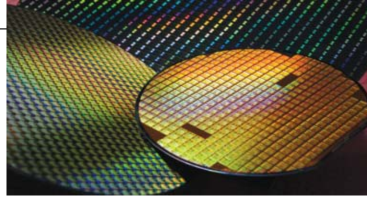
- Properties and reactivity of the surface will depend on:
  - Bonding geometry of molecules to the surface
  - Physical topography
  - Chemical composition
  - Chemical structure
  - Atomic structure
  - Electronic state



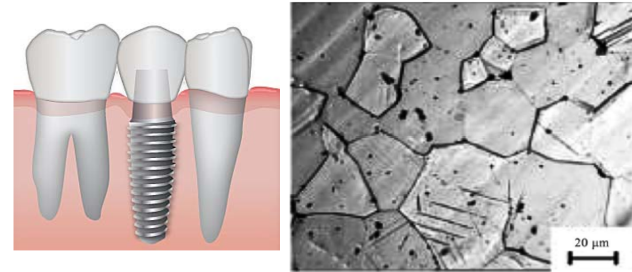
→ Careful selection of 'tools' needed

Surface Analysis: Industrial Examples

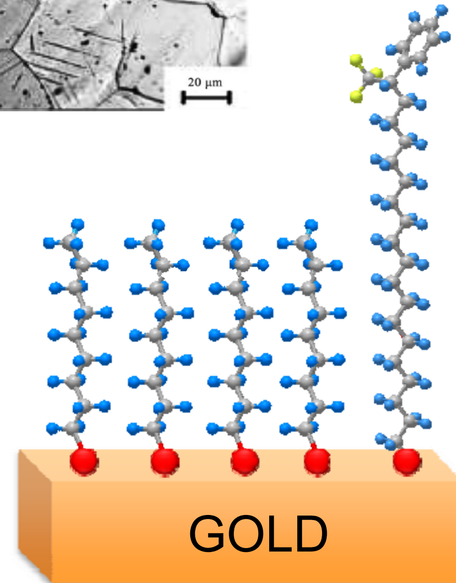
- Semi-conductors



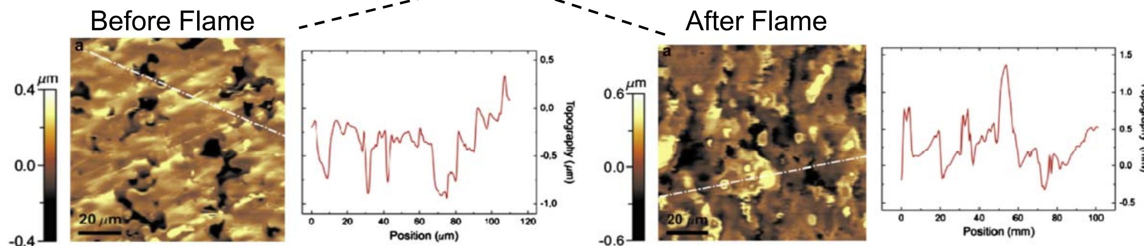
- Bio technology

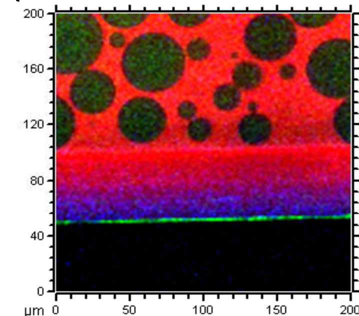


- Self assembled monolayers (SAMs)



- Thin films / coatings & adhesion
- Plasma / flame treated surfaces

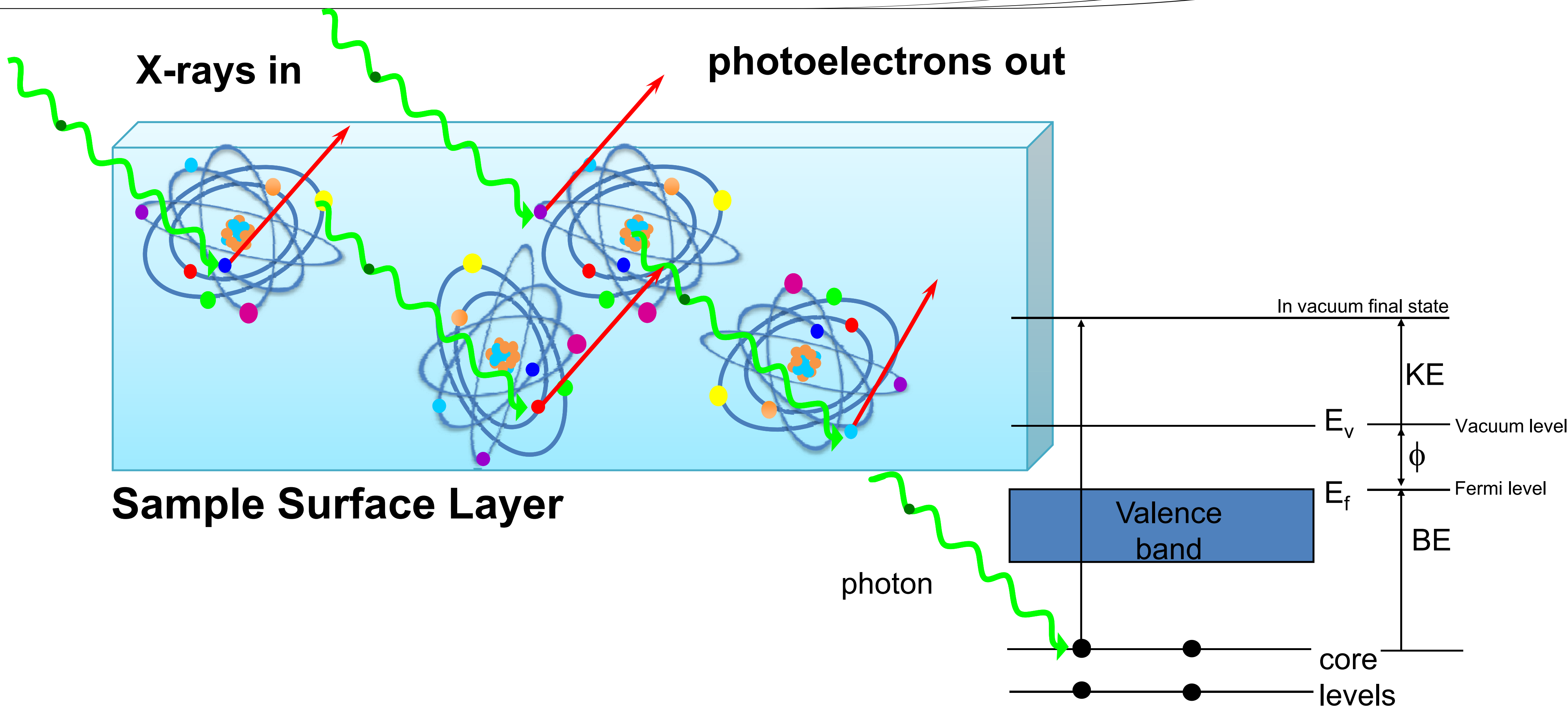




Journal of Biomaterials and Nanobiotechnology, 2012, 3, 87-91
Polymer, 2010, 51, 3591-3605

XPS Theory & Spectra Signals

The Photoelectron Process



binding energy (eV) = photon energy - kinetic energy - work function

$$BE\ (eV) = h\nu - KE - \phi$$

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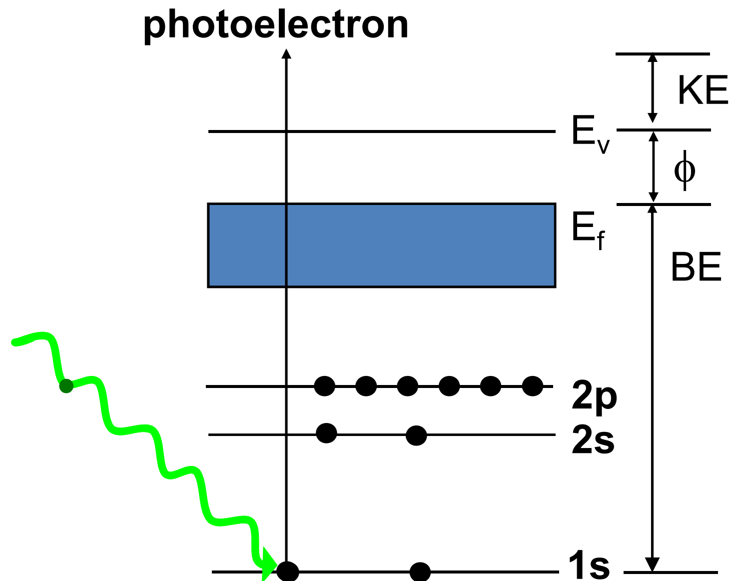
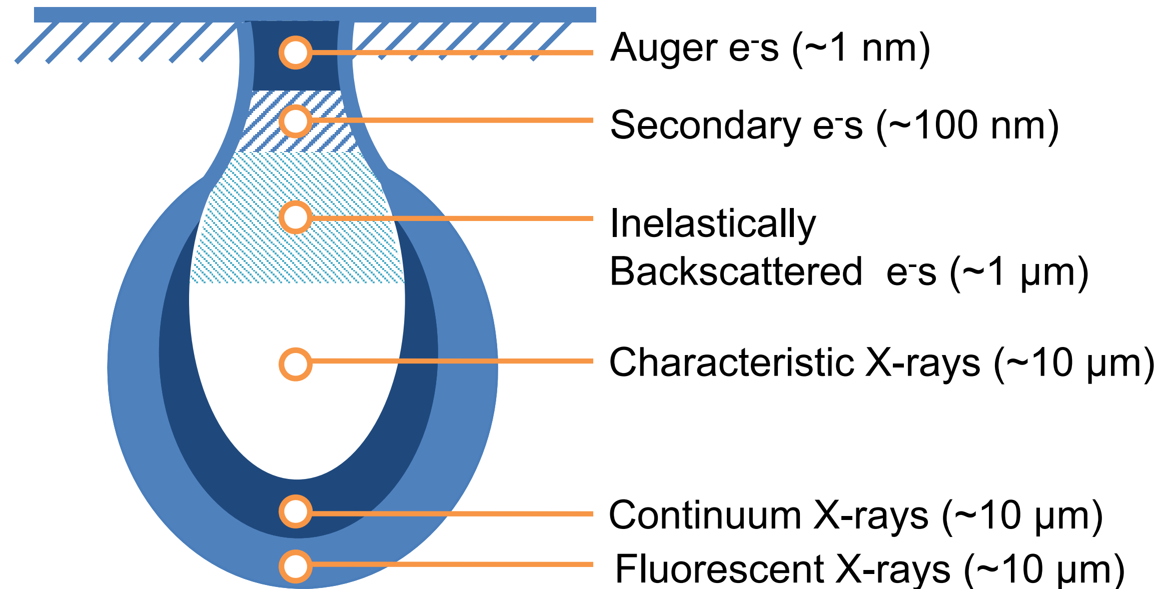
The Photoelectron Process

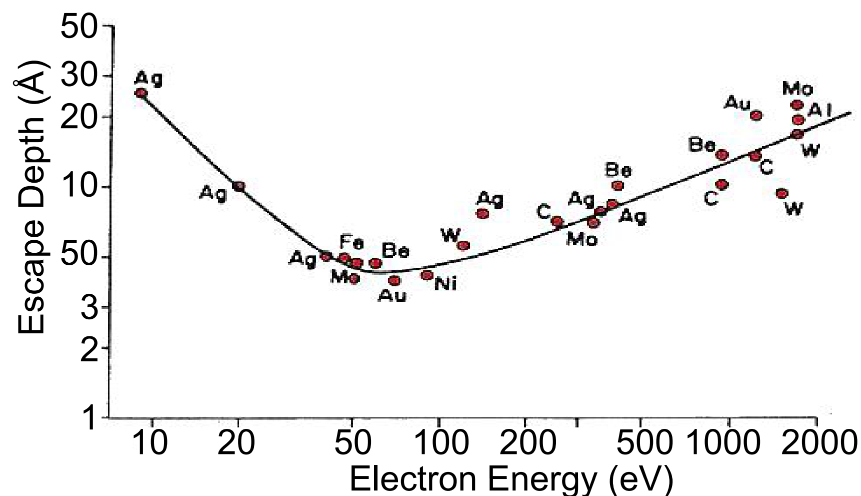




- **Each element → unique set of binding energies**
- **X-ray source energy ≥ B.E. of electron in atom → a secondary electron elastically scattered**
- Core level electrons in solid-state atoms are quantized→ spectra exhibit resonance peaks characteristic of the electronic structure for atoms at sample surface
- **X-rays penetrate deep** into the specimen, **but** only the surface electrons can ***escape*** with sufficient energy for analysis
    - i.e. ejected electrons from depths >10nm →low probability of leaving the surface without undergoing an energy loss event (contribute to the background signal)

Surface Sensitivity of XPS

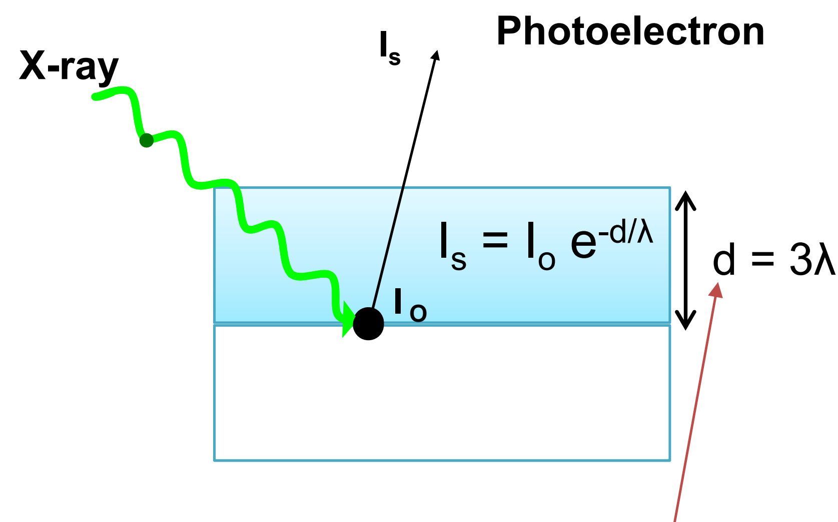
- The **inelastic mean free path** (λ_i) determines the depth at which photoelectrons are able to escape from the sample surface without inelastic scattering
- X-rays penetrate deep into the specimen, but only the surface electrons can escape with sufficient energy for analysis → Penetration depth of the X-ray radiation is 10^2-10^3 nm



- For an electron of intensity (I_o), emitted at a depth 'd' below the surface, the intensity is attenuated according to the Beer-Lambert law:
  - Intensity (I_s) of the electron as it reaches the surface is given by:

$$I_s = I_o e^{-d/\lambda}$$

- With a path length of one λ, 63% of all electrons are scattered



Sampling depth = av. distance from the surface for which 95% of photoelectrons are detected

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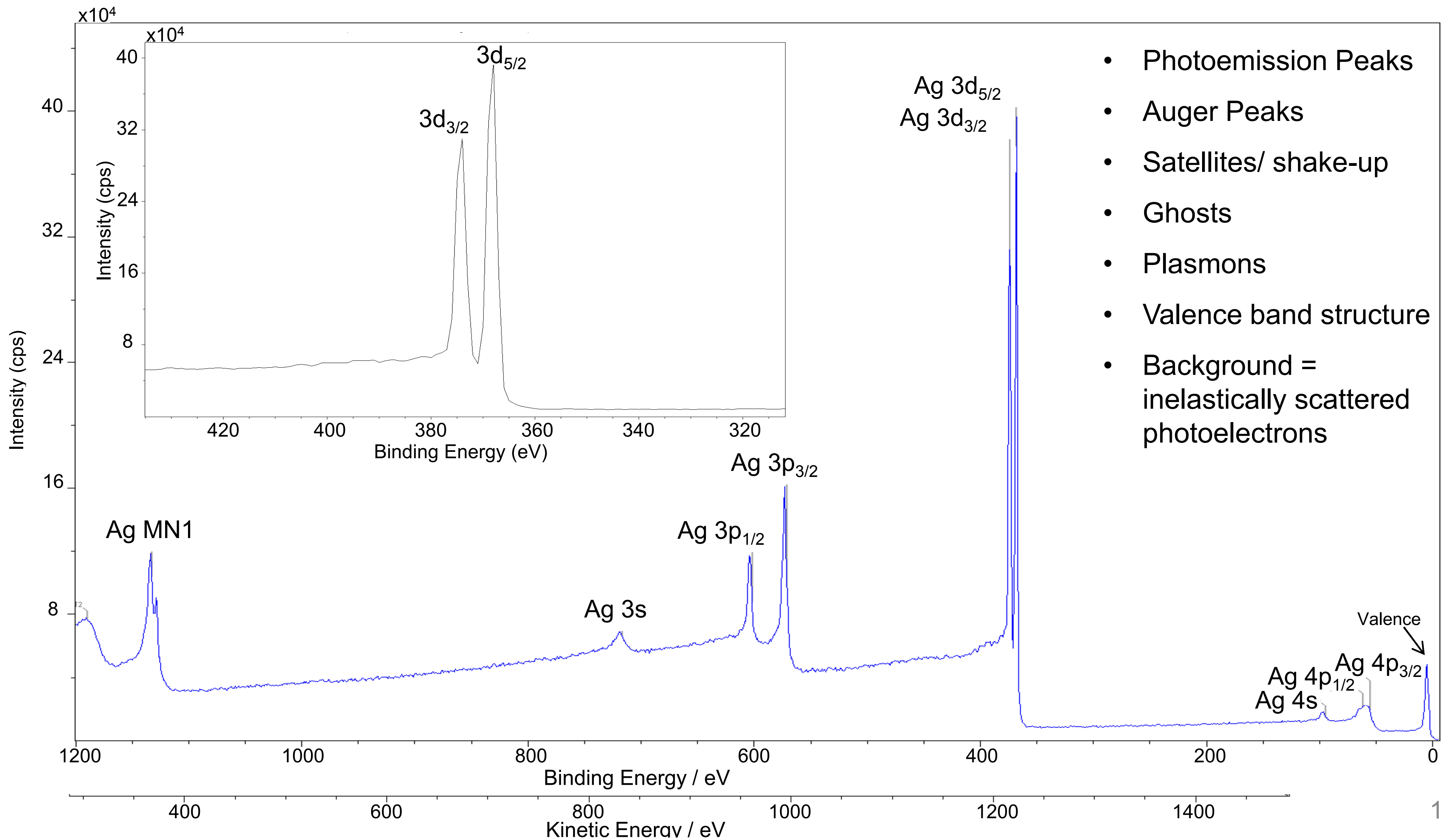
The Photoelectron Spectrum



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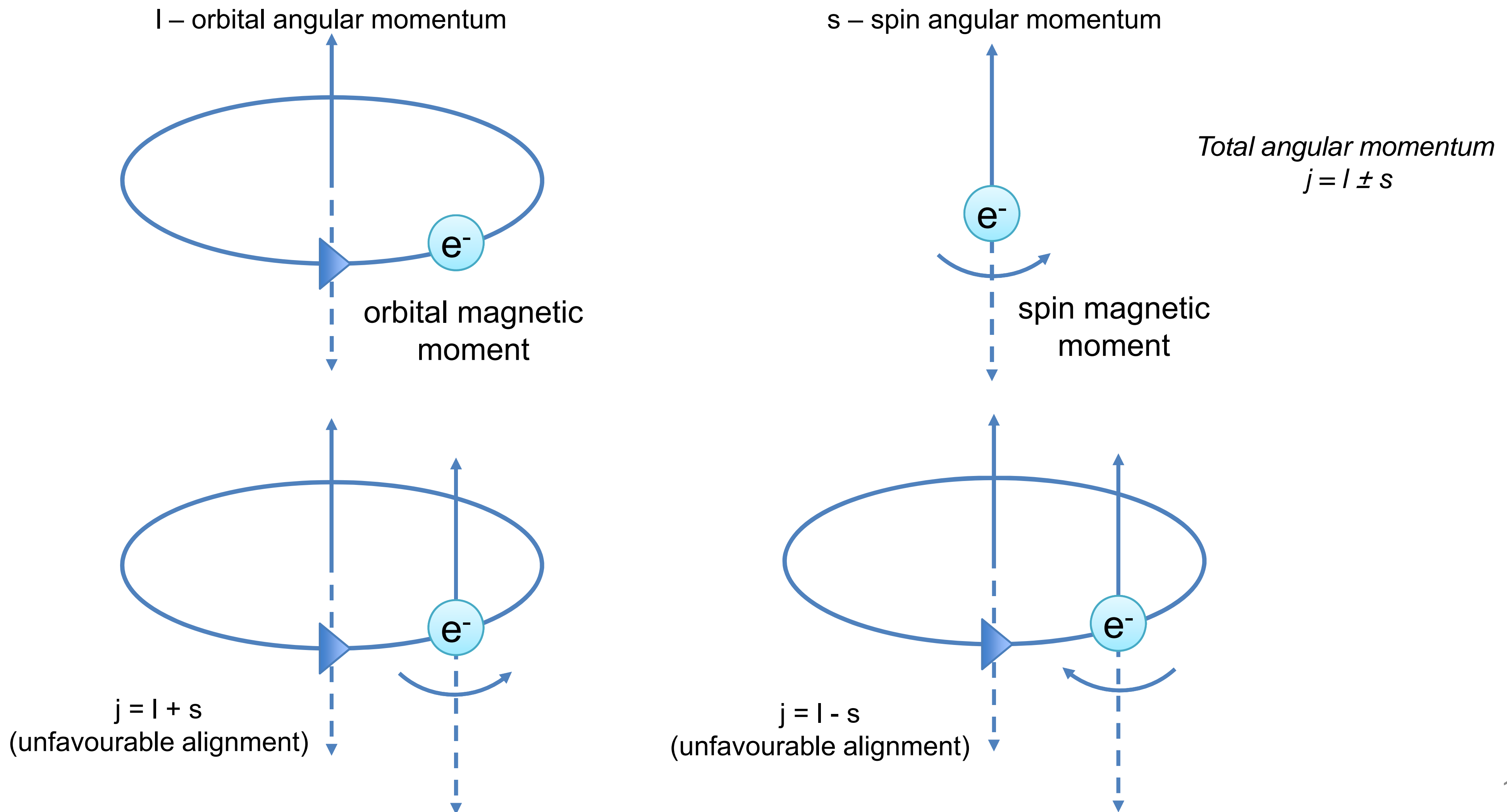
Photoemission Peaks: Spin-Orbit Coupling

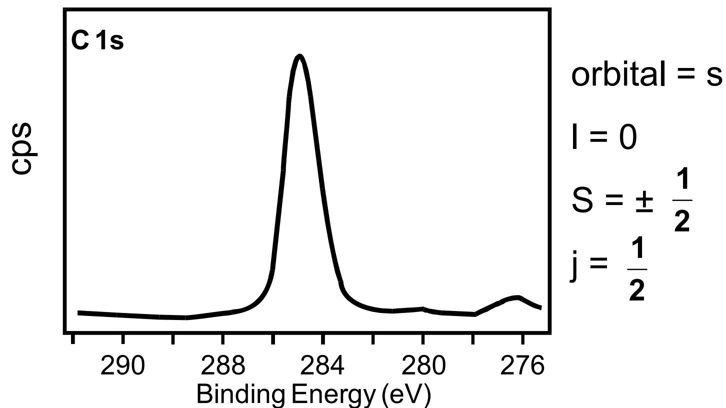
- For an electron in orbital with orbital angular momentum, coupling between magnetic field spin (s) and angular momentum (l) occurs



Spin-Orbit Coupling

- The spin-orbit coupling causes doublets to be observed for all photoemission peaks that originate from an orbital where $l > 0$ (p,d,f)

$j = l \pm s$

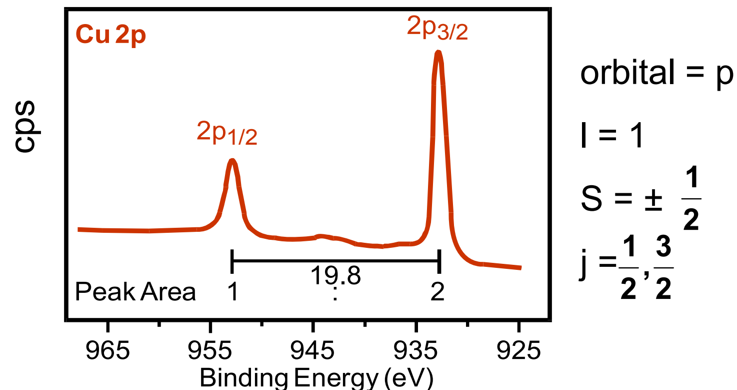


orbital = s

l = 0

$S = \pm \frac{1}{2}$

$j = \frac{1}{2}$

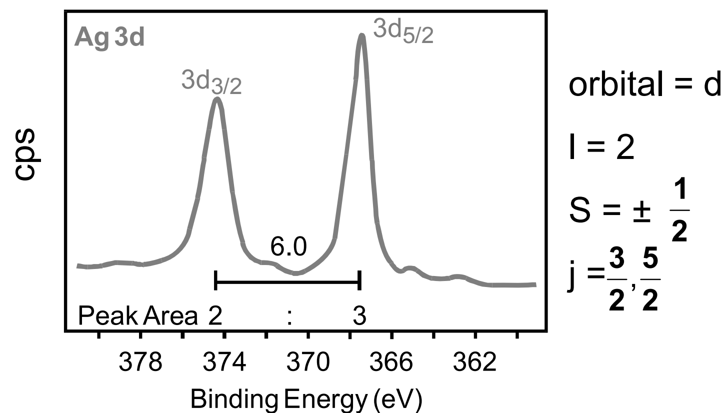


orbital = p

l = 1

$S = \pm \frac{1}{2}$

$j = \frac{1}{2}, \frac{3}{2}$

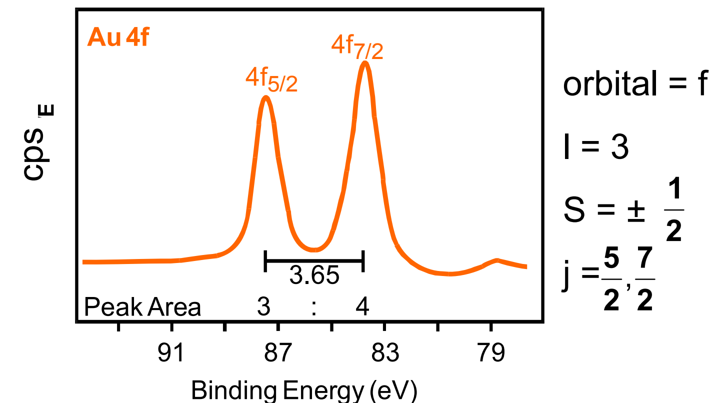


orbital = d

l = 2

$S = \pm \frac{1}{2}$

$j = \frac{3}{2}, \frac{5}{2}$



orbital = f

l = 3

$S = \pm \frac{1}{2}$

$j = \frac{5}{2}, \frac{7}{2}$

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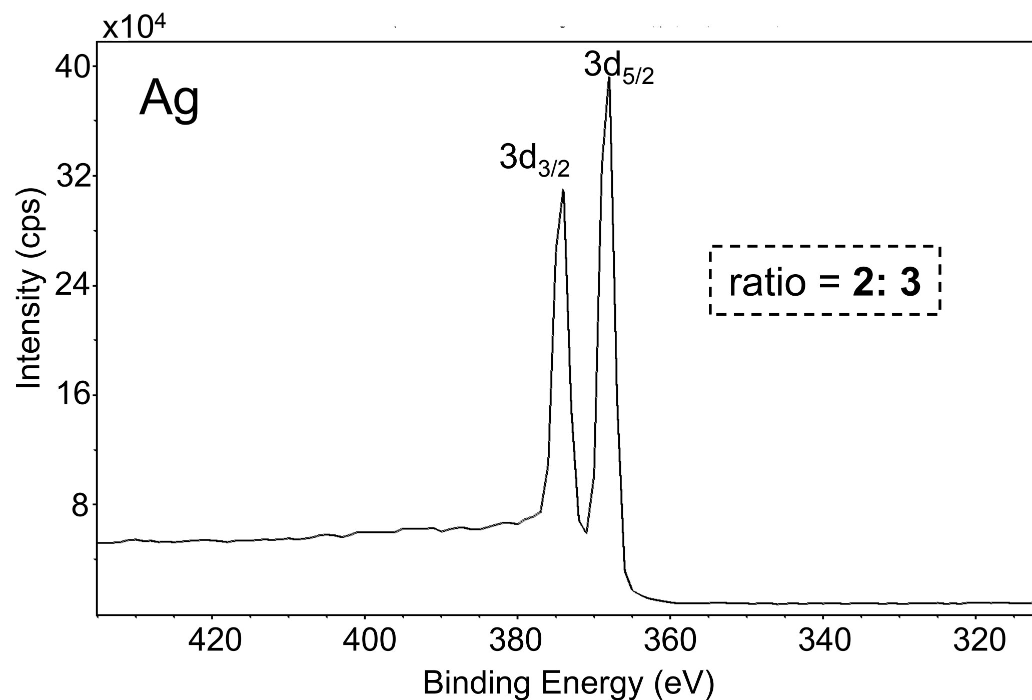
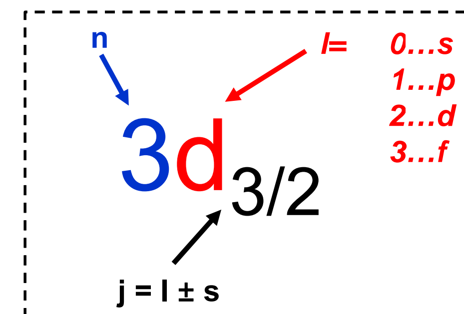
Spin-Orbit Coupling

- Doublet = two states →differ slightly in **energy** and their **degeneracy**
- Degeneracy (number of spin-orbit split levels at each j value) = 2j + 1 → doublet peaks vary in intensity



Subshell	j values	Degeneracy
s	$\frac{1}{2}$	-
p	$\frac{1}{2},\frac{3}{2}$	2, 4 = **1, 2**
d	$\frac{3}{2},\frac{5}{2}$	4, 6 = **2, 3**
f	$\frac{5}{2},\frac{7}{2}$	6, 8 = **3, 4**

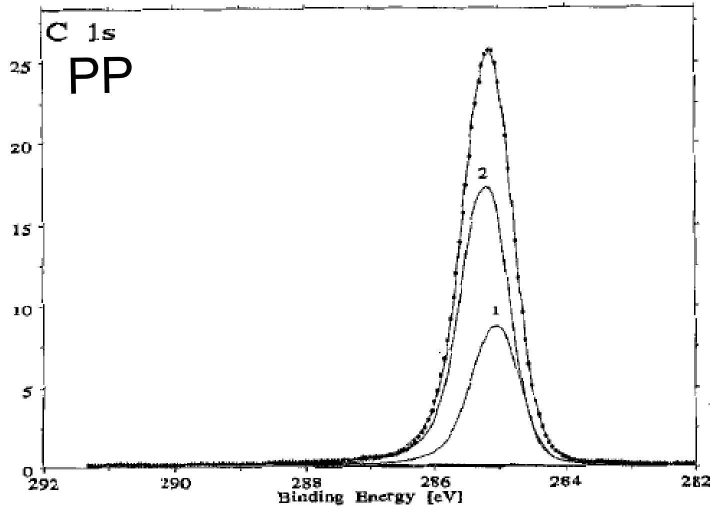
- B.E. of lower J value in doublet is higher (B.E. $3d_{3/2}$ > B.E. $2p_{5/2}$)
- Magnitude of spin-orbit coupling splitting increases with z
- Magnitude of spin-orbit splitting decreases with distance from nucleus (as *l* increases for a constant *n*) →increased nuclear shielding

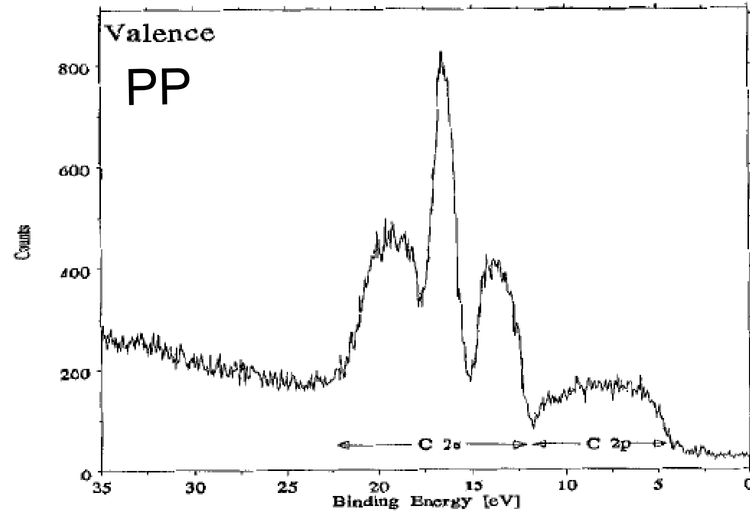


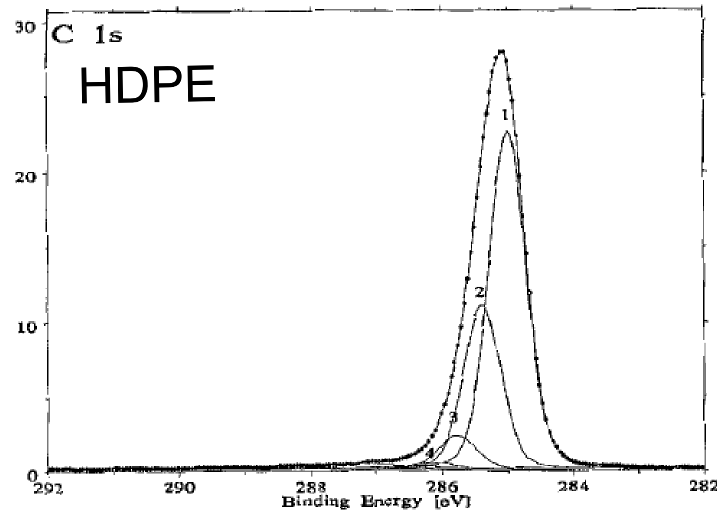
What information do we get from XPS?

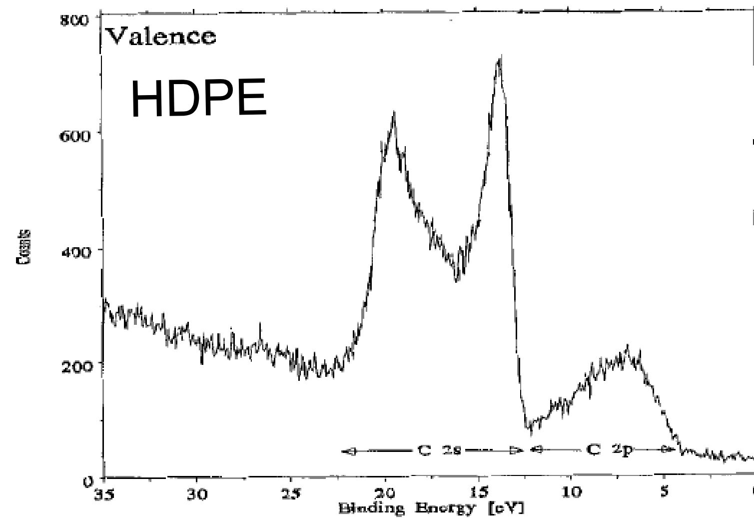
- **Surface sensitivity** - photoelectron signal from first 1-10 layers of atoms and molecules.
- **Element identification** (except H & He) at concentrations from 0.1 atomic %
- **Quantitative** determination of the elemental composition
- **Chemical state** information - molecular environment of the element
- **Non-destructive** analysis, including depth profiles, from the top 10 nm (angle resolved XPS)
- **Destructive depth profiles** of inorganic materials or organic materials (e.g. using a gas cluster source for sputtering the surface)
- **Imaging** - lateral variations in surface composition
- **‘Finger printing’** of materials using valance band

Valence Band (VB) spectra









- Photoemission lines near the Fermi level (0eV B.E.)
- Photoemission of most weekly bound electons from
  - → MO’s
  - → Solid state energy bands
- Insulating sample
  - → low no. of electrons near Fermi level
- Metallic sample
  - → high no. of electrons near Fermi level
- ‘Fingerprint’ like region
  - e.g. can distinguish PP & PE

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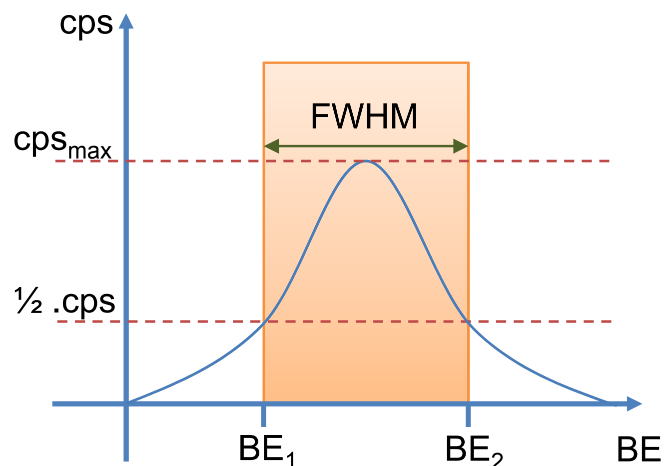
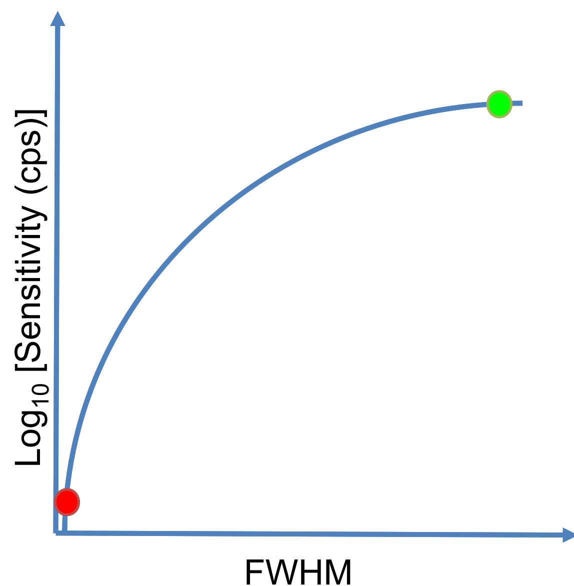
Resolution & Sensitivity

- Tailor experiments for **sensitivity** & **resolution** (full width half maximum, FWHM)





- **Full width half maximum** (**FWHM**) is a measure of resolution in XPS = full width at half of the maximum value (i.e. half of the cps recorded at the peak height)
  - High FWHM → low resolution
  - Low FWHM → high resolution

- **Counts per second (cps)** is the number of signals detected
  - High cps → greater sensitivity
  - Low cps → lower sensitivity

🟢 Use high pass energy for low concentration elements
→ max sensitivity, but lower resolution

🔴 Use low pass energy for chemical state information
→ lower sensitivity, but high resolution

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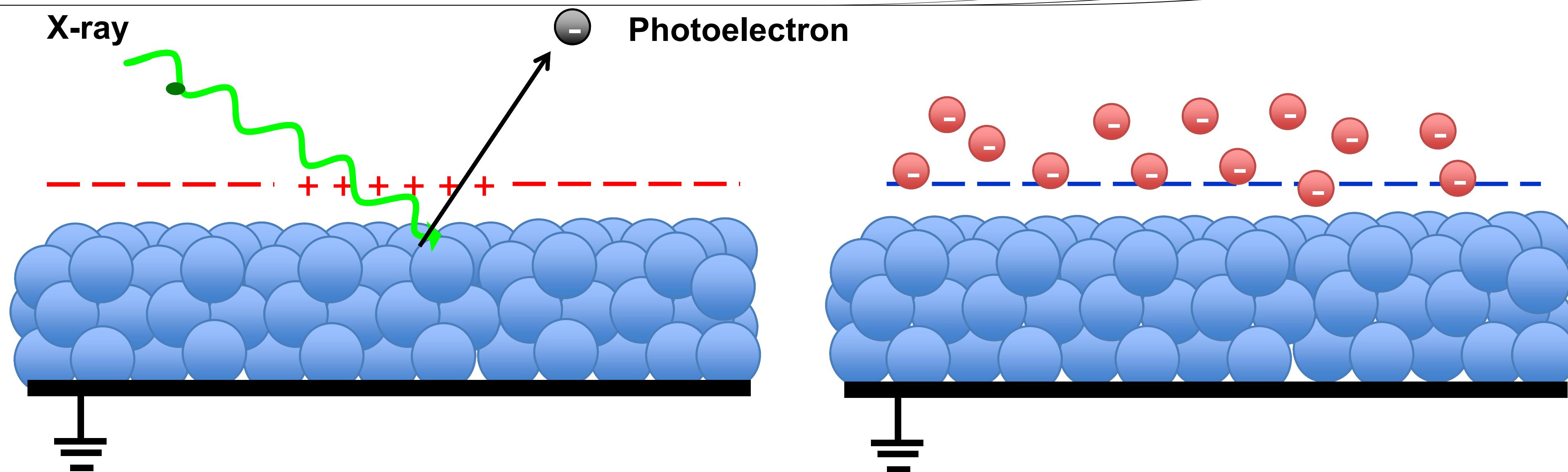
Insulating Samples

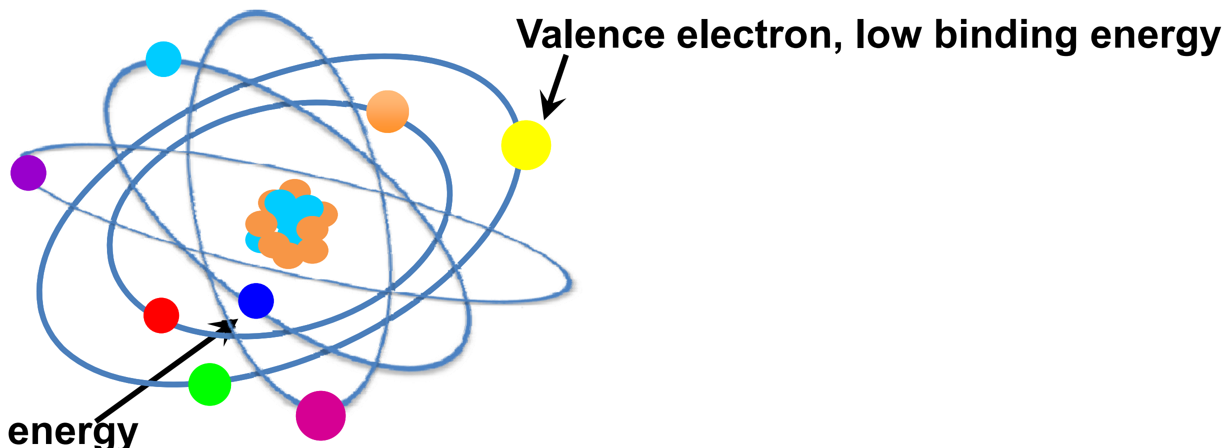


- For conductive sample, the sample is grounded, and no surface charge is built on the sample surface
- For insulate sample, the sample can not be grounded, and surface charge is built on the sample surface
- Surface charge lead to kinetic energy loss of emitted electrons, leading to shift of XPS peak position

→Low-energy electrons alleviates build up of positive charge

Chemical State Information

- The **binding energy** of an electron is dependent on the atomic orbital the electron occupies & the chemical environment of the atom



- XPS therefore provides information on the chemical state of the atom or ion

C 1s photoemission peaks from organic materials

	Functional group	B.E (eV)
hydrocarbon	C-H, C-C	285.0
amine	C-N	286.0
alcohol, ether	C-O-H, C-O-C	286.5
fluorocarbon	C-F	287.8
carbonyl	C=O	288.0
2F bound to a carbon	$-CH_2CF_2-$	290.6
3F bound to a carbon	$-CF_3$	293-294

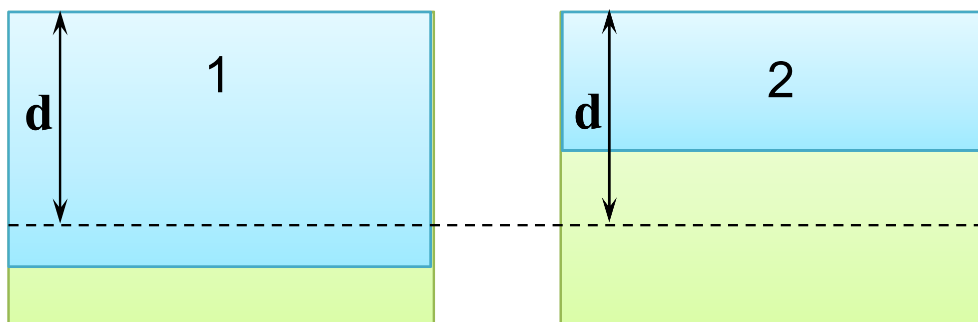
O 1s photoemission peaks from organic materials

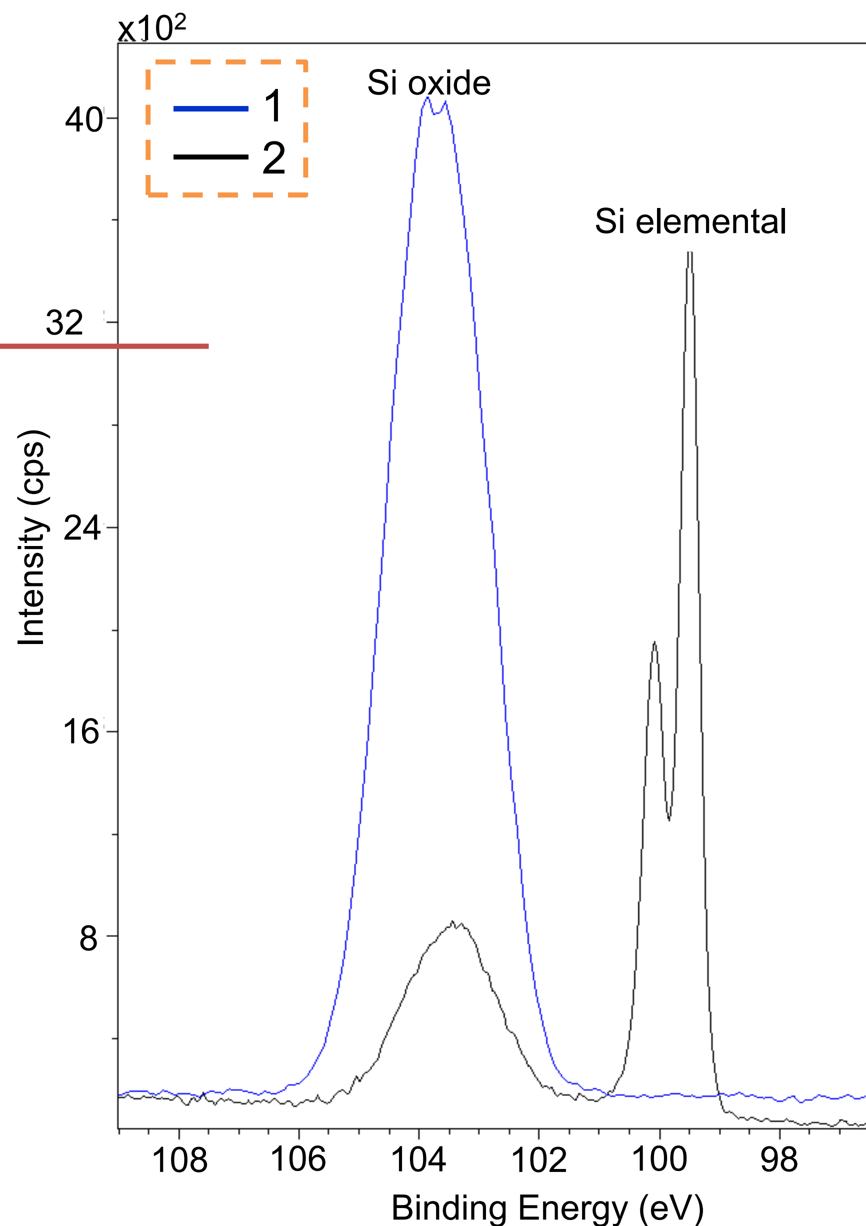
Functional group		B.E. (eV)
carbonyl	-C=O, O-C=O	532.2
alcohol, ether	-O-H, O-C-O	532.8
ester	C-O-C=O	533.7

Chemical State: Si

- **Two** samples:
  1. Thick film SiO_2 film on Si
  2. Thin film SiO_2 film on Si

→Large chemical shift between elemental Si & silicon dioxide peaks





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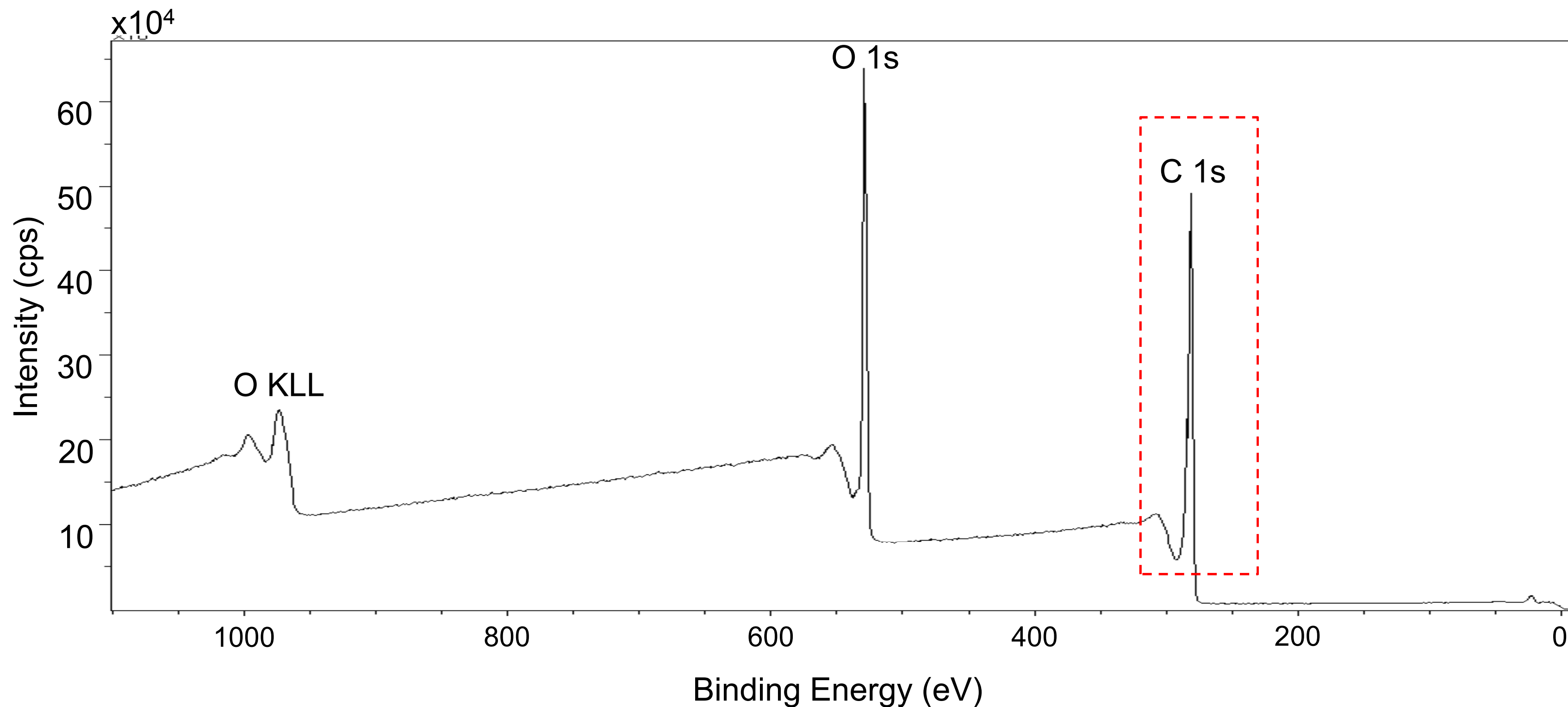
Quantitative Surface Analysis

Poly(ethylene terephthalate) - PET → Large Area Survey



Peak	Position B.E. (eV)	Atomic Conc. (%)
C 1s	282	74.54
O 1s	530	25.46

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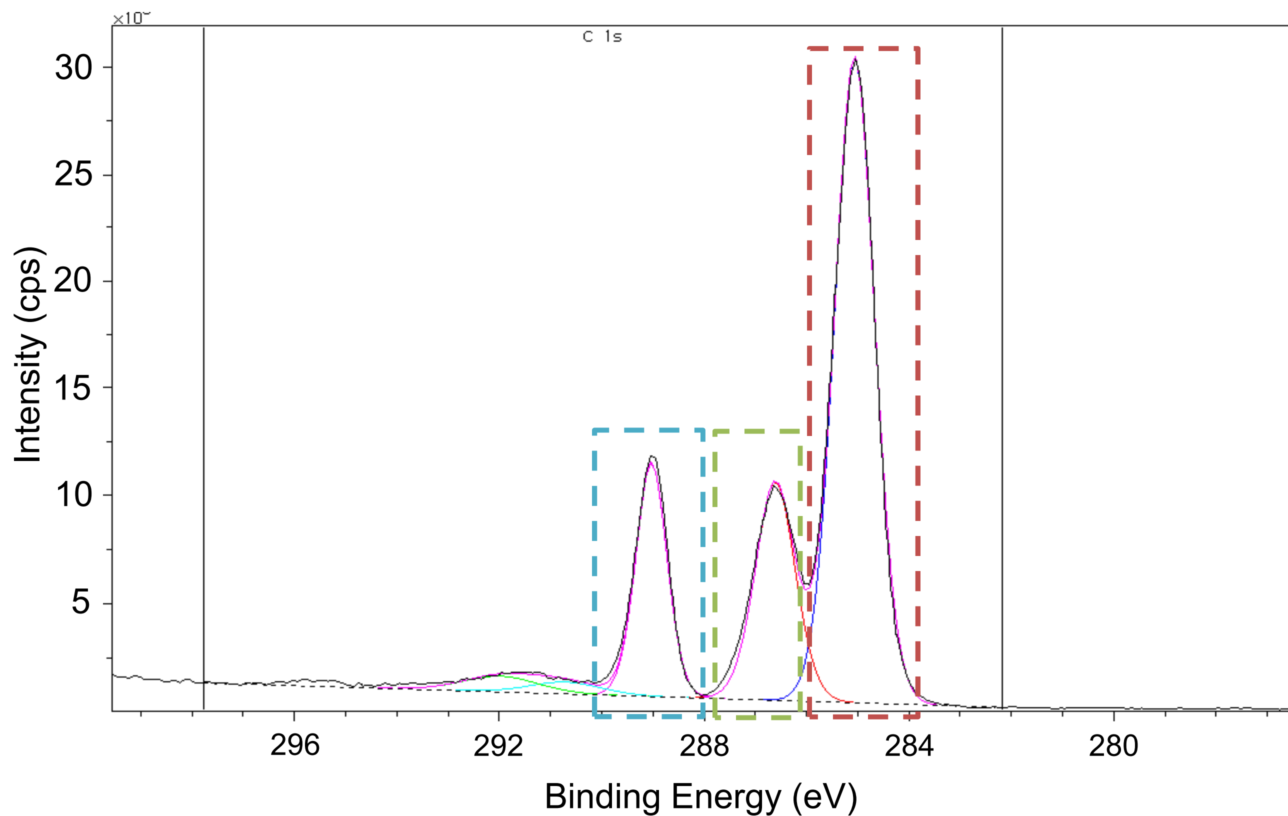
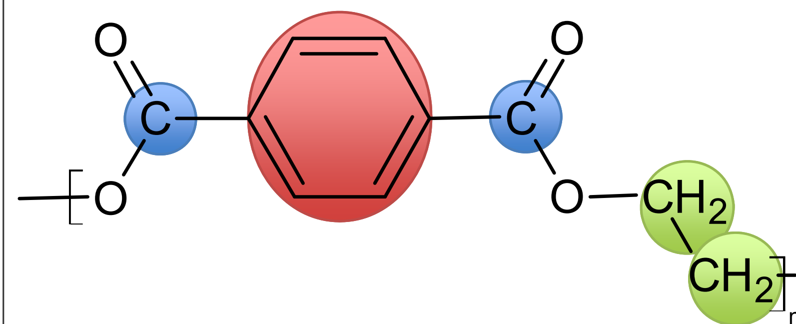
Neutralisation of Insulating samples

Poly(ethylene terephthalate) - PET → Narrow region





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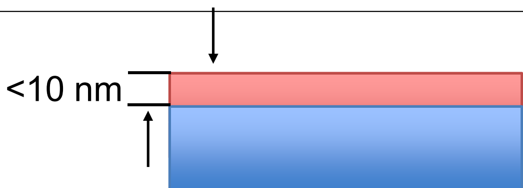
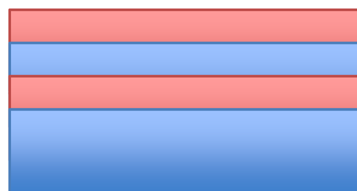
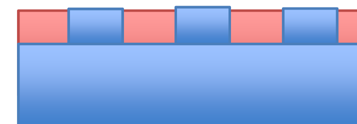
Beyond Large Area Spectroscopy



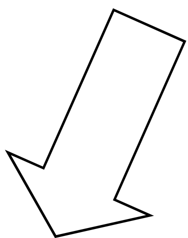


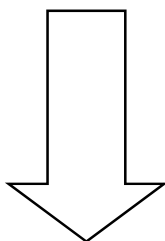


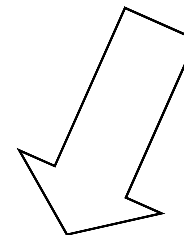
Thin film

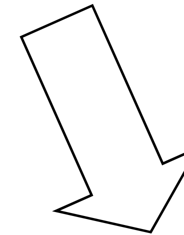
Thicker layer or multilayers

Heterogeneous surface







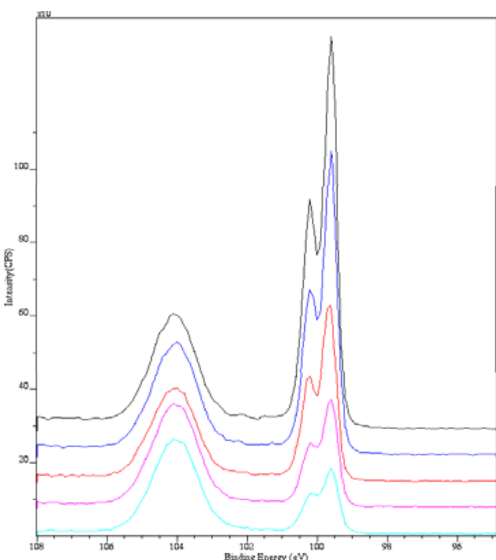


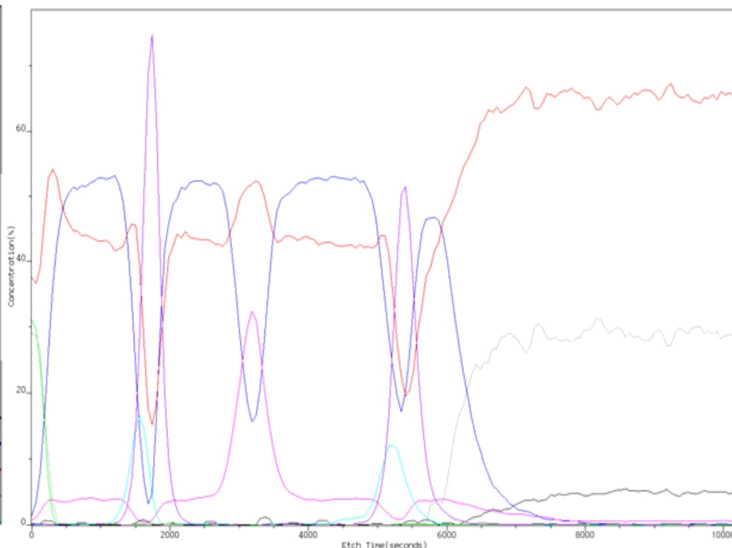
Angle resolved XPS

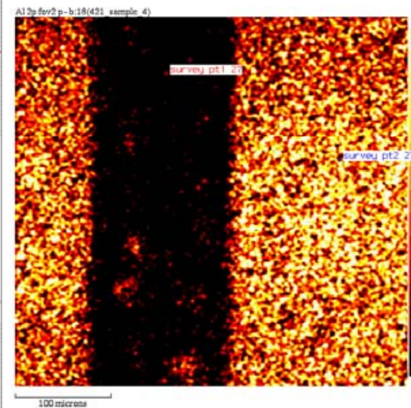
Depth profile

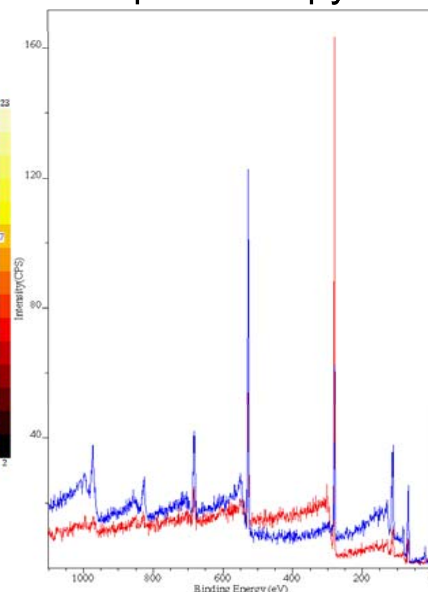
Surface imaging

Selected area spectroscopy

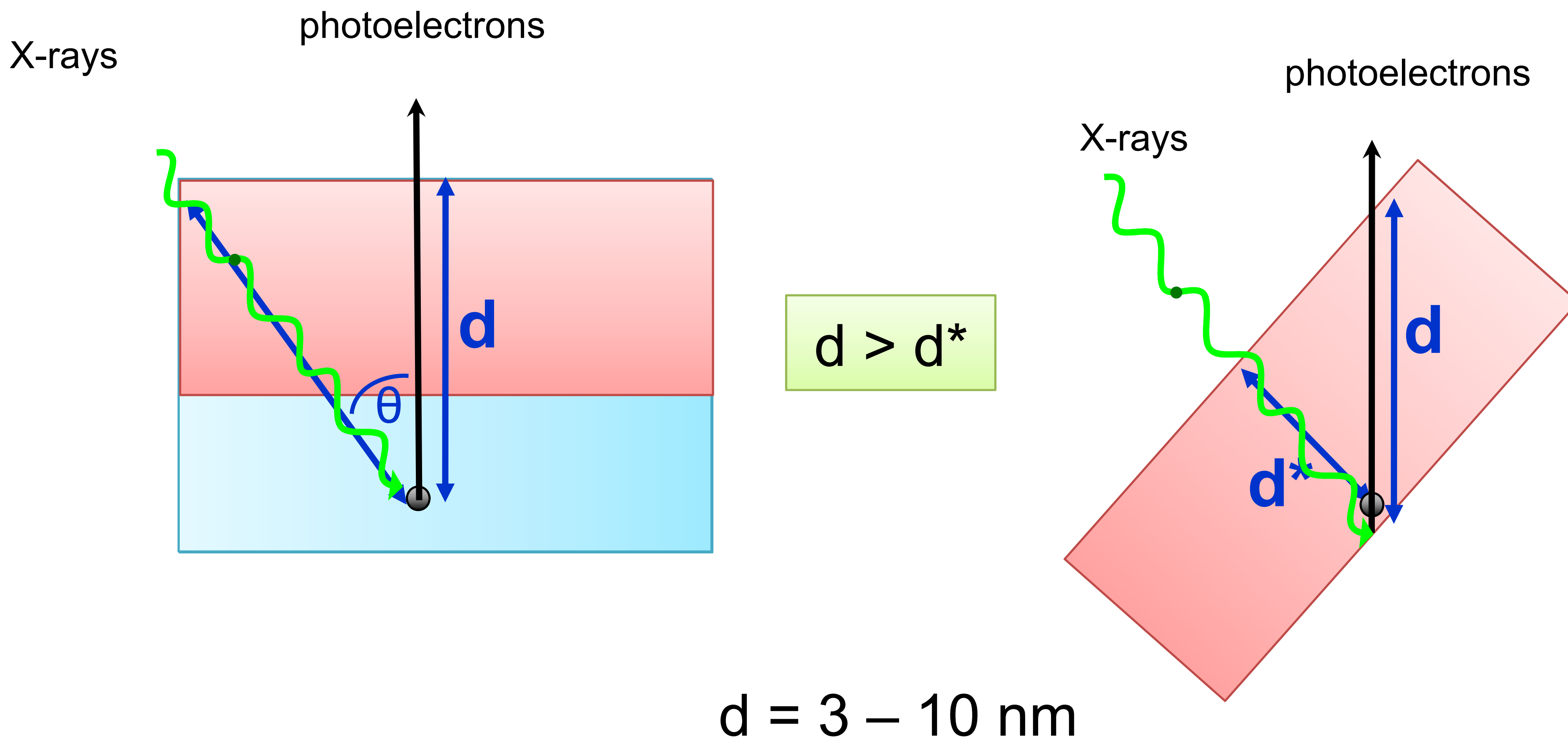








Angle Resolved XPS



d = 3 – 10 nm

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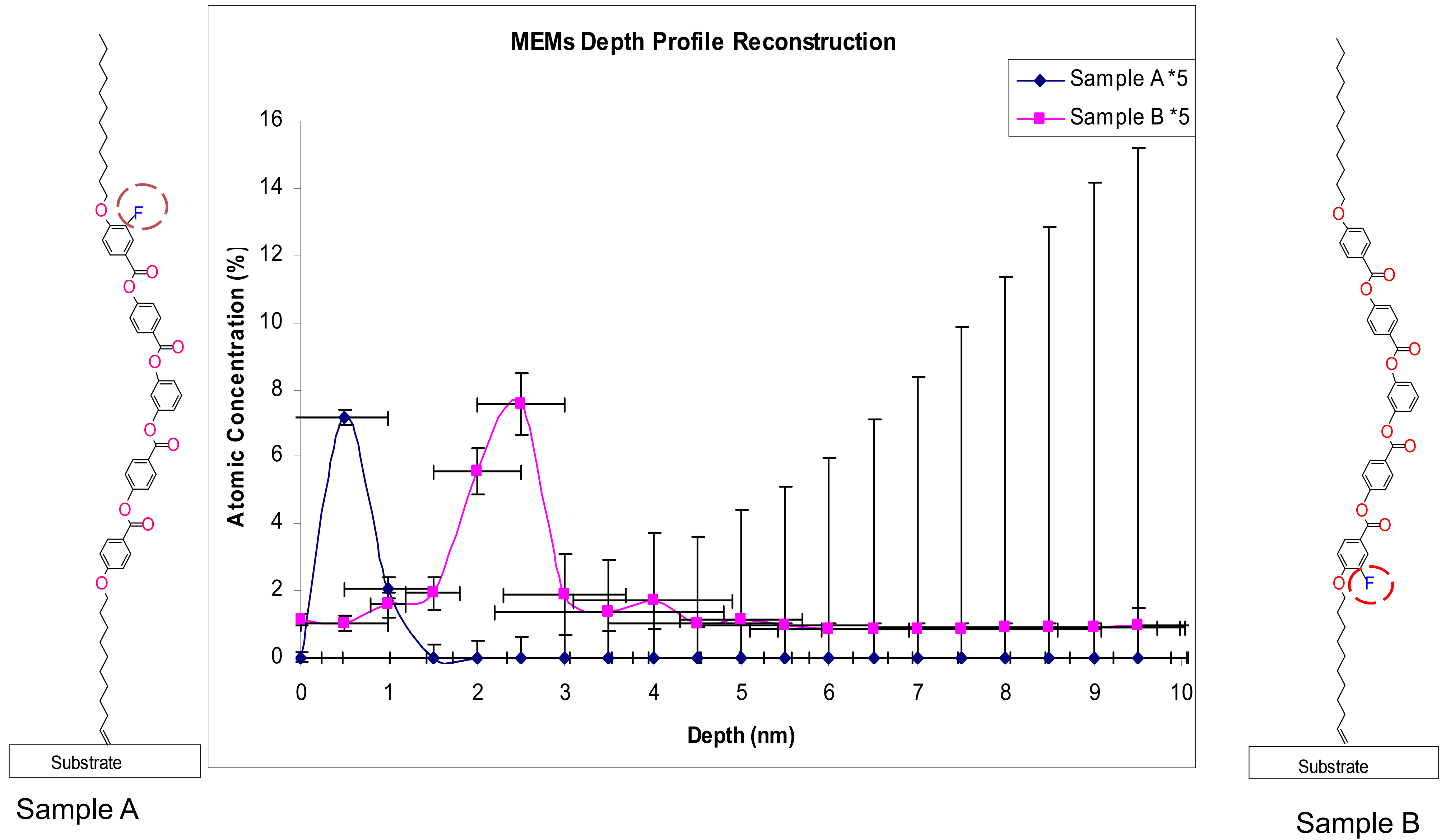
MEMs Depth Profile Reconstruction
– Depth Distribution of Fluorine



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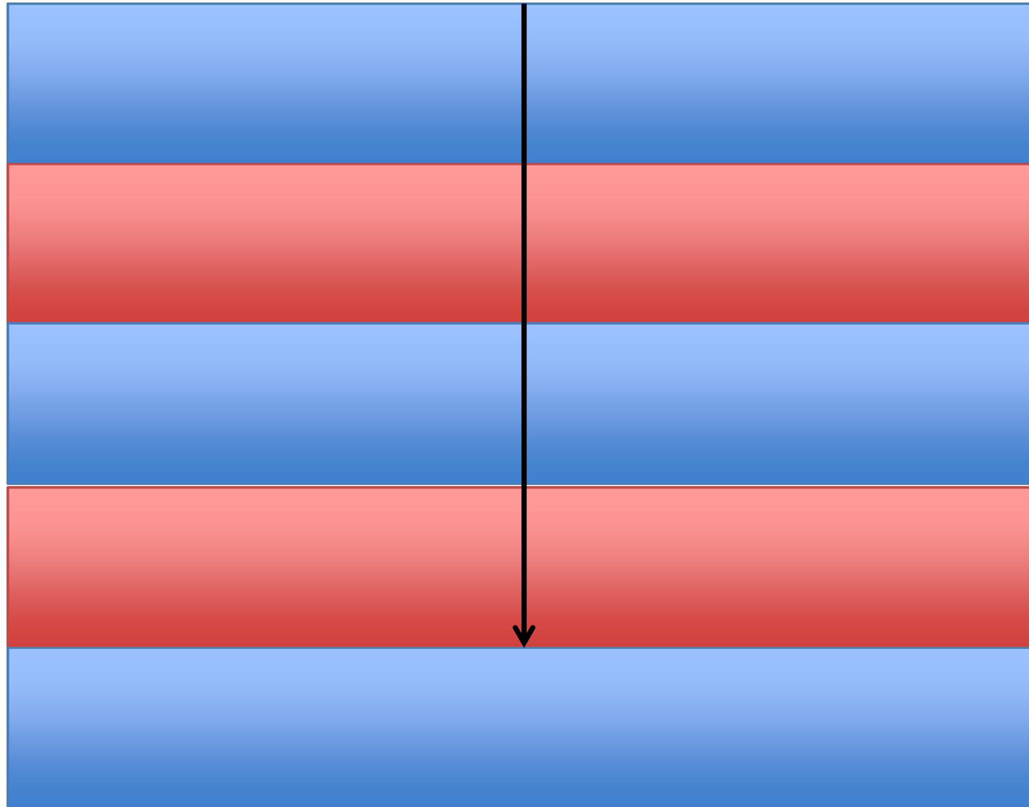
Depth Profiling

Multi-layered Structure:



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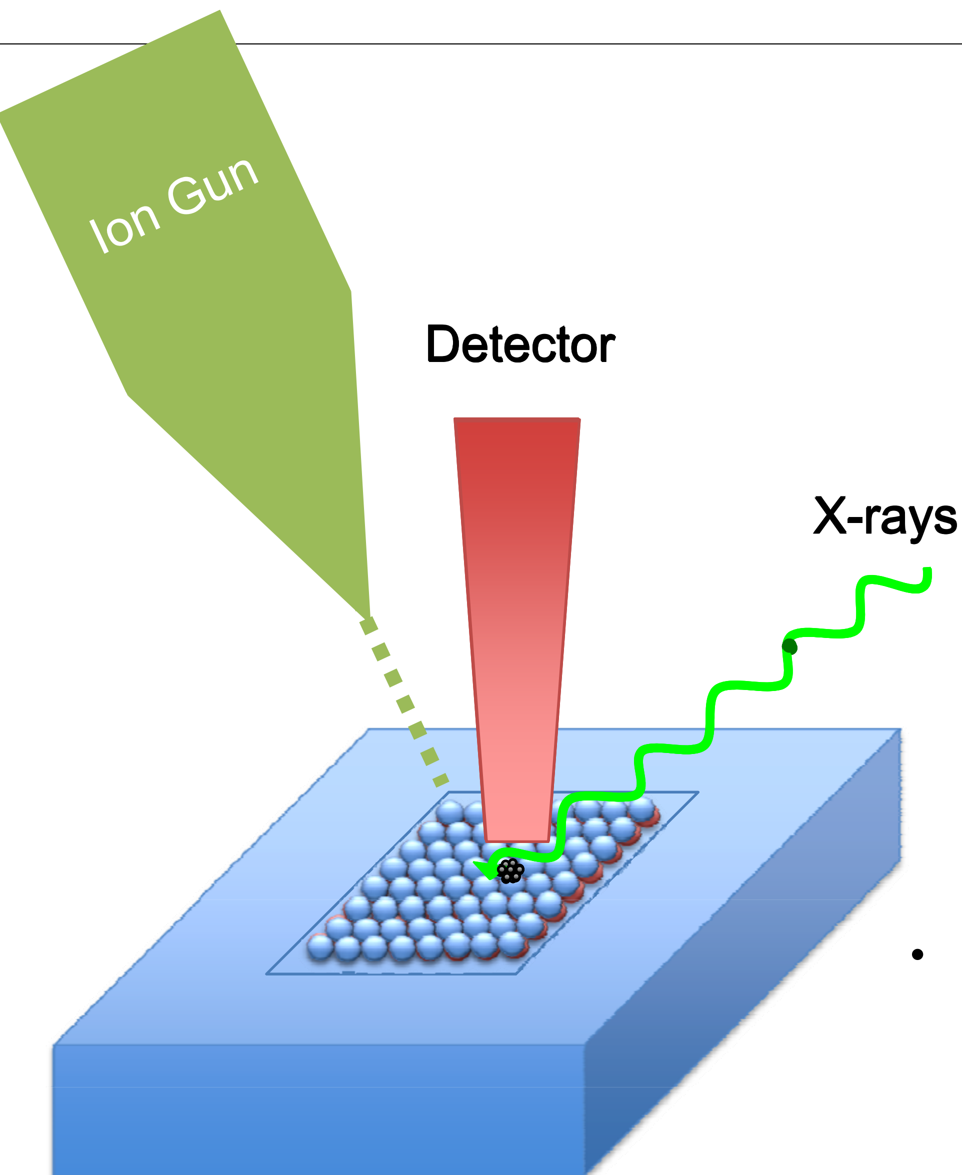
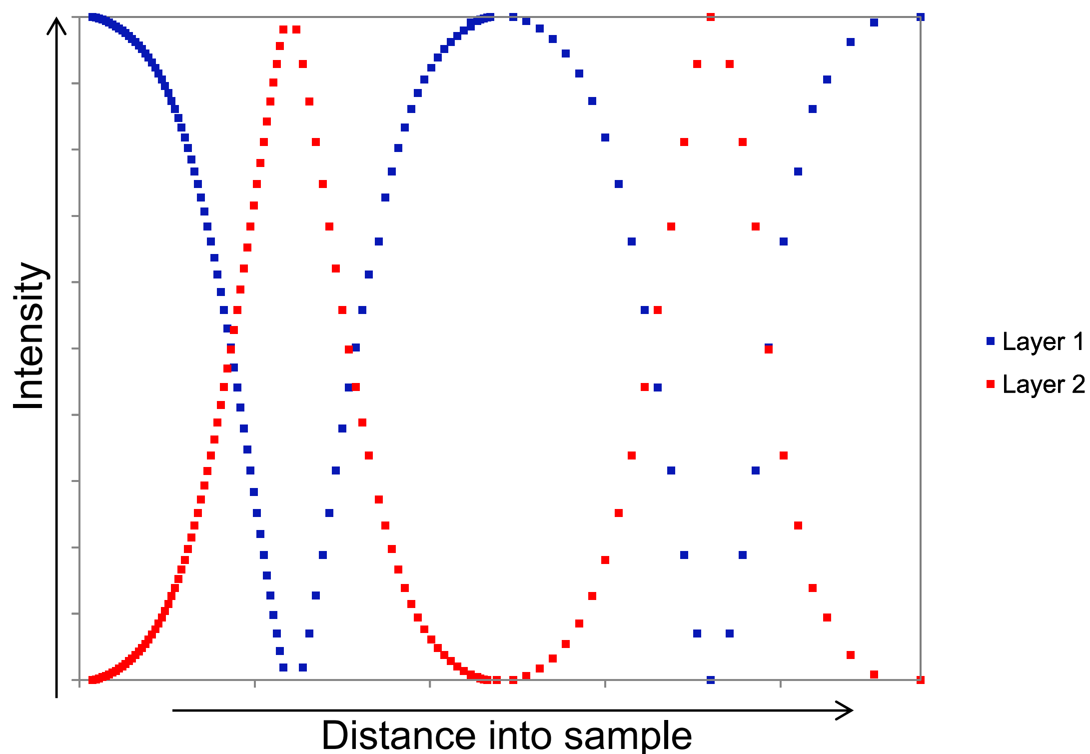
Depth Profiling

X-rays

Ion gun





- **Depth profiling** allows the identification of the chemical nature buried beneath the surface layers
  - The rate of etching depends on material properties
  - Organic and inorganic materials is possible

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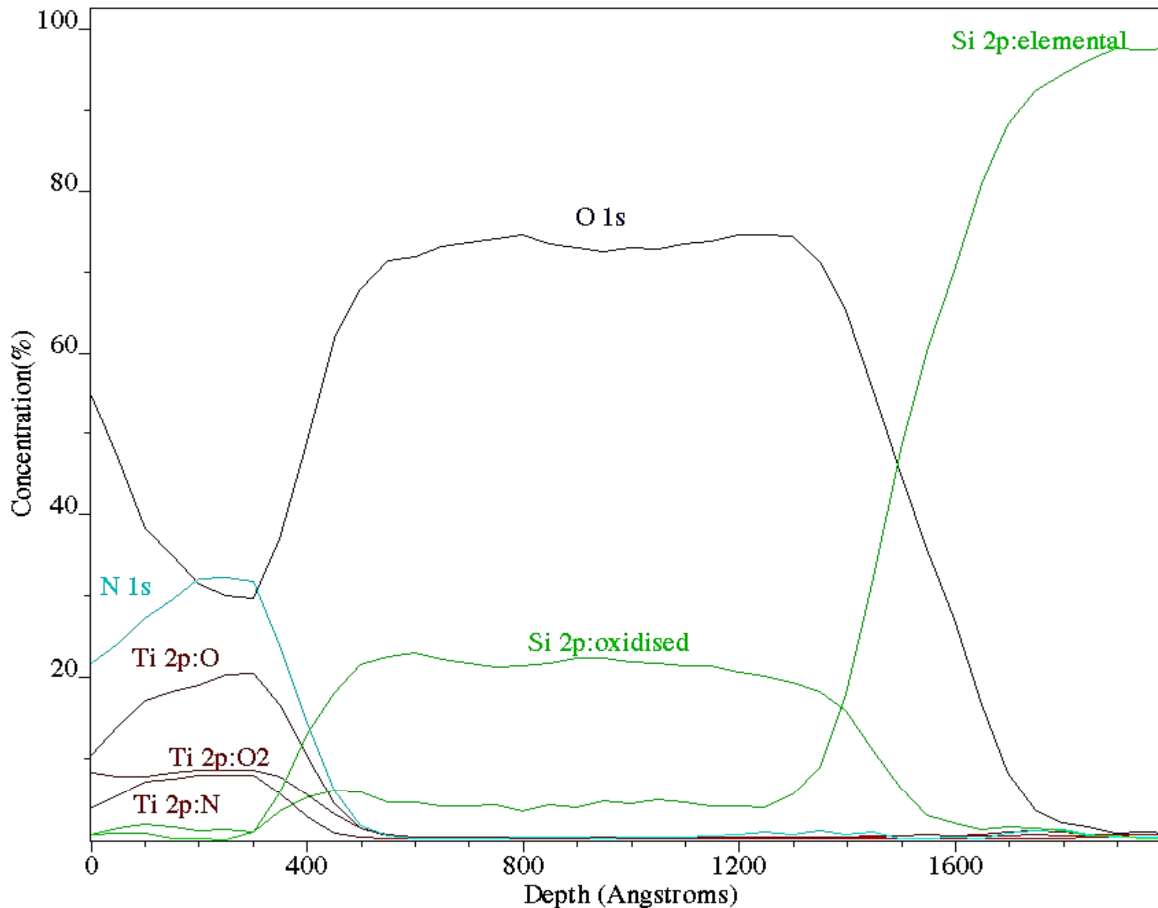
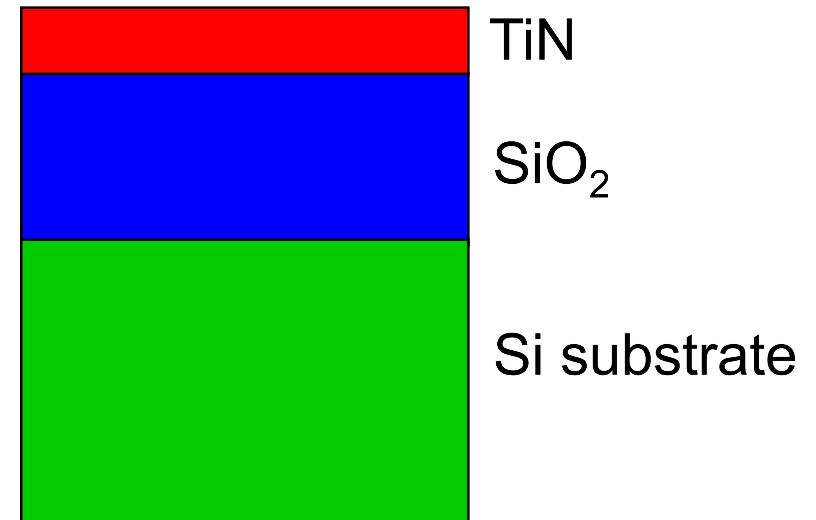
Depth Profiling

- Full chemical state concentration depth profile through TiN film:
- Can determine film thickness





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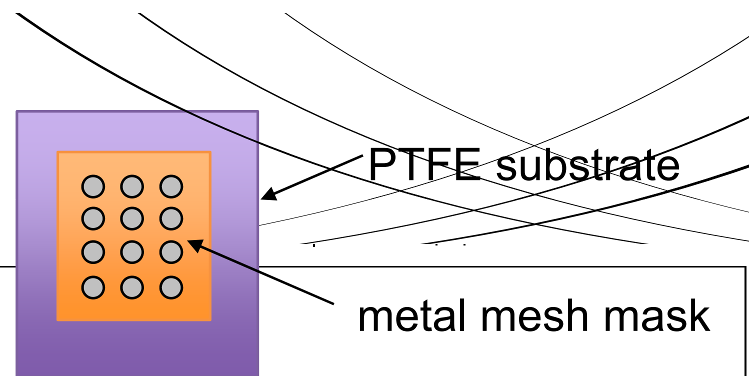
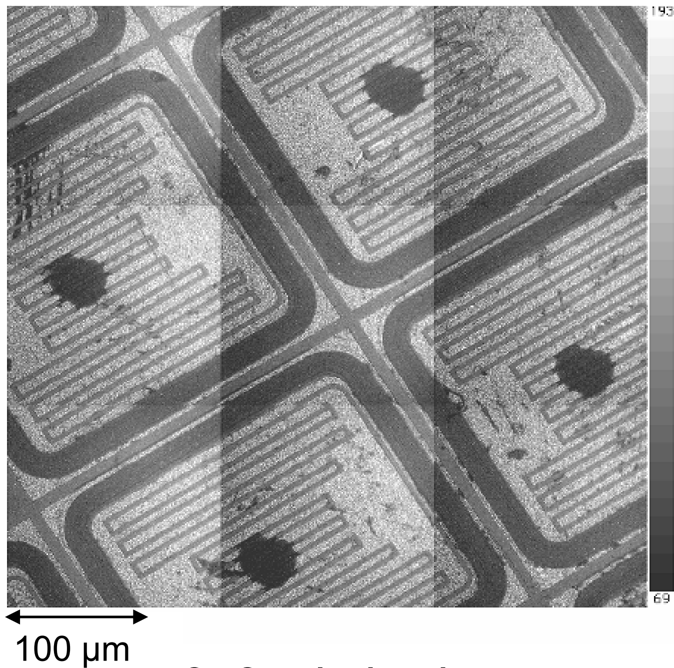
Imaging



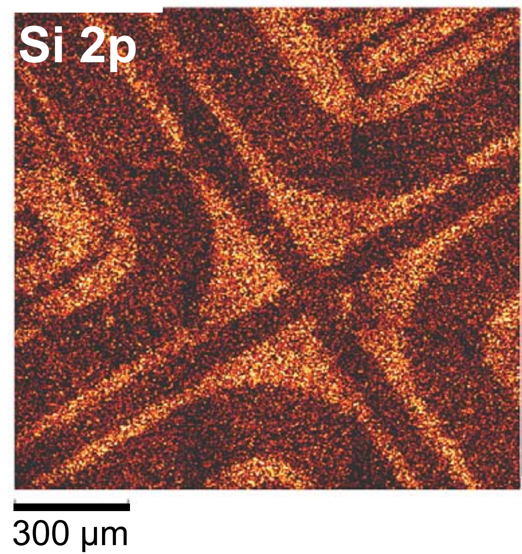
- **Imaging** allows the identification of inhomogeneity
  - 1 µm lateral resolution
  - Stitching of images allows larger area analysis

Imaging

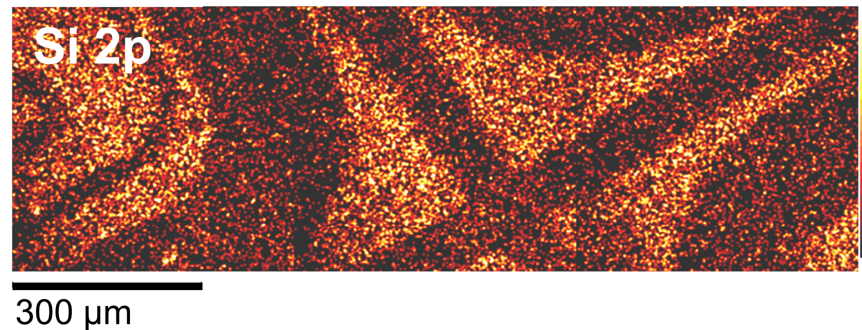
- Stitching of images allows larger area analysis:



3x3 stitched



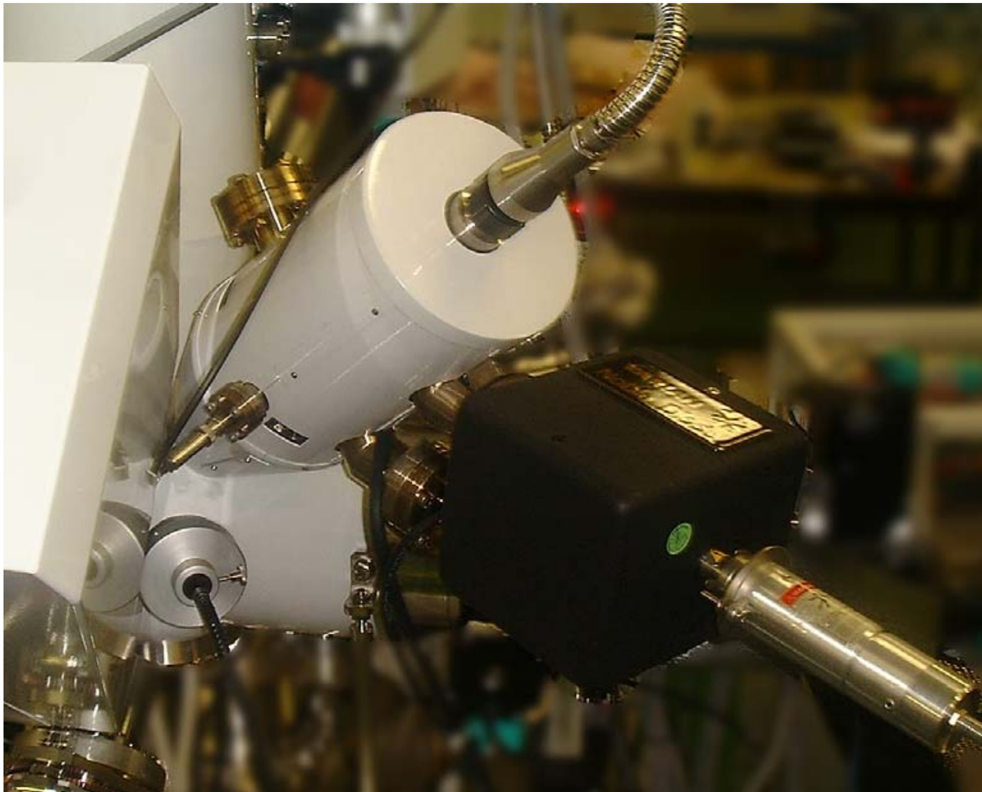
3x3 stitched parallel image

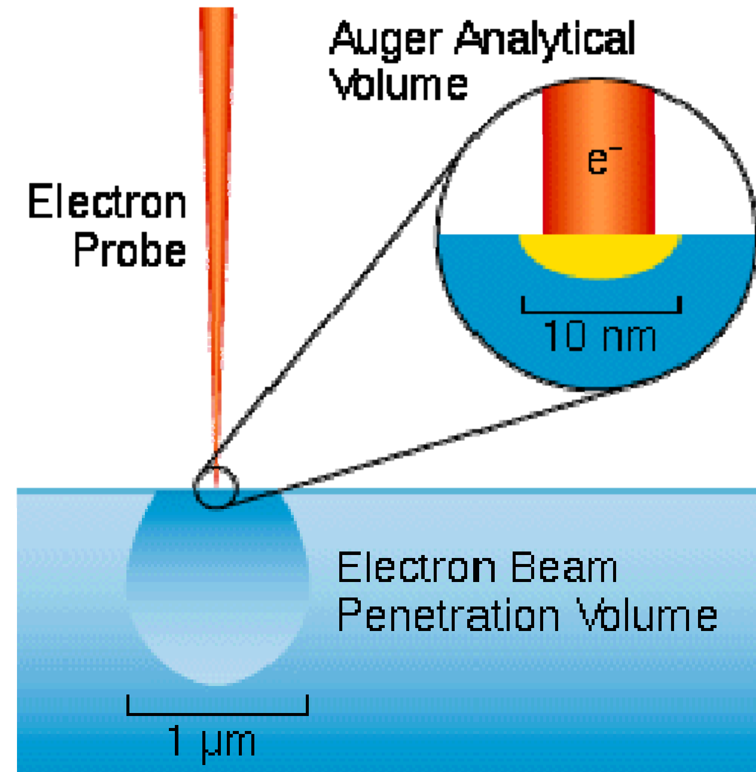


1x3 stitched parallel image

Related Techniques

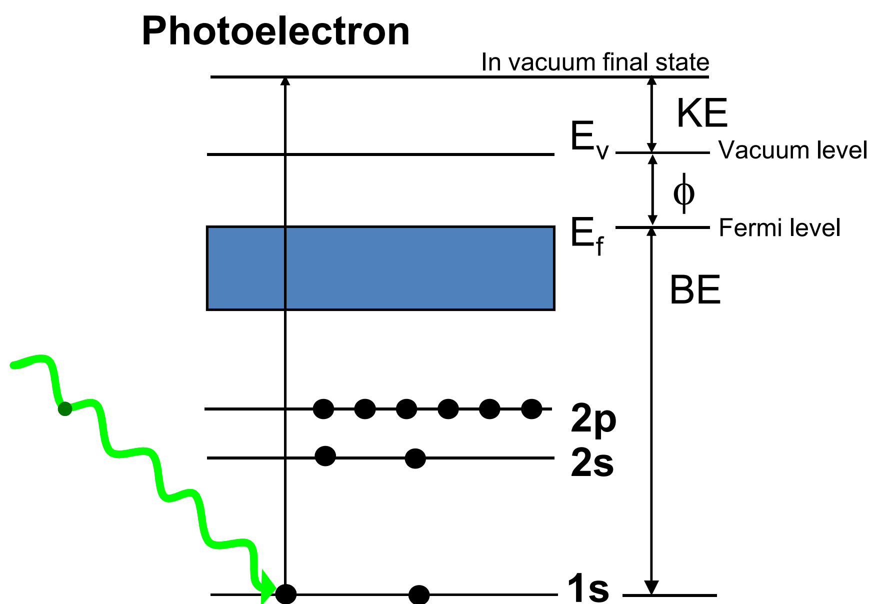
Auger Electron Spectroscopy



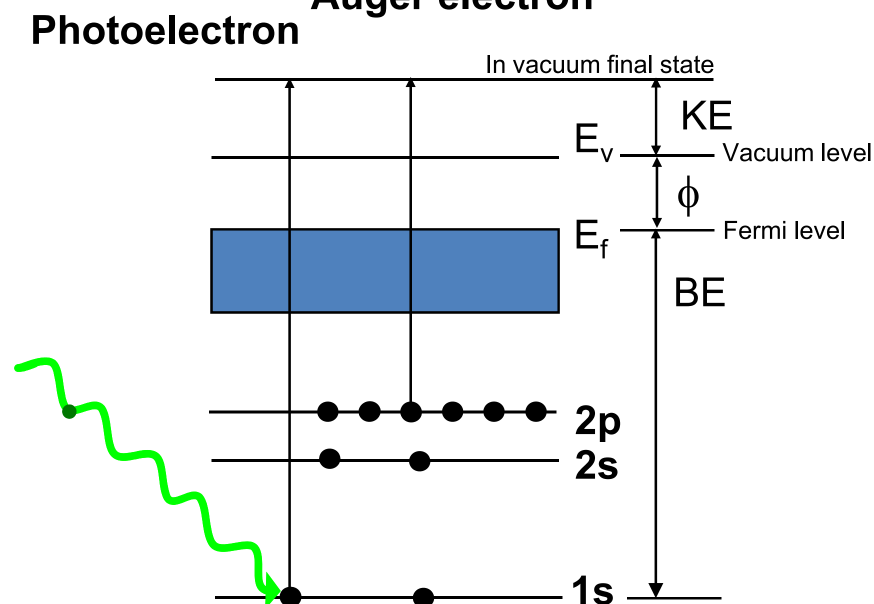


XPS & Auger Spectroscopy

- XPS



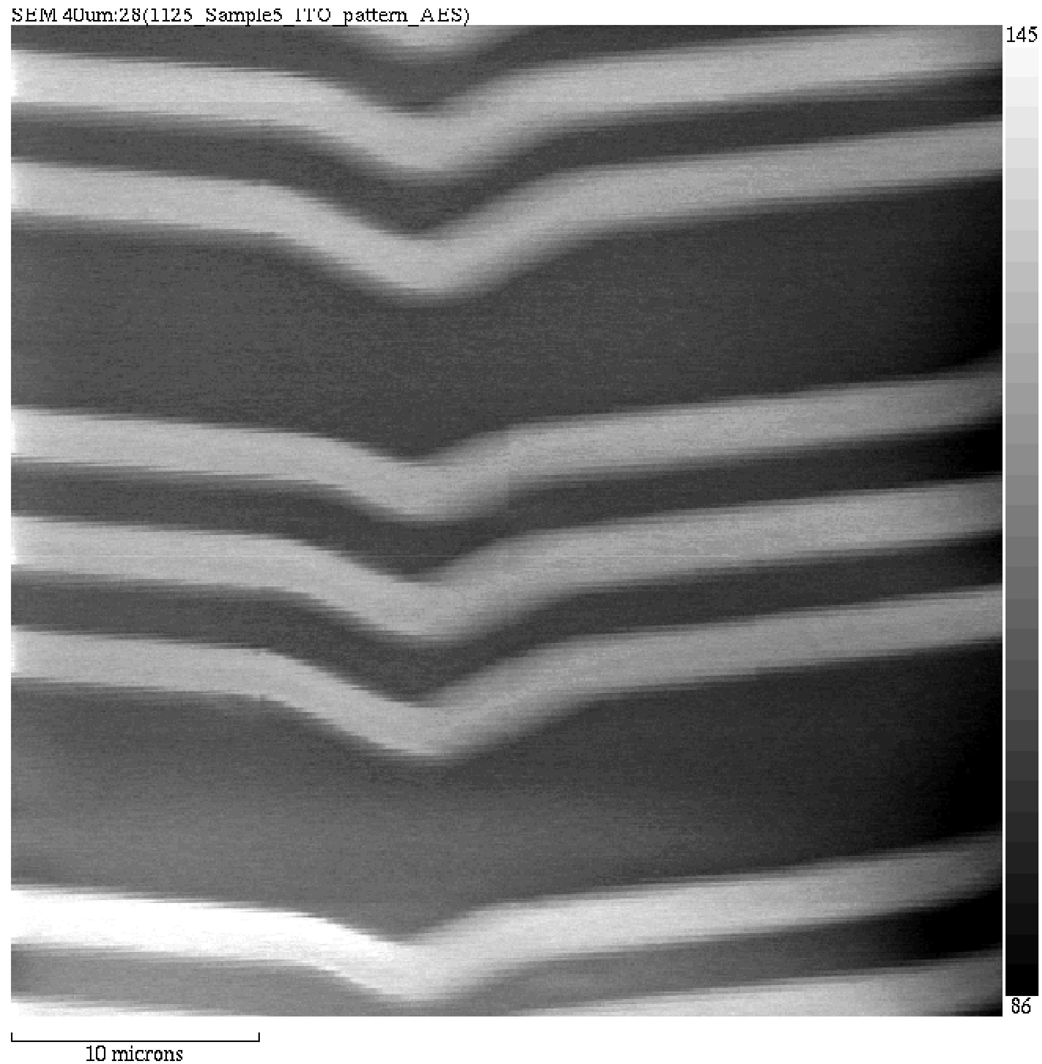
- Auger



SEM image of an ITO pattern

SEM image of an ITO pattern surface recorded using the FEG source.

Image field of view is 40 um.



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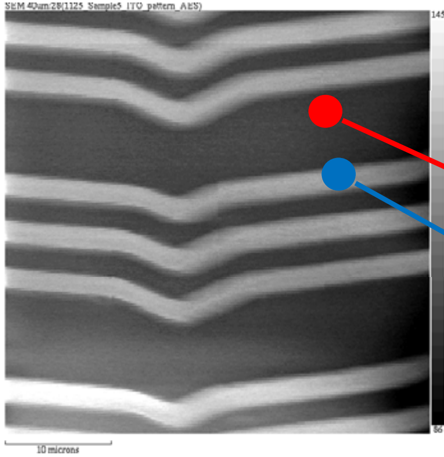
Auger spectra



Auger spectra were recorded from positions defined by the above SEM map.

These spectra are displayed opposite, red from the substrate and blue from the line feature.

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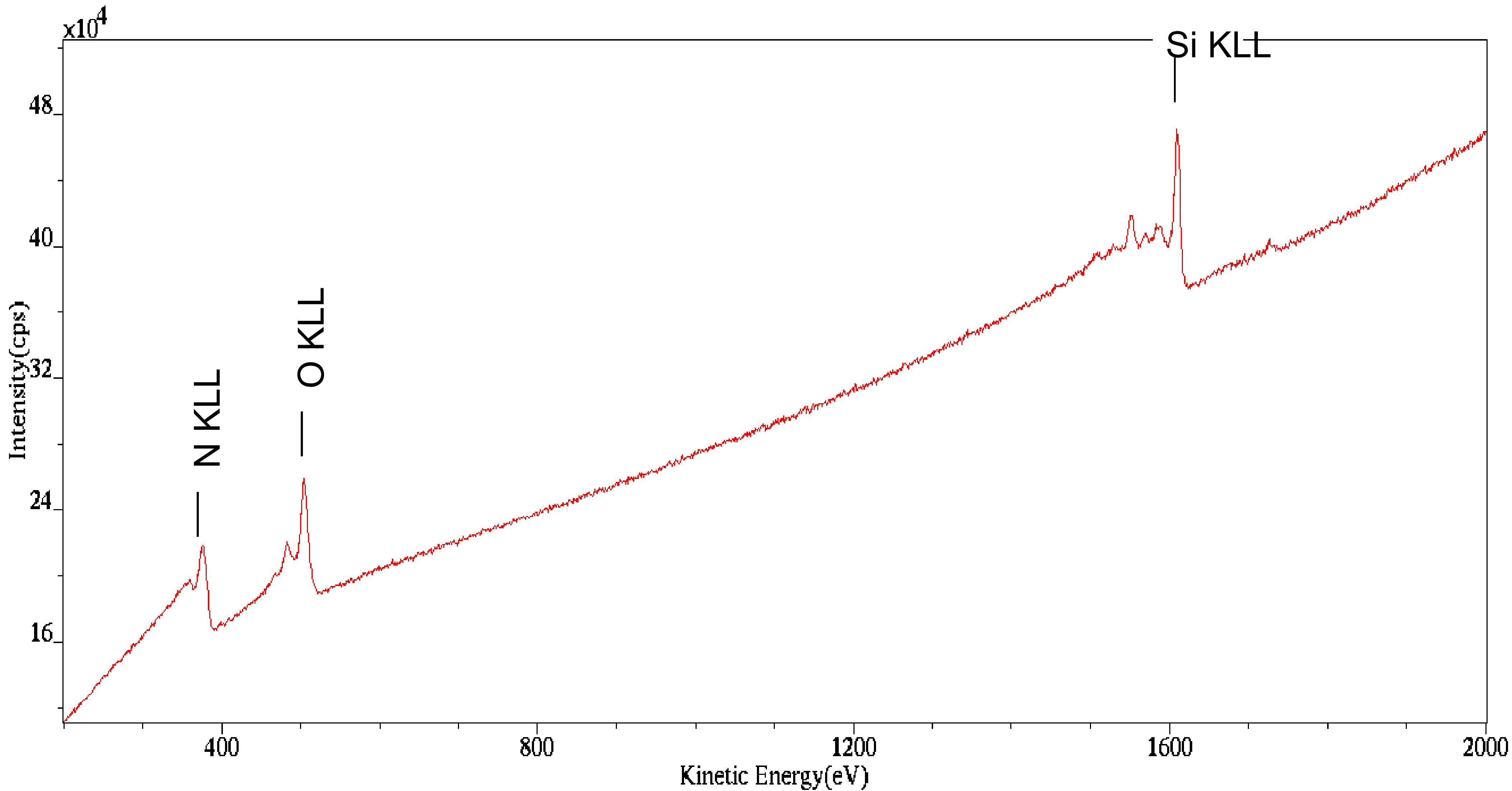
Auger spectrum – substrate region



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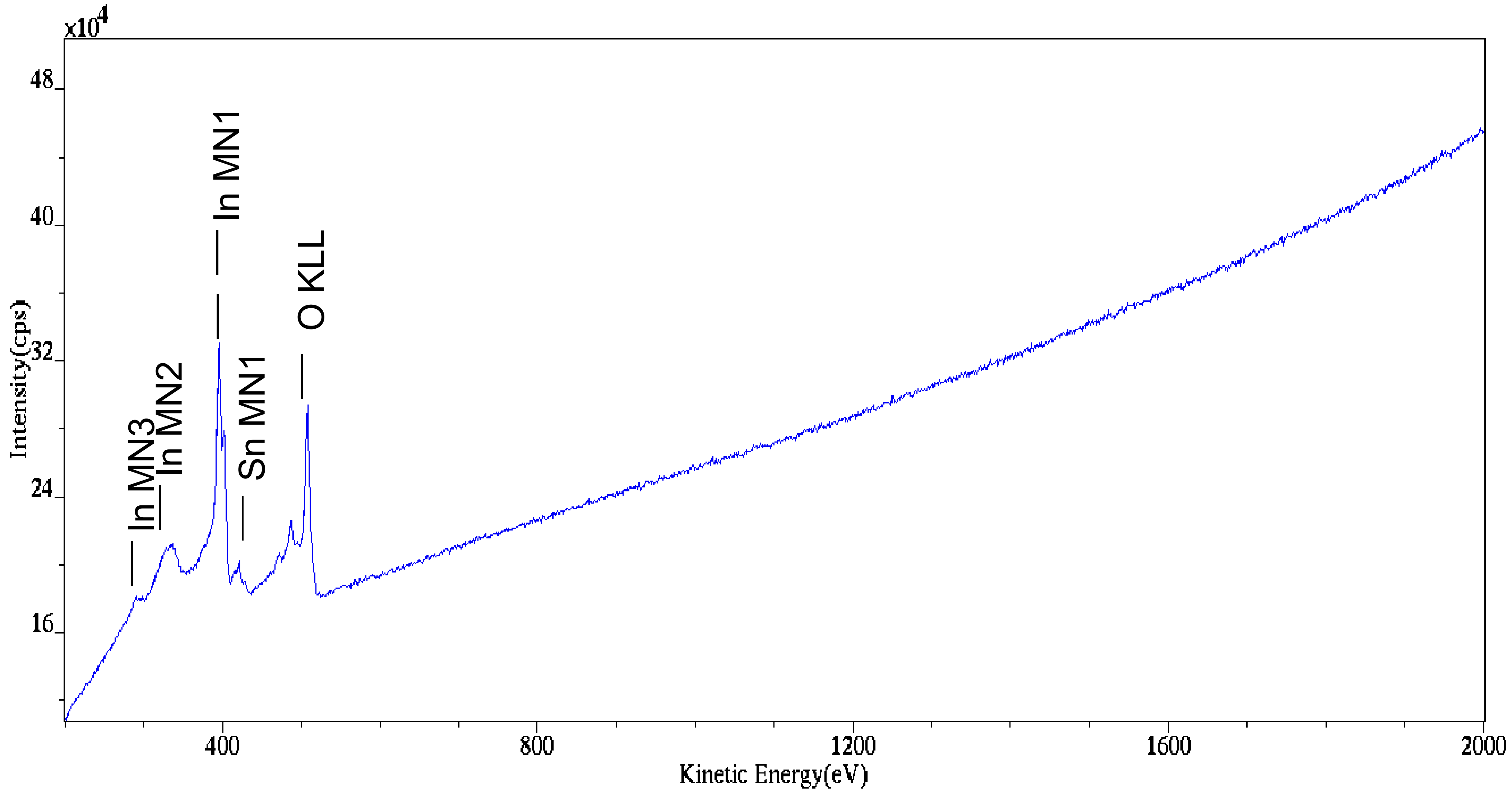
Auger spectrum – line region



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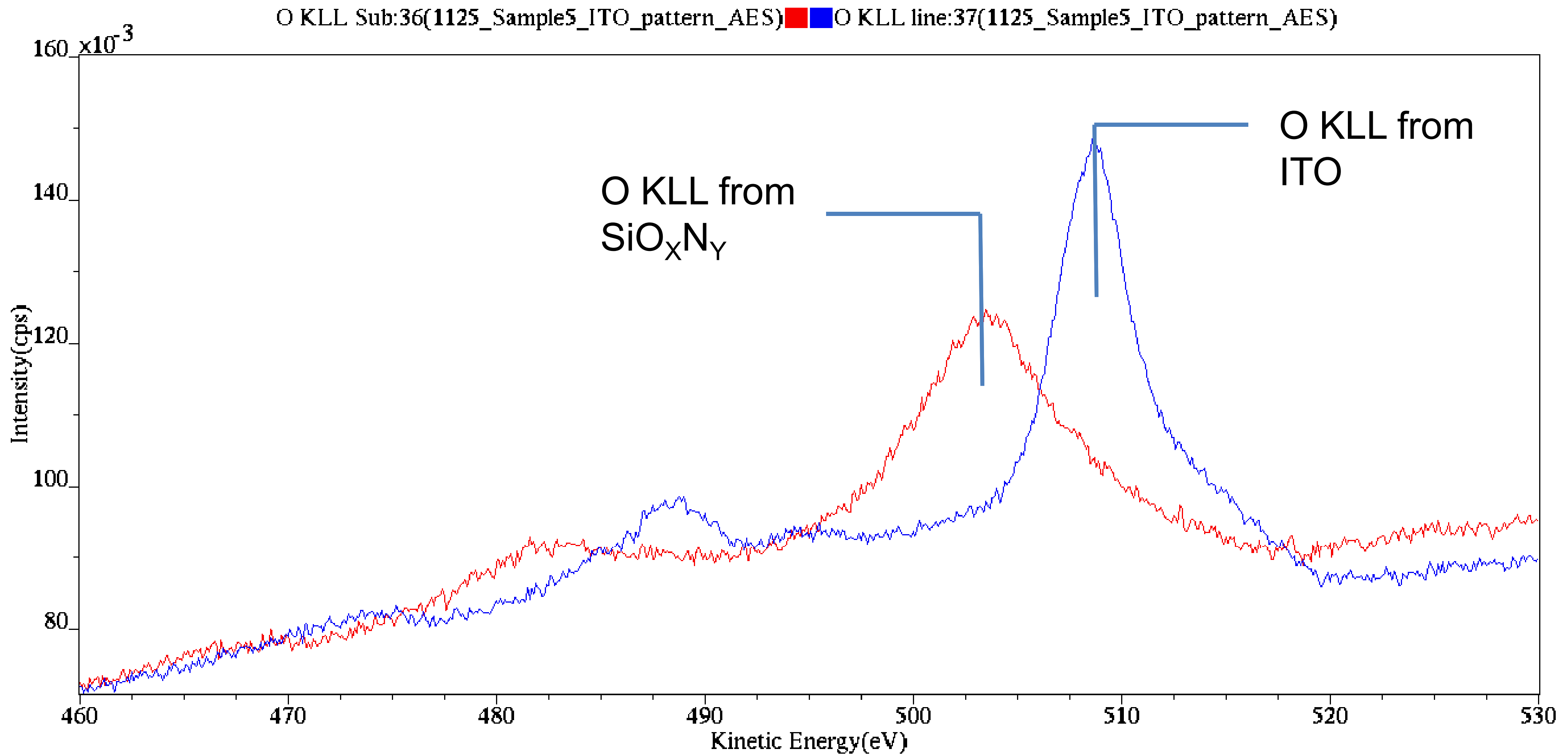
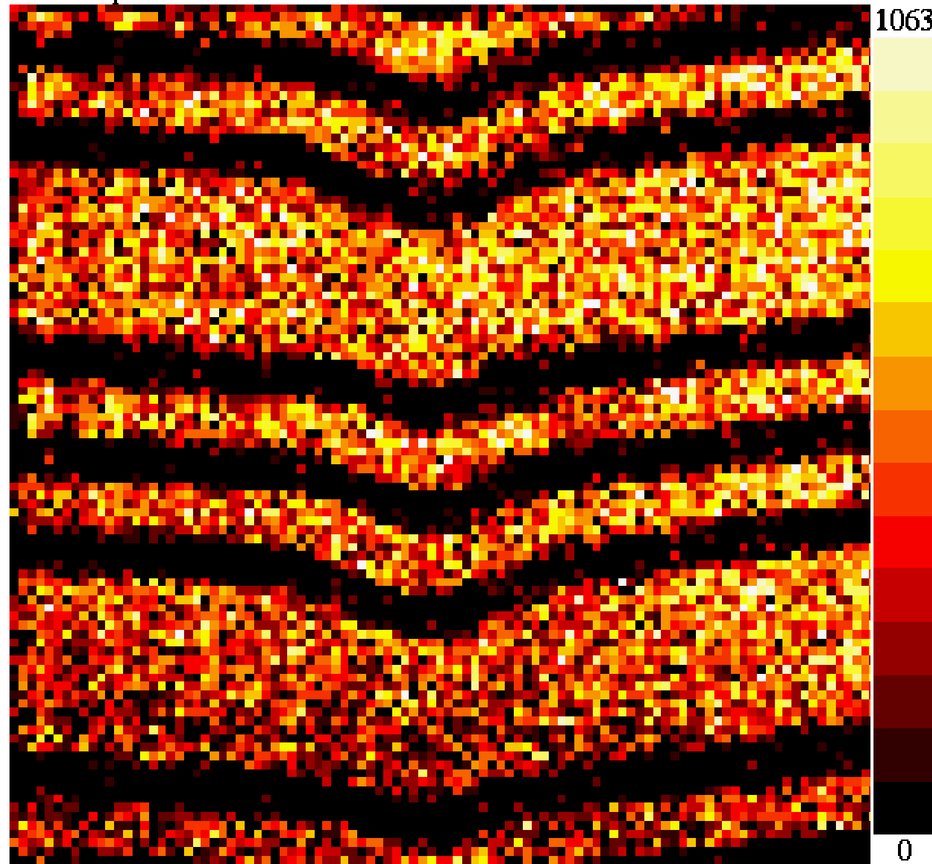
High resolution Auger O KLL spectra

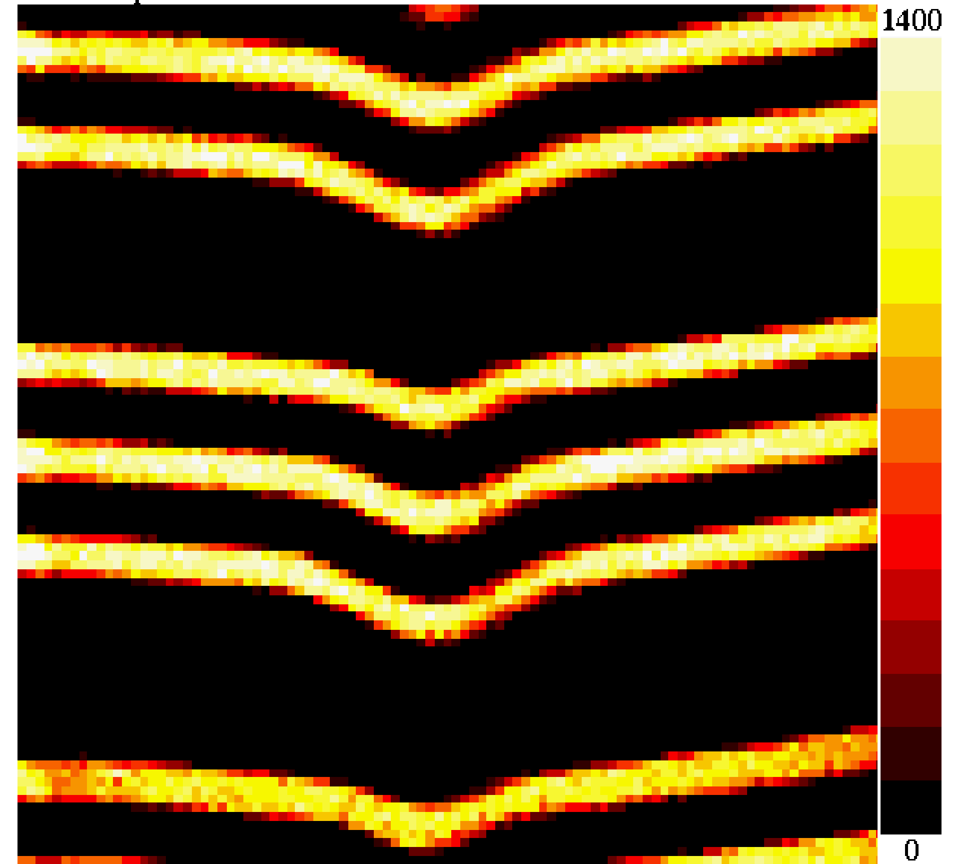
High resolution O KLL Auger spectra recorded from the substrate (red) and from the line (blue) demonstrating the different O chemistry. Spectra were normalised to unit area to aid comparison.



Scanning Auger Microscopy

Auger maps recorded of the 40 micron area. Si KLL peak minus background map (left) and In MNN peak minus background map (right). Each map was recorded with 100 x 100 pixels with a total acquisition time of 800 s.





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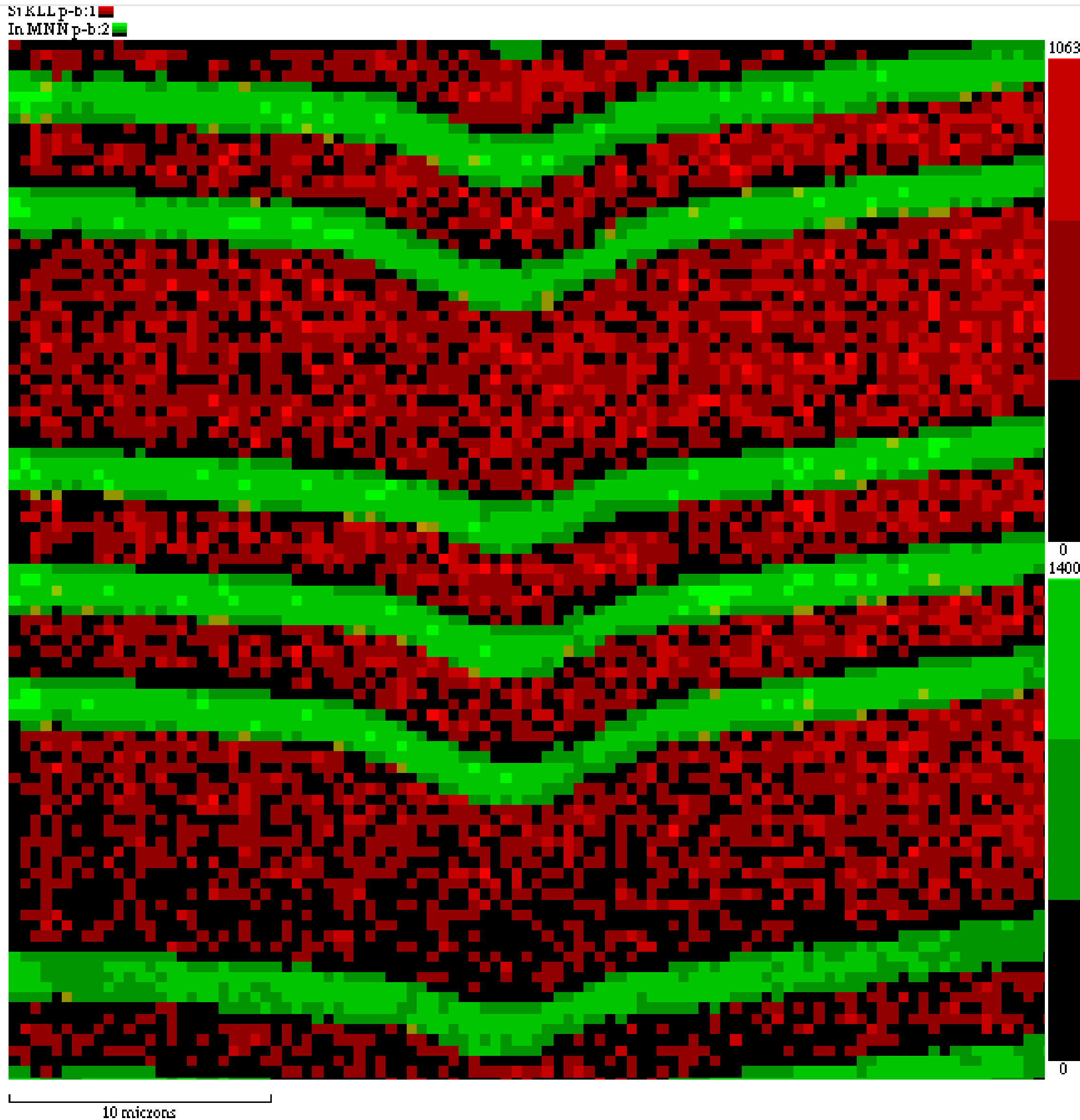
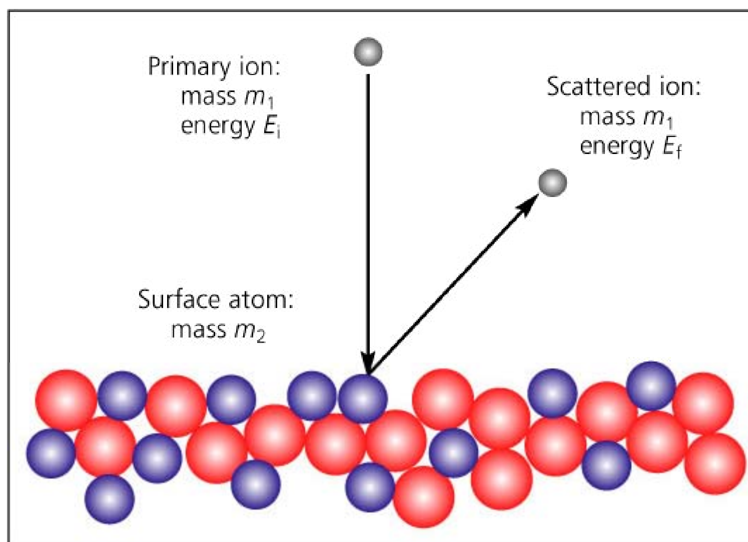
Scanning Auger Microscopy



Overlay of Si KLL peak minus background map (red) and In MNN peak minus background map (green).

Ion Scattering Spectroscopy (ISS)

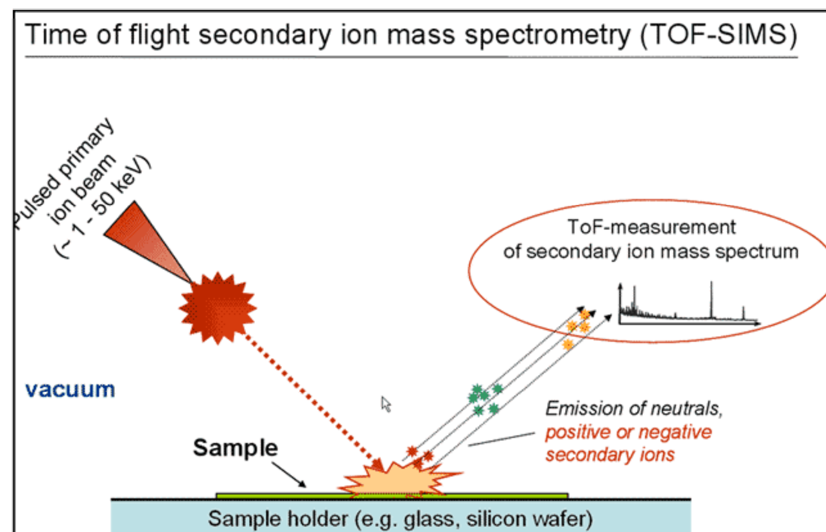
- Surface-sensitive analytical technique used to characterize the chemical and structural makeup of materials (can be semi-quantitative)
- ISS measures **the change in kinetic energy of a low-energy primary ion that is scattered elastically from the sample surface.** If the ion penetrates below the first atomic layer, the probability of inelastic scattering also becomes high, and, through the resulting multiple collisions, the ion loses a significant fraction of its energy. Thus, ion-scattering spectra usually consist of a series of elastic scattering peaks superimposed on a broad background from the inelastically scattered ions.
- Involves **directing a stream of charged particles known as ions** at a surface and making observations of the positions, velocities, and energies of the ions that have interacted with the surface



- Data that is collected can be used to **deduce information about the material such as the relative positions of atoms in a surface lattice and the elemental identity of those atoms.**

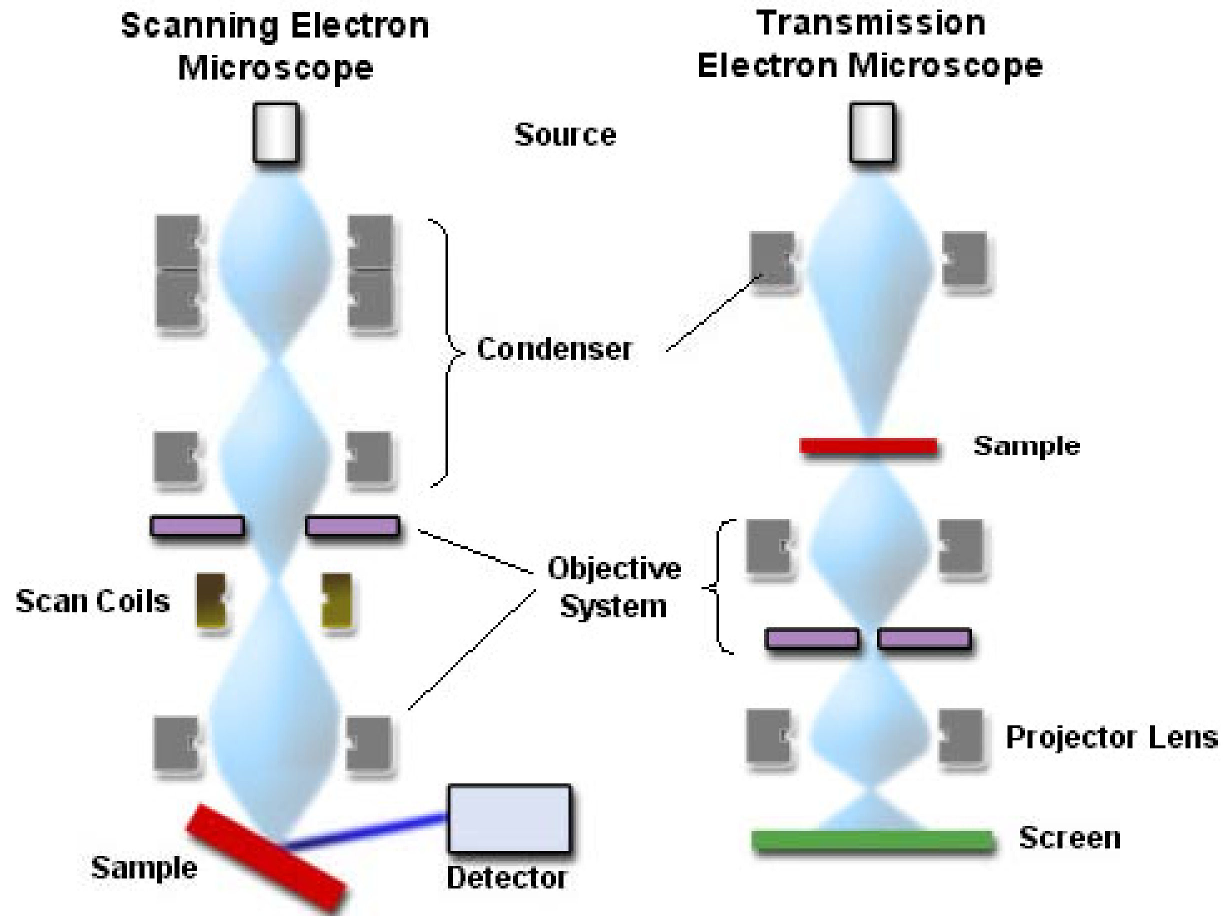
Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

- ToF-SIMS is a surface-sensitive analytical method that uses a pulsed ion beam (Cs or microfocused Ga) to remove molecules from the very outermost surface of the sample
- The particles are removed from atomic monolayers on the surface (secondary ions)
- These particles are then accelerated into a "flight tube" and their mass is determined by measuring the exact time at which they reach the detector (i.e. time-of-flight)
- Three operational modes are available using ToF-SIMS: surface spectroscopy, surface imaging and depth profiling



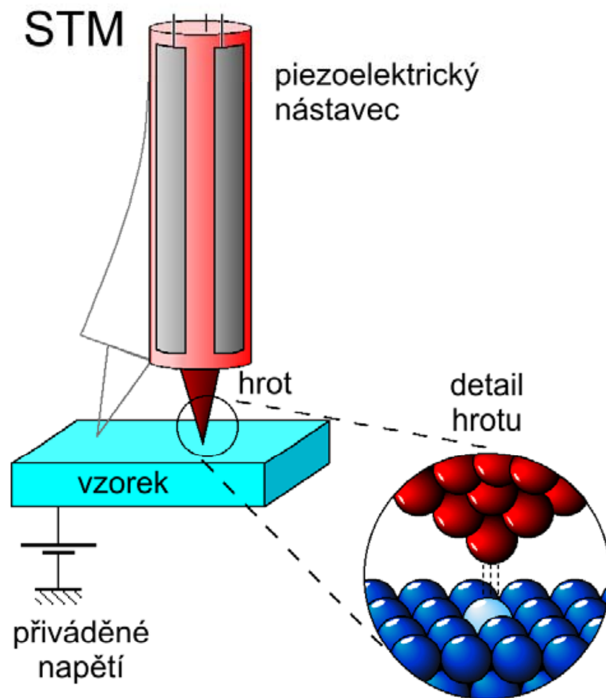
SEM & TEM

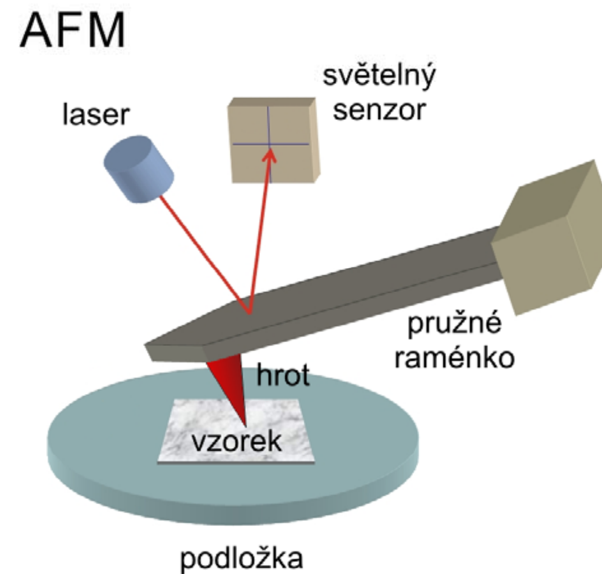
- Surface morphology (chemical information from EDX)
- Resolution of SEM ~ 3.5 nm
- Resolution of TEM ~ 0.2 nm



STM & AFM

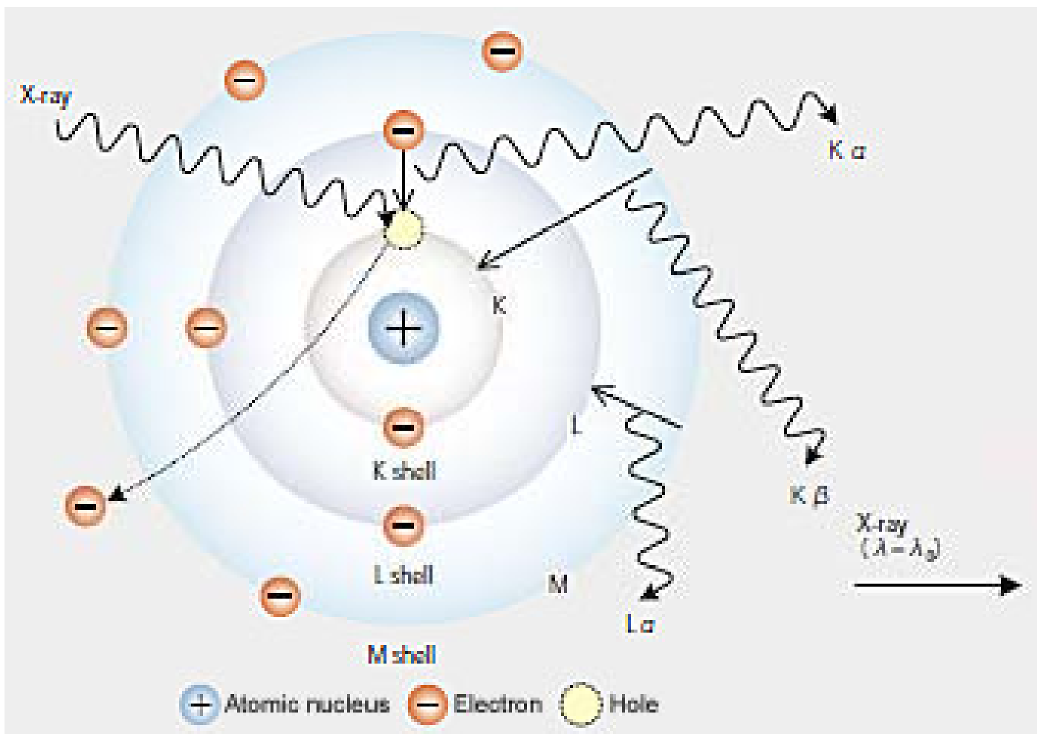
- Surface roughness / surface morphology / adhesive forces with functionalised tips
- STM – tunnelling current between a metallic tip & a conducting sample (close proximity but NO contact
- AFM – van der Waals forces between the tip & the surface (short range repulsive force in contact mode or larger range attractive force in non-contact mode)





Energy Dispersive X-ray Spectroscopy

- Elemental analysis or chemical characterization of a sample



- Energy resolution: 130 eV (Full Width Half Max) at Mn Kα
- Limit of detection: 1000 – 3000 ppm; >10% wt%
- Elements identified: elements heavier than Beryllium
- Spatial resolution: Low atomic number (Z): 1-5 um^3; High Z: 0.2 – 1 um^3

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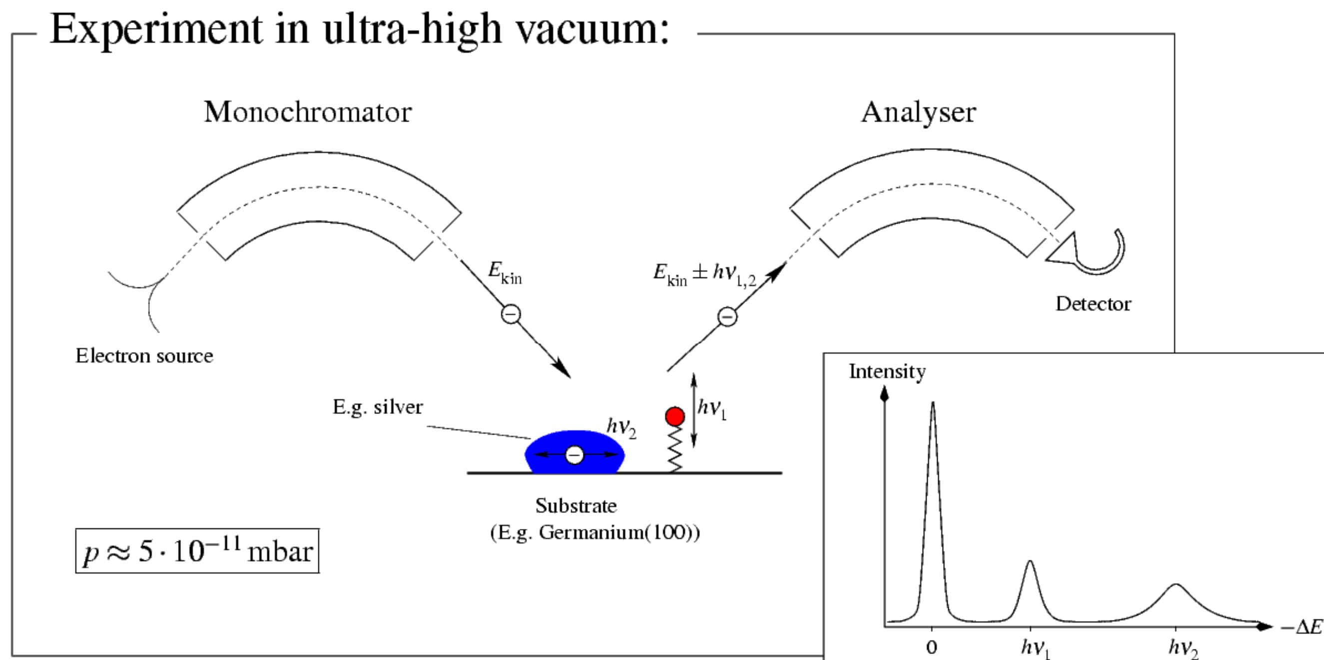
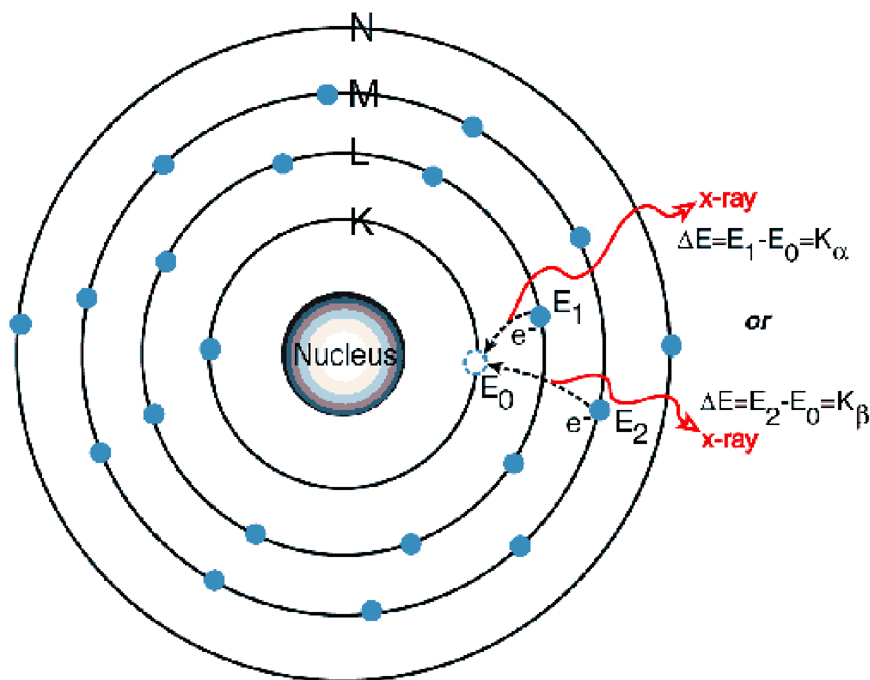
Electron Energy Loss Spectroscopy (EELS)

- Detect the elemental components of a material
- **Material is exposed to a beam of electrons** with a known, narrow range of kinetic energies
- Some of the **electrons** will undergo inelastic scattering, which means that they lose energy and have their paths slightly and randomly deflected
- The amount of energy loss can be measured via an electron spectrometer and interpreted in terms of what caused the energy loss



X-ray Fluorescence Spectroscopy (XRF)

- **Emission of characteristic "secondary" (or fluorescent) X-rays** from a material that has been excited by bombarding with **high-energy X-rays** or gamma rays.
- The phenomenon is widely used for elemental analysis and chemical analysis, particularly in the investigation of metals, glass, ceramics and building materials, and for research in geochemistry, forensic science and archaeology.



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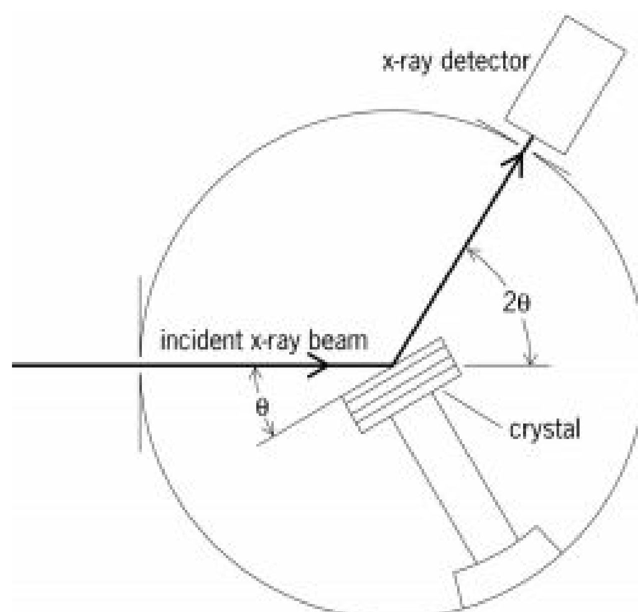
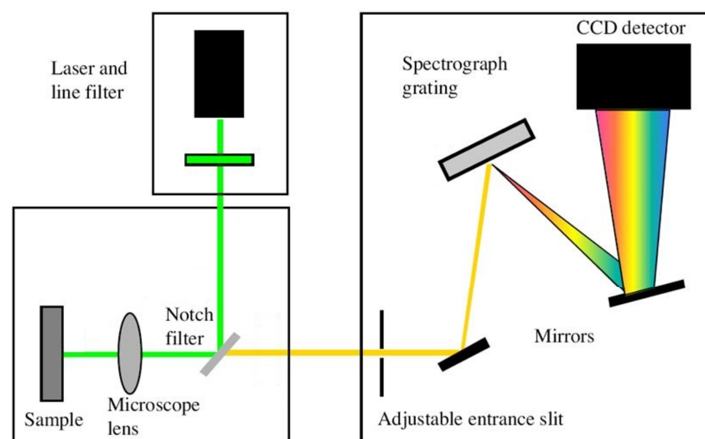
X-ray Diffraction
(XRD)

- Identification and characterization of compounds based on their diffraction pattern
- A crystal is mounted on a goniometer and gradually rotated while being bombarded with X-rays, producing a diffraction pattern of regularly spaced spots known as *reflections*
- The two-dimensional images taken at different rotations are converted into a three-dimensional model of the density of electrons within the crystal using the mathematical method of Fourier transforms, combined with chemical data known for the sample



Raman

- A spectroscopic technique **used to observe vibrational, rotational, and other low-frequency modes** in a system
- It relies on **inelastic scattering, or Raman scattering, of monochromatic light**, usually from a laser in the visible, near infrared, or near ultraviolet range
- The laser light interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down.
- The shift in energy gives information about the vibrational modes in the system.
- Infrared spectroscopy yields similar, but complementary, information.



Thank You For
Listening!

Back-up

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Acronyms & Definitions

AES	Auger electron spectroscopy
BE	Binding energy (eV)
eV	electron volt
FWHM	full width half maximum
IMFP	Inelastic mean free path length
ISS	Ion scattering spectroscopy
KE	Kinetic energy (eV)
SAM	scanning Auger microscopy
SEM	Secondary electron microscopy
SIMS	Secondary ion mass spectrometry
ToF	Time of flight
UPS	Ultra violet photoelectron spectroscopy
XPS	X-ray photoelectron spectroscopy

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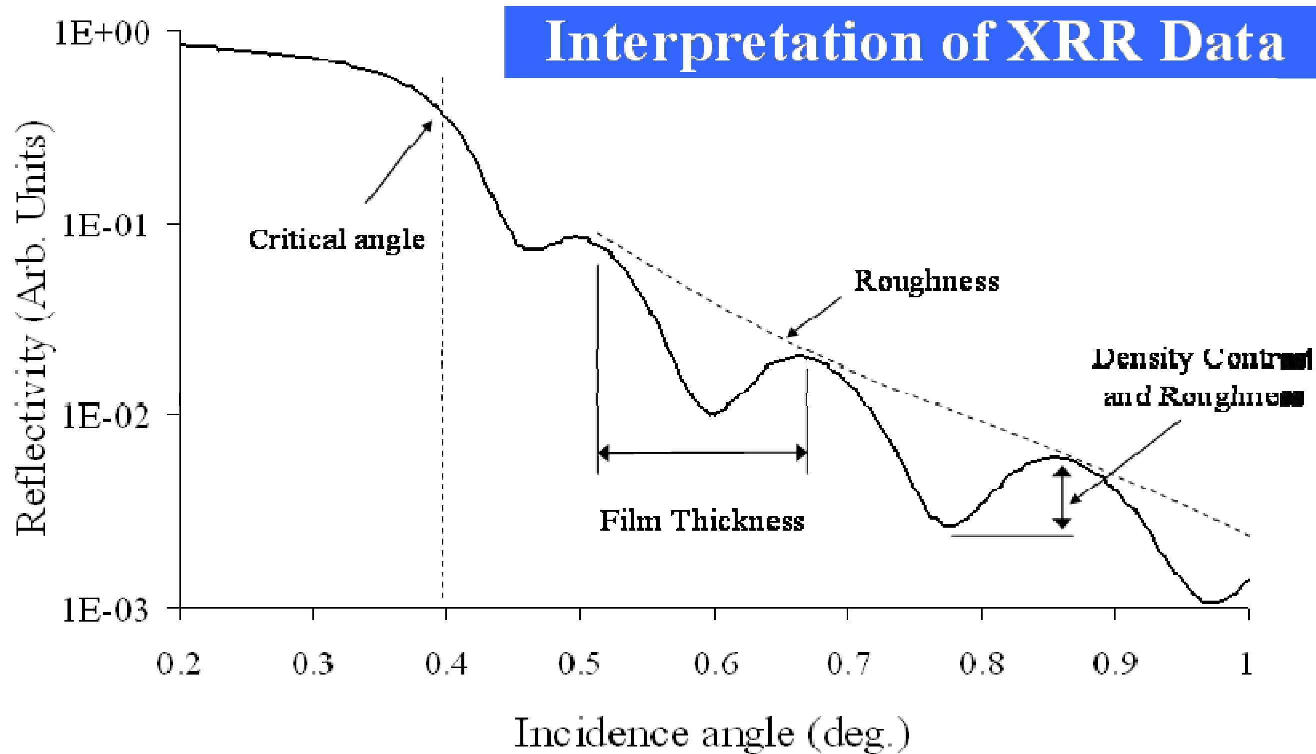
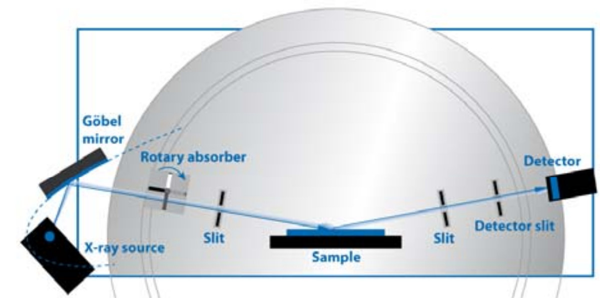
X-Ray Reflectivity (XRR)

- Calculation of the **electron density**, **thickness** and **interface roughness** for each particular layer

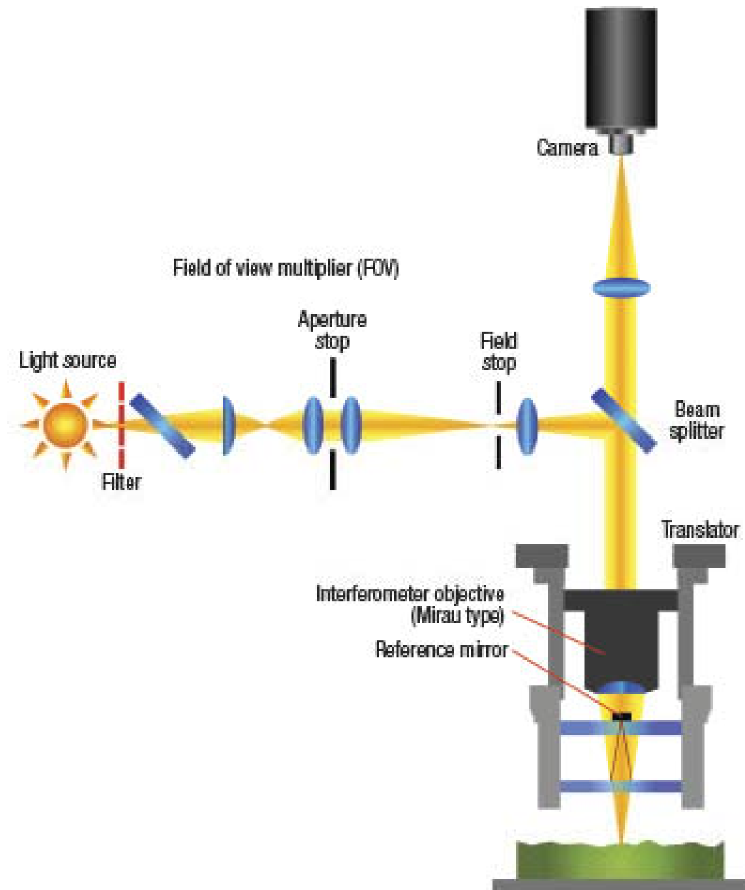




E Bontempi, "X-Ray Reflectivity for the characterization of thin films" in Recent Research Development in Chemical Physics, Transworld Research Network (ed.), 5 (2004) 461-488, ISBN 81-7895-155-X

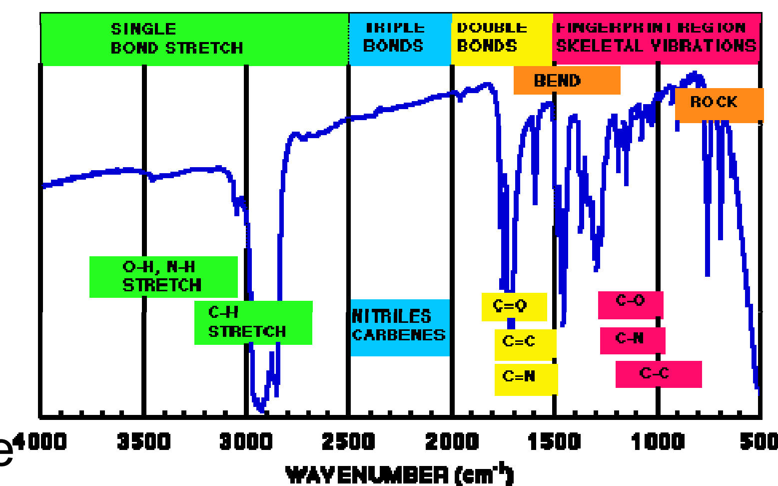
White Light Interferometry

- **White light interferometry** is a non-contact optical method for surface height measurement on 3-D structures with surface profiles varying between tens of nanometers and a few centimetres



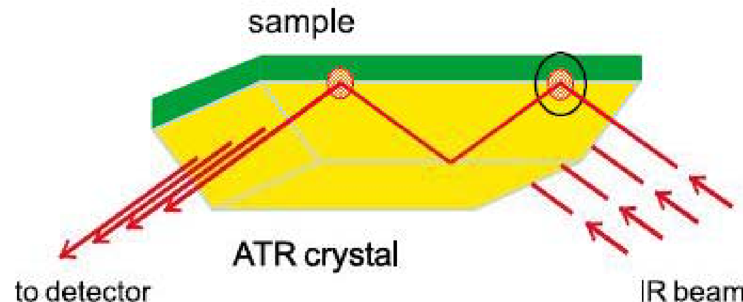
Fourier Transform Infrared Spectroscopy (FTIR)

- IR radiation is passed through a sample
- Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted)
- The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample
- Like a fingerprint no two unique molecular structures produce the same infrared spectrum
- It can identify unknown materials
- It can determine the quality or consistency of a sample
- It can determine the amount of components in a mixture



Attenuated Total Reflection Infrared Spectroscopy (ATR-IR)

- **Attenuated total reflection** (ATR) is a sampling technique used in conjunction with IR which enables samples to be examined directly in the solid or liquid state without further preparation
- ATR uses a property of total internal reflection resulting in an evanescent wave
- A beam of IR light is passed through the ATR crystal in such a way that it reflects at least once off the internal surface in contact with the sample
- This reflection forms the evanescent wave which extends into the sample
- The penetration depth into the sample is typically between 0.5 and 2 micrometres, with the exact value being determined by the wavelength of light, the angle of incidence and the indices of refraction for the ATR crystal and the medium being probed



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Techniques 1

Technique	Auger Electron Spectroscopy	X-Ray Photoelectron Spectroscopy	Energy Dispersive Spectroscopy
Abbreviation	AES	XPS or ESCA	EDS
Primary Excitation	Electron	X-Ray	Electron
Detected Secondary	Auger Electron	Photoelectron	X-Ray
Elemental Range	3-92	3-92	6-92
Lateral Resolution	5 nm	1 µm	1 µm
Detected Depth	10 nm	10 nm	1 µm
Detection Limit	1%	0.01%	0.1%
Quantitative?	Semi	Semi	Yes
Accuracy ±	10%	10%	10%
Depth Profile?	Yes	Yes	No
Analyze Insulator	Yes	Yes	Yes
Identify Organics?	No	Some	No
Chemical State ID?	Some	Yes	No

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Techniques 2

Technique	X-Ray Fluorescence	X-Ray Diffraction	Secondary Ion Mass Spectrometry, Dynamic	Time - of - Flight SIMS, Static
Abbreviation	XRF	XRD	SIMS	TOF-SIMS
Primary Excitation	X-Ray	X-Ray	Ions	Ions
Detected Secondary	X-Ray	X-Ray	Substrate ions	Substrate ions
Elemental Range	6-92	Crystalline materials	1-92	1-92
Lateral Resolution	1 cm	30 µm	60 µm	2000 Å
Detected Depth	Bulk	0.1-10 µm	0-10 µm	15 Å
Detection Limit	ppb	1%	ppm	ppm
Quantitative?	Yes	Semi	Yes	Semi
Accuracy ±	10%	10%	30%	100%
Depth Profile?	No	Yes, with angles	yes	No
Analyze Insulator	Yes	Yes	Yes	Yes
Identify Organics?	No	Some crystalline	No	Yes
Chemical State ID?	No	Yes	No	Molecular species

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Techniques 3

Technique	Fourier Transform Infrared	Raman Microprobe	Atomic Force/ Scanning Tunnelling Microscope
Abbreviation	FTIR	Raman	AFM/STM
Primary Excitation	IR radiation	Laser	
Detected Secondary	IR radiation	Photons	Surface Topography
Elemental Range	NA	NA	NA
Lateral Resolution	10-100 μm	2 μm	<0.1 Å
Detected Depth	20 Å-1μm	0.2-10 μm or more if transparent	0.1 Å (vertical resolution)
Detection Limit	ppm	0.1%	NA
Quantitative?	Yes	Poor	NA
Accuracy ±	5%	100%	1-2 Å
Depth Profile?	Yes	Variable	No
Analyze Insulator	Yes	Yes	Yes
Identify Organics?	Yes	Yes	No
Chemical State ID?	Chemical Bond Information	Molecular species	No

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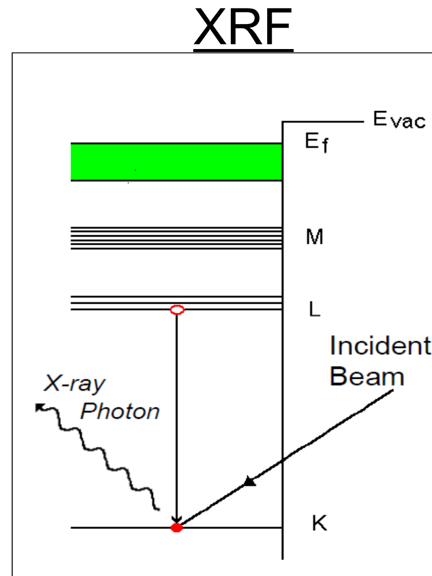
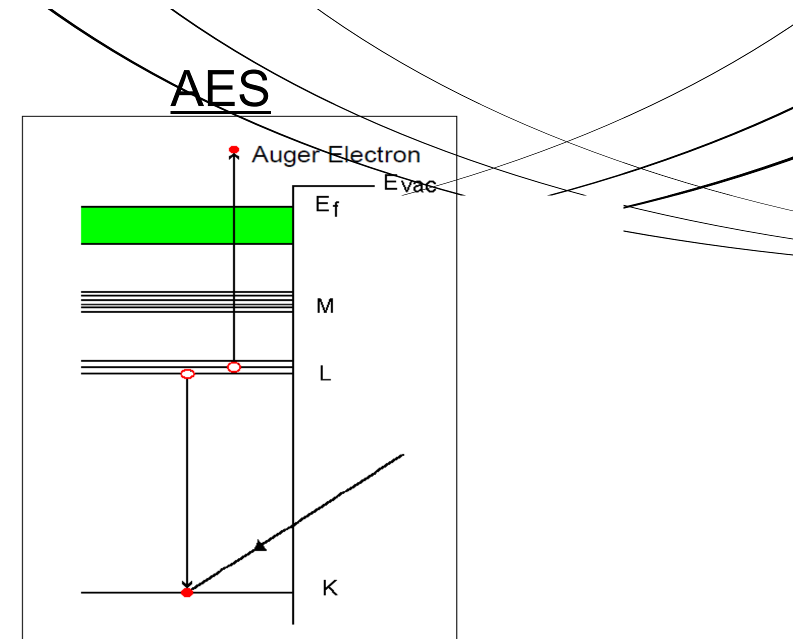
XRF & AES





Example

- A hole is created on the K level in the initial ionisation step
- This requires a primary energy greater than the binding energy of the electron in that shell
- The hole can be produced by either the primary beam, or the backscattered secondary electrons
- The atom relaxes by filling the hole with an electron coming from an outer level, in the example shown as L1.
- As a result, the energy difference EK – EL1 becomes available as excess energy, which can be used in two ways.
- The emission of an X-ray at that energy may occur or the energy may be given to another electron, either in the same level or in a more shallow one, as is the case in the example, to be ejected.
- The first of the two competing processes is X-ray fluorescence, the second Auger emission.