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Introduction to X-ray Photoelectron Spectroscopy
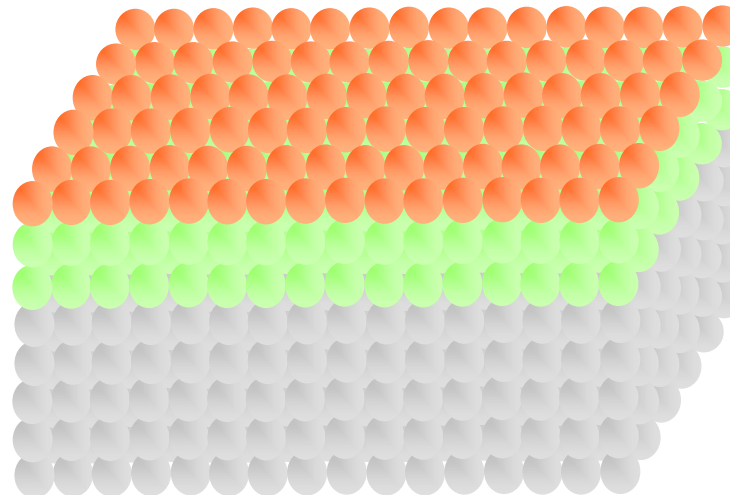
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What is the surface?

- What happens at surfaces is extremely important in a vast range of applications from environmental corrosion to medical implants.

- A surface can be thought of as the interface between different phases (solid, liquid or gas).

- We can think of the surface as the top layer of atoms but in reality the state of this layer is very much influenced by the 2 – 10 atomic layers below it (~0.5 – 3 nm).

- Surface modification treatments are often in the range of 10 – 100 nm thick. >100 nm can be thought of as the bulk.

- Surface analysis encompasses techniques which probe the properties in all these ranges.

Why is Surface Analysis Important?

Scale of
surface region:

0 – 0.2 nm

0 to 10 nm

> 10 nm

Surface: typically controls chemical interaction with other materials and environment.

Bulk material: controls materials physical properties – density, strength, flexibility etc.

The surface of the material is very often chemically distinct from the bulk material and standard analytical techniques can not provide any information about it's composition.

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SURFACE SCIENCE

Surface ..what it means

0.1 micron

bulk

10 nm

1 nm

• Depth profiling*

•By sputtering in situ

•Information on atomic layers below the surface as a function of depth

•Destructive or nondestructive

• Elemental analysis of the outermost atom layer

• Detail knowledge of the Chemical Binding state

• Surface homogeneity

• Nature of absorbates

• Surface characteristics has great impact : example : adhesion, bond-ability, reactions, etc.

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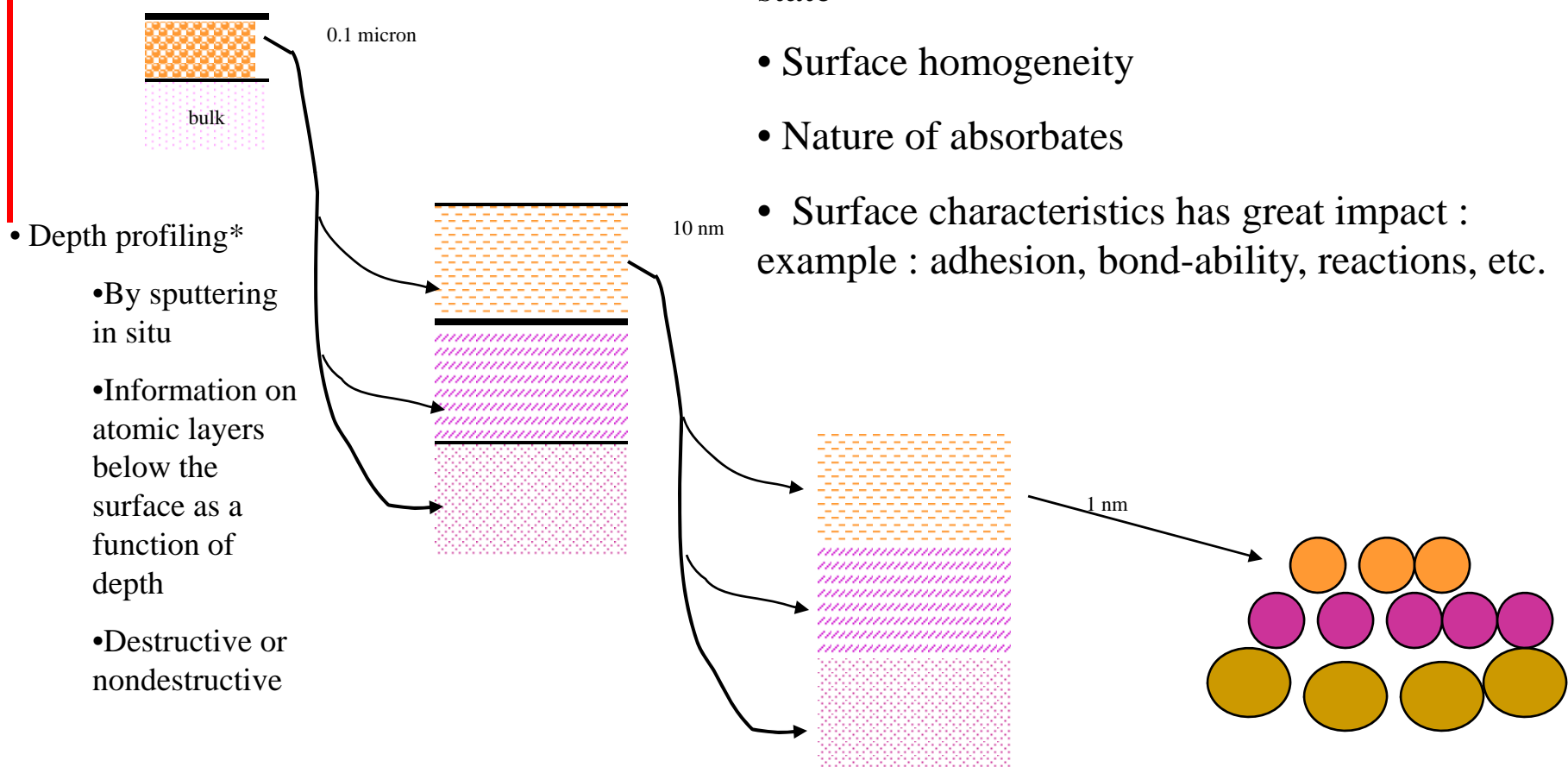
What does a surface technique do ?

• Qualitative

•Quantitative, semi-quantitative

•Chemical bonding

•Mapping (Scanning ESCA/Auger/TOF-SIMS/FTIR/EDX/WDX)

•Depth profiling

•Film thickness (thin film)

Area of Interest

D,thickness

surface

BULK
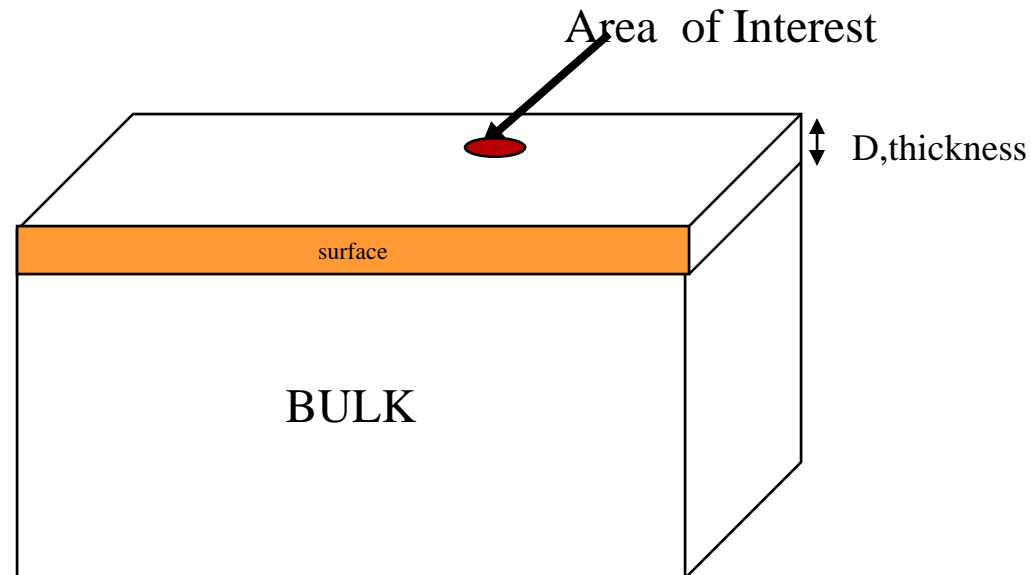
Lateral: 10 microns to a few hundred microns

Depth : < 5 nm

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Surface Analysis - Techniques Available

- 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

No one technique can provide all these pieces of information. However, to solve a specific problem it is seldom necessary to use every technique available.

EXCITATION

photons

ions

electrons

EMISSION

Interaction with material

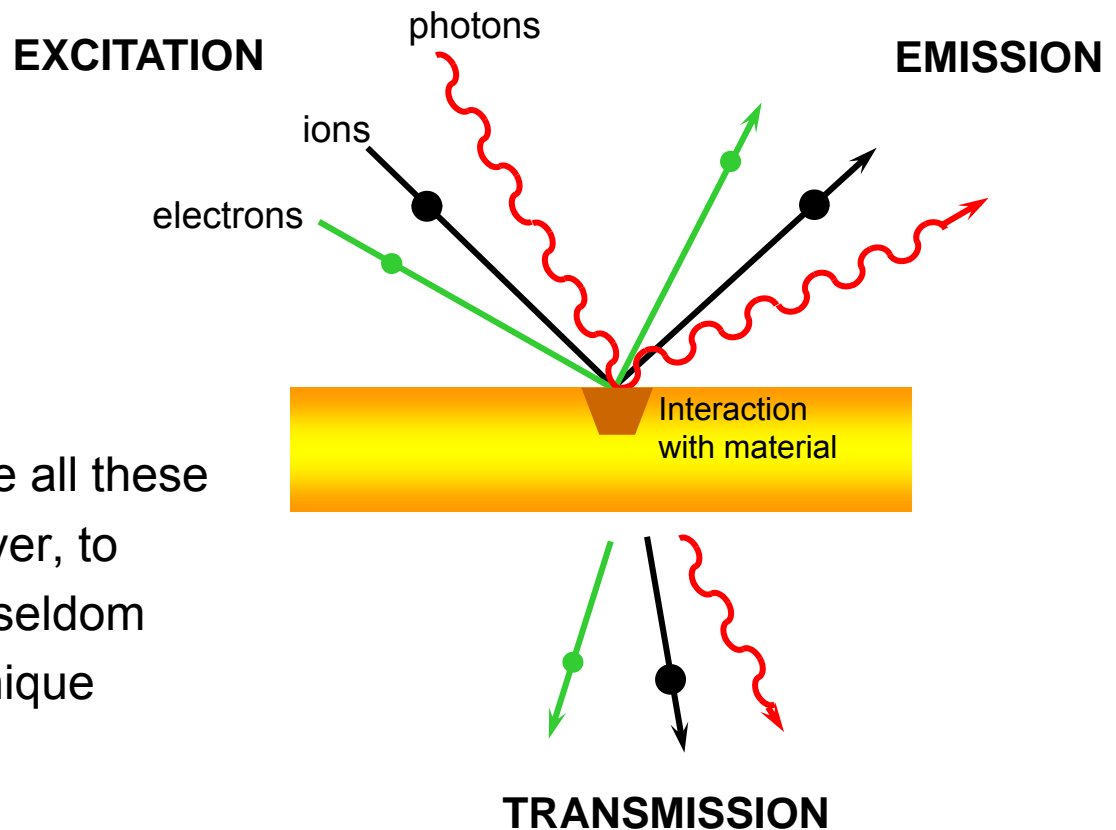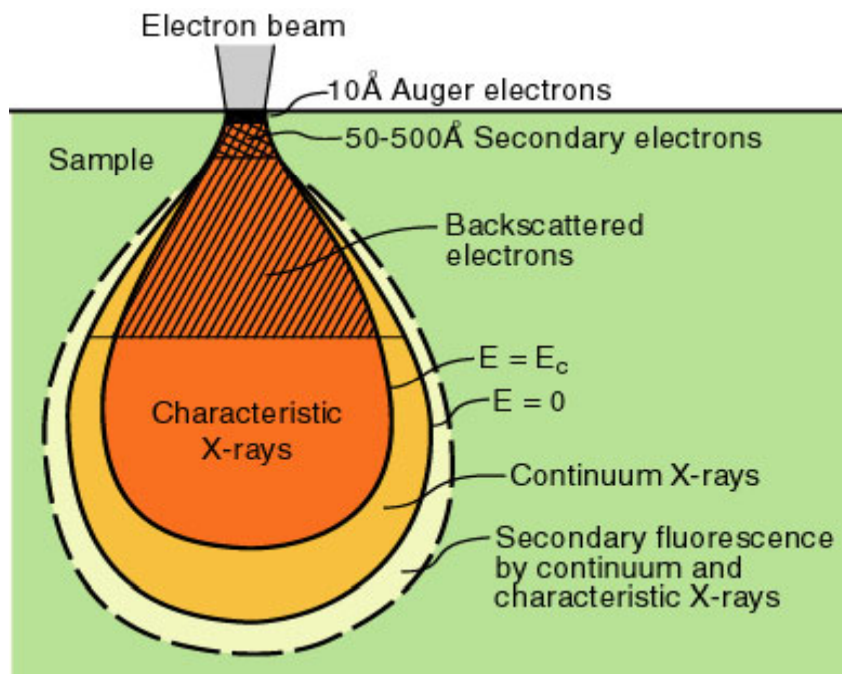**TRANSMISSION**

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Figure 2.1b. Generalized illustration of interaction volumes for various electron-specimen interactions. Auger electrons (not shown) emerge from a very thin region of the sample surface (maximum depth about 50 Å) than do secondary electrons (50-500 Å).

Electron beam

—10Å Auger electrons

—50-500Å Secondary electrons

Sample

Backscattered electrons

E = E_c

E = 0

Characteristic X-rays

Continuum X-rays

Secondary fluorescence by continuum and characteristic X-rays

1. Pls take note of the effective beam diameter (influencing the "spot size)
2. common SEM with a spot beam of about 5 nm, the diameter of the volume sampled, the so-called "interaction volume" may be up to 5 hundred times larger
3. It is caused by electrons, and other resulting radiations scattering and diffusing thru' the sample, before emerging and being detected
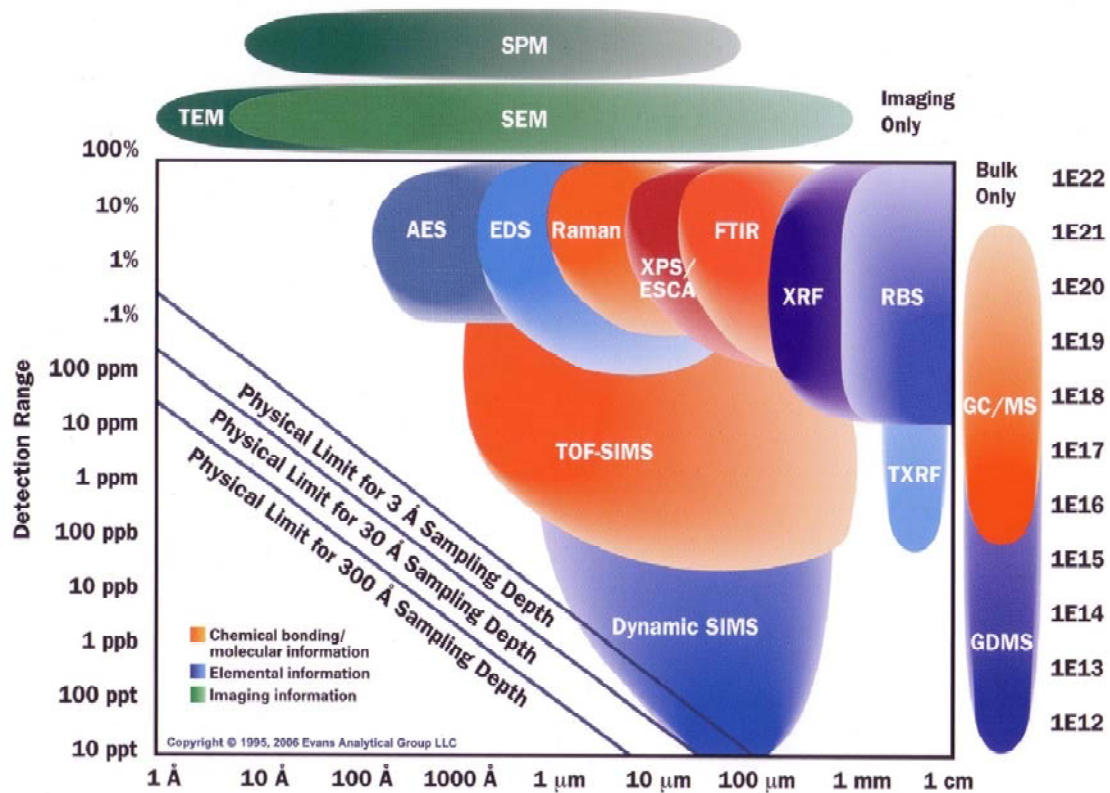
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Surface Analysis - Techniques Available

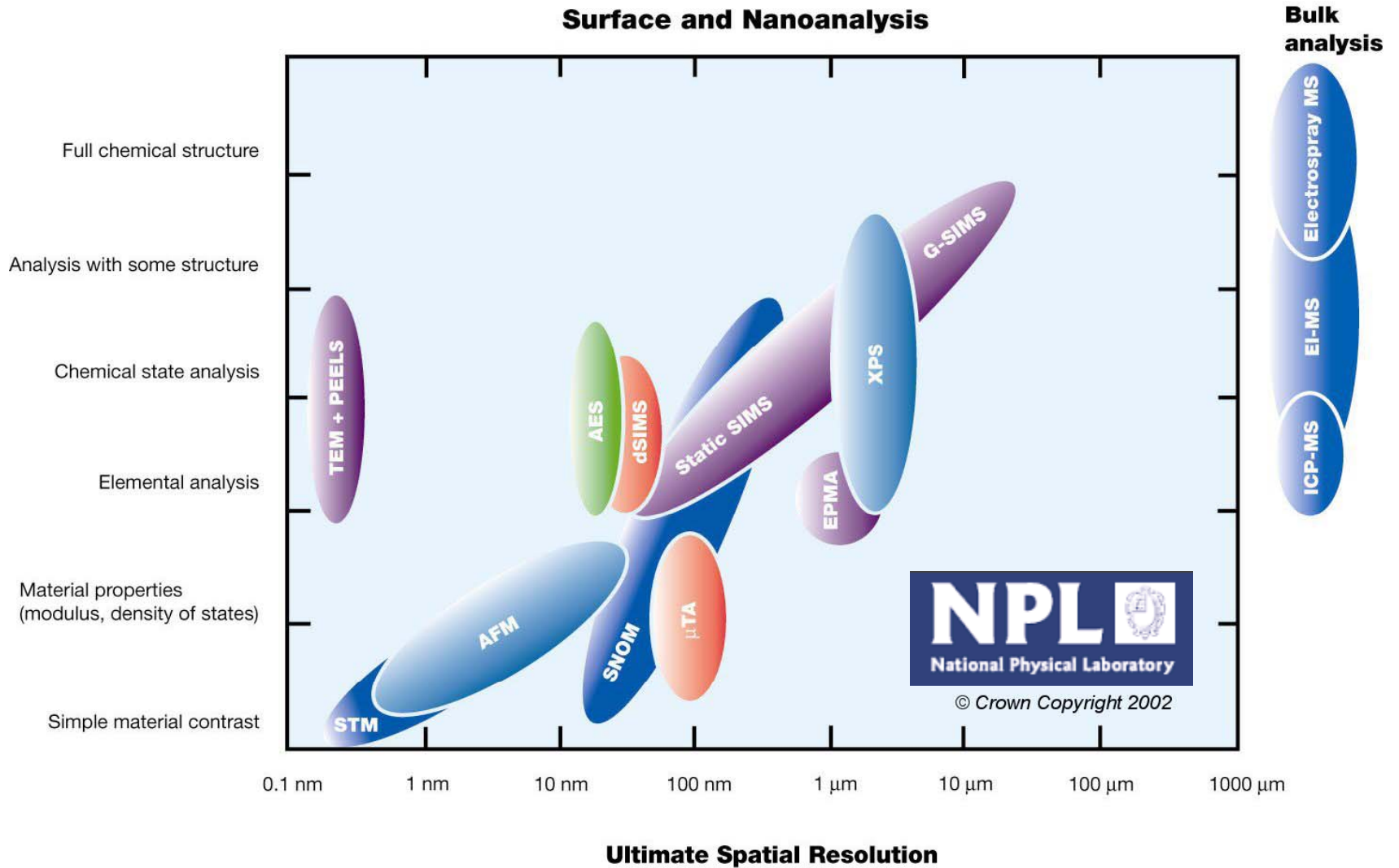| Analytical Technique	Signal Measured	Elemental Range	Depth Resolution	Surface info.
SIMS (secondary ion mass spectrometry)	Secondary Ions	H-U	5 - 30 Å	Chemical composition Chemical structure
TOF-SIMS (time-of-flight SIMS)	Secondary Ions	H-U, Large Organic Molecules / Cluster Ions	2000 Å (Scanning Mode)	Adsorbate bonding
TEM (transmission electron microscopy)	Transmitted Electrons X-Rays	Na-U EDX	N/A	
FE-SEM, EDX (field emission SEM)	Backscattered or Secondary Electrons and X-Rays	Na-U	1 - 5 micrometres	
ISS (ion scattering spectroscopy)	Ions	H- U	monolayer	atomic structure chemical composition
AES/SAM (Auger electron spectroscopy, scanning Auger microscopy)	Auger Electrons	Li-U	1 - 5 nm	chemical composition
ESCA/XPS (electron spectroscopy for chemical analysis, X-ray photoelectron spectroscopy)	Photoelectrons	Li-U	1 – 10 nm	chemical composition chemical structure
RAIRS (reflection-absorption infra-red spectroscopy)	IR photons	organic, some inorganics	monolayer	Adsorbate bonding
STM (scanning tunnelling microscopy)	-	solid surfaces	upper most atoms	physical topography

Analytical Technique	Signal Measured	Elemental Range	Depth Resolution	Surface info,

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Surface Analysis - Techniques Available

Surface Analysis - Techniques Available

Surface and Nanoanalysis — Bulk analysis

Full chemical structure
Analysis with some structure
Chemical state analysis
Elemental analysis
Material properties (modulus, density of states)
Simple material contrast

0.1 nm   1 nm   10 nm   100 nm   1 µm   10 µm   100 µm   1000 µm

Ultimate Spatial Resolution

TEM + PEELS, AES, dSIMS, Static SIMS, G-SIMS, XPS, EPMA, AFM, STM, SNOM, µTA, Electrospray MS, EI-MS, ICP-MS

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National Physical Laboratory
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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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ESCA/XPS

- XPS or ESCA ? Why ?
- Initial name given is XPS : X-ray Photoelectron Spectroscopy. Work mostly done by Physicists in the early '50. Wilson Chamber experiment, etc
- Photoelectric effect
- Einstein, 1921 Nobel prize
- Interpretations and applications pioneered by the Chemists
- mid '70… Professor Kai Siegbahn coined the name Electron Spectroscopy for Chemical Analysis,ESCA (note: the Professor was awarded a Nobel prize for his work in this area,1981

- Used as an analytical tool
- Surface sensitive
- Qualitative (elemental analysis)
- Quantitative
- Insight into the chemical state of sample (chemical bonding)
- Imaging capability

Incoming X-ray

e⁻
Photo- electron

nucleus

05-10-2017

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Photo emission process

X ray

e,photoelectron

K.E

E_v

0

E_f

Valence band

3s

2p

2s

1s

B.E.
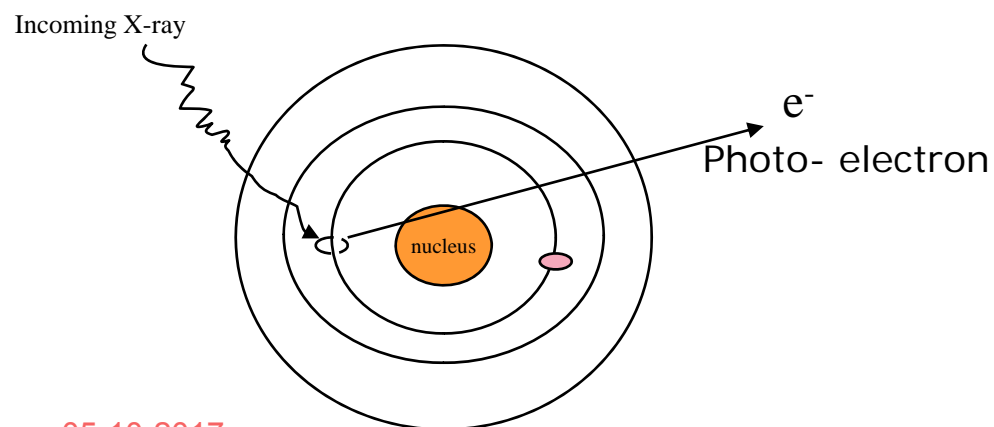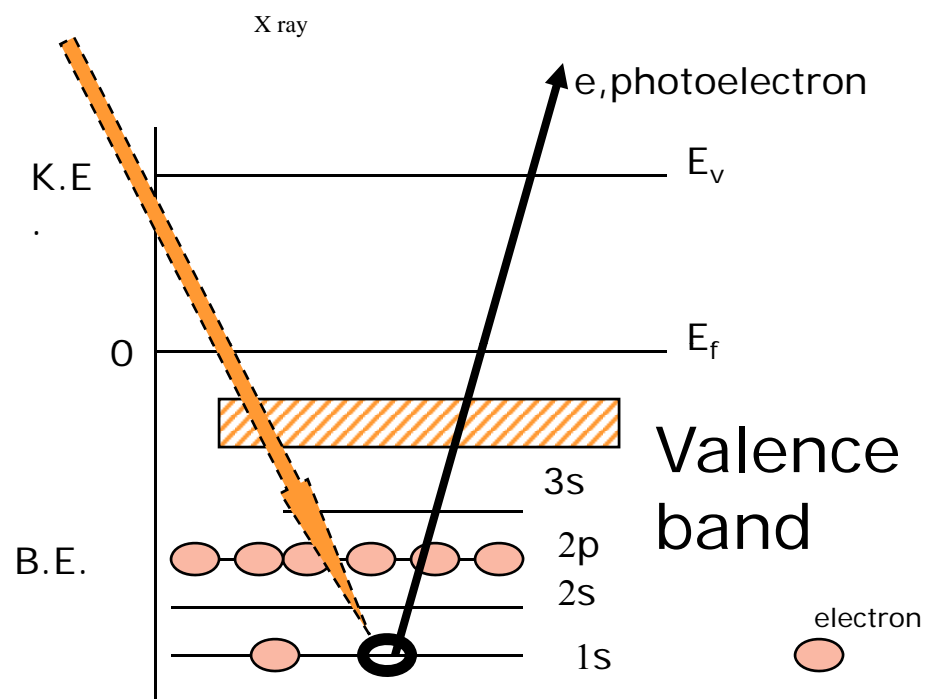
electron

❖ The surface is bombarded by the monoenergetic x-ray, emitting a photoelectron

❖This photoelectron can be analysed and used (we have the XPS/ESCA)

❖ What happens to the excited atom ?

❖ It would undergo a relaxation process as the excited atom is unstable

❖ See next slide for the relaxation

❖ relaxation by a X ray fluorescence

❖ relaxation by an Auger electron escaping

The BE is now taken to be a direct measure of the energy required to just remove the electron concerned from its initial level to the vacuum level and the KE of the photoelectron is again given by #

The Energy is given by Einstein's' equation # : $E = h\upsilon$,

and

$h\upsilon = K.E. + B.E + work function$

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X-ray Fluorescence, XRF

Energy level transition forming x-ray fluorescence analysis XRF. The energy of the released x ray is independent of the incident x ray

When the electronic transition occurs,energy is conserved by the emission of a photon (x ray).the other process is a radiation-less transition ,see the next slide

vacuum

Fermi level

Valence band

L_{23} (2p)

L_1(2s)

XRF

E

K (1s)
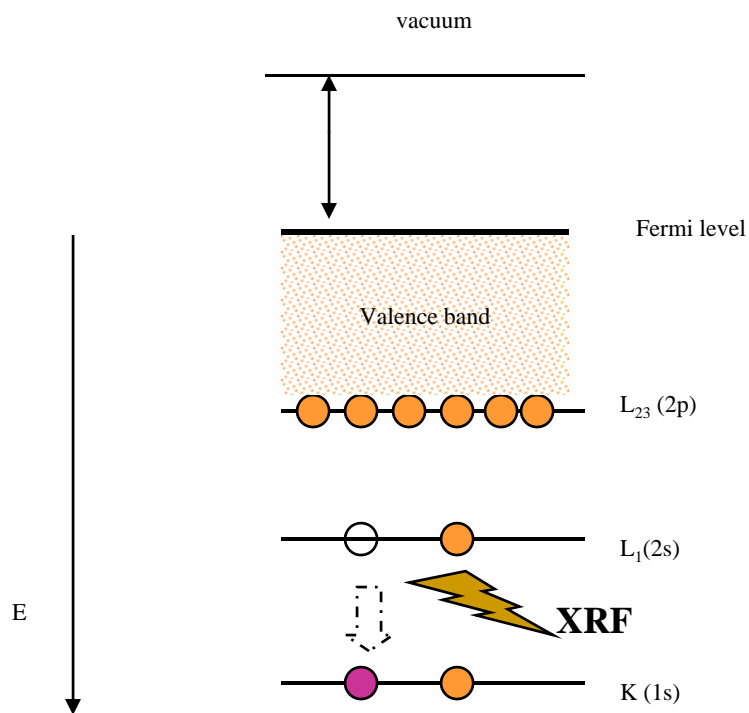
ESCA instrument does not have a x-ray detector to collect the secondary x-ray signals

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The Auger electron process

vacuum

Nomenclature : Auger line XYZ

A Core hole in level X is filled by an electron in level Y and an electron is ejected from level Z

$$E = E_K - E_{L1} - E_{L23} + Q$$

Auger electron, KL_1L_{23}

Fermi level

Valence band

L_{23} (2p)

L_1(2s)

K (1s)

E
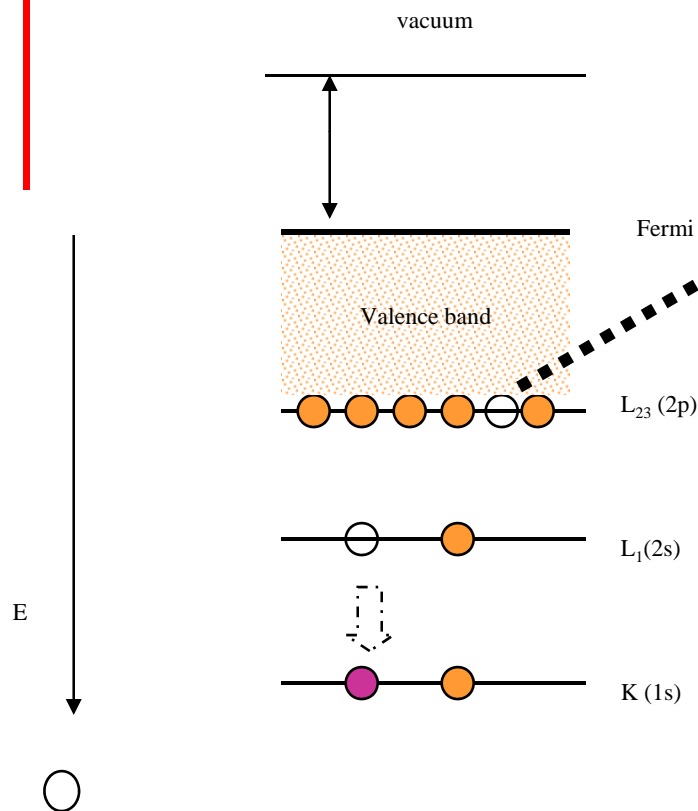
In addition to the photoelectron emitted in the photoelectric process, Auger electrons are emitted due to relaxation of the energetic ions remained after the photoemission.This Auger electron emission occurs roughly 10^{-14} seconds after the photoelectric effect

In the Auger process, as shown, an outer electron gets into the inner orbital vacancy,and the second electron is emitted carrying off the excess energy (kinetic energy of the auger electron

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Note on Auger electron emission

- The Auger process can occur anytime we create a hole in a core orbital (level)

- Holes are created using x-rays (in ESCA) , electrons (in AES), ions (in SIMS), and others

- Auger electron signals provides supplementary information in a ESCA spectrum

- AES also provides an alternative stand-alone surface analysis tool (to be elaborated later)
  - Use electron beam as a probe
  - Spot size of the electron beam can be as small as 50-100 nm, hence useful as an analysis tool for the area of interest on a sample with <1 micron

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How ESCA works

- It involves irradiating a solid in vacuo,with mono-energetic soft x-rays. The X-rays interact with atoms in this surface region by photo electric effect,causing electrons to be emitted. Core electrons are involved
- The emitted electrons have kinetic energy defined by Einstein equation :
- $E = h\upsilon = B.E.+ K.E + \Phi$
- Where E is the energy of the photon (x-ray)
- BE= the binding energy of the ejected photoelectron
- KE = the kinetic energy of the ejected photoelectron (measured by electron analyzer)
- Φ = the spectrometric work function
- using soft (200-2000 eV) x-ray excitation to examine core-levels
- The Mg and Al Kα x-rays are chosen as radiation source . Both have limited penetrating power monochromatic radiation
- Mg K α = 1253.6eV
- Al K α x rays = 1486 eV
- Binding energy is a characteristic of an element.No two atoms have the exact set of values of their atomic binding energies. Hence, ESCA can be used for elemental analysis.
- Involves 3 electrons. Applicable to Li and above.
- ESCA spectrum is a plot of counts (Intensity) versus Binding energy
- Intensity ,in general , indicates the amount of the element present

Typical Sampling Depths of Techniques
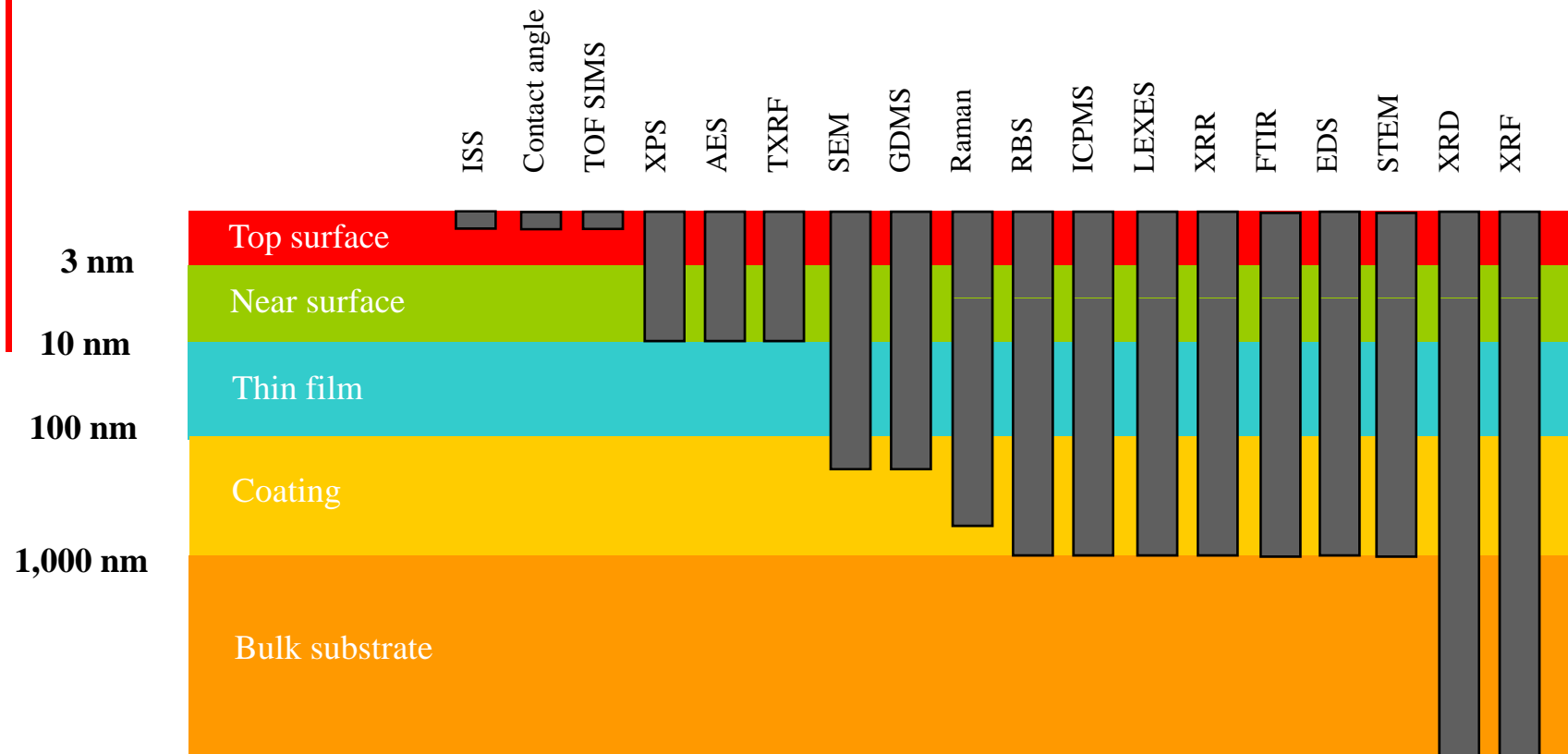
The X-ray Photoelectron Spectroscopy Experiment

- Prof. Kai Siegbahn, (1918 – 2007) Uppsala University, pioneered the technique of XPS, producing the first well defined spectrum in 1954.

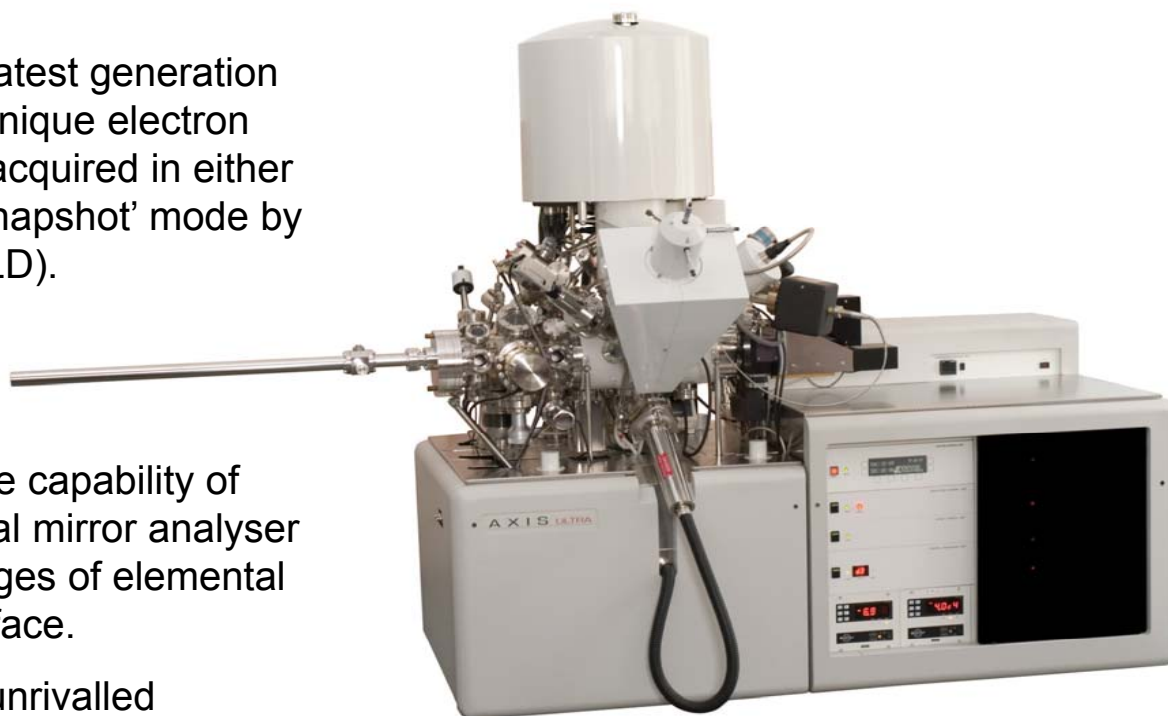- He shared the 1981 Nobel prize in physics for his work in spectroscopy.

- Since then the basic building blocks of the X-ray photoelectron spectrometer have not changed.

- However, UHV technology and electronics have improved!

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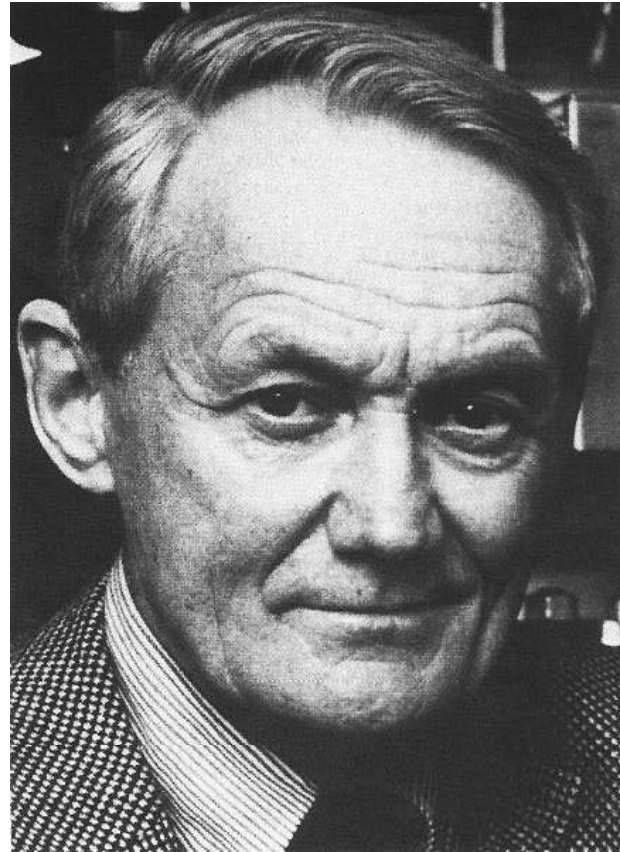
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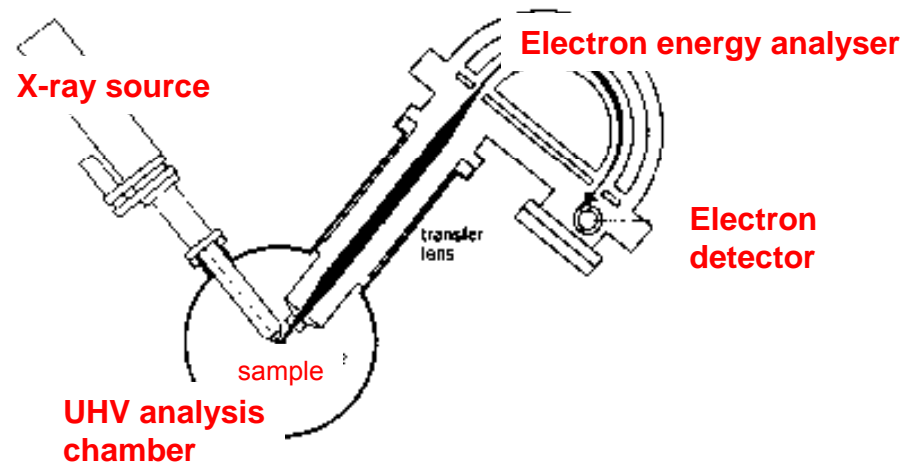
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AXIS Ultra^{DLD}

The AXIS Ultra^{DLD} provides the latest generation tool for high sensitivity muti-technique electron spectroscopy. Spectra may be acquired in either scanned or rapid un-scanned 'snapshot' mode by using the delay-line detector (DLD).

The AXIS Ultra^{DLD} has the unique capability of parallel imaging using a spherical mirror analyser providing lateral distribution images of elemental and chemical species at the surface.

As with all AXIS spectrometers unrivalled performance on insulators is guaranteed by the use of the coaxial charge neutalisation system.

What information do we get from XPS?

- **Surface sensitivity** - photoelectron signal from first 1-10 layers of atoms and molecules.
- **Identification** of all elements (except H & He) at concentrations >0.1atomic%*.
- **Quantitative** determination of the elemental composition.
- Information about the **chemical state** (molecular environment) of the element.
- **Non-destructive** analysis, including depth profiles, from the top 10 nm.
- Destructive **depth profiles** of inorganic materials for 100s of nm.
- **Lateral variations** in surface composition at >3μm resolution.
- **'Finger printing'** of materials using valance band.

- *Sensitivity - a sample with a surface of size 1 cm^2 - this will have ca. 10^{15} atoms in the surface layer. In order to detect the presence of impurity atoms present at the 1% level, a technique must be sensitive to ca. 10^{13} atoms. Contrast this with a spectroscopic technique used to analyse a 1 cm^3 bulk liquid sample i.e. a sample of ca. 10^{22} molecules. The detection of 10^{13} molecules in this sample would require 1 ppb (one *part-per-billion*) sensitivity - very few techniques can provide anything like this level of sensitivity.

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Principles & Theory of XPS

When a surface is exposed to electromagnetic radiation above a certain threshold frequency (typically visible light for alkali metals, near ultraviolet for other metals, and extreme ultraviolet for non-metals), the radiation is absorbed and electrons are emitted

In 1839 Alexandre Edmond Becquerel discovered the photovoltaic effect while studying the effect of light on electrolytic cells.

In 1899, J. J. Thomson investigated ultraviolet light in Crookes tubes Influenced by the work of James Clerk Maxwell, Thomson deduced that cathode rays consisted of negatively charged particles, later called electrons

In 1905, Albert Einstein descried light as composed of discrete quanta, now called photons, rather than continuous waves. Einstein theorized that the energy in each quantum of light was equal to the frequency multiplied by a constant, later called Planck's constant. A photon above a threshold frequency has the required energy to eject a single electron, creating the observed effect. This discovery led to the quantum revolution in physics and earned Einstein the Nobel Prize in Physics in 1921

1907, P.D. Innes experimented with a Röntgen tube, Helmholtz coils, a magnetic field hemisphere (electron energy analyzer) and photographic plates to record broad bands of emitted electrons as a function of velocity, in effect recording the first XPS spectrum.

Kai Siegbahn and his group in Uppsala (Sweden) developed several significant improvements in the equipment and in 1954 recorded the first high-energy-resolution XPS spectrum of cleaved sodium chloride (NaCl) revealing the potential of XPS – which he called electron spectroscopy for chemical analysis (ESCA). A few years later in 1967, Siegbahn published a comprehensive study on XPS bringing instant recognition of the utility of XPS. In cooperation with Siegbahn, Hewlett-Packard in the USA produced the first commercial monochromatic XPS instrument in 1969. Siegbahn received the Nobel Prize in 1981 to acknowledge his extensive efforts to develop XPS into a useful analytical tool.

The Photoelectron Process

X-rays in

photoelectrons out

Sample Surface Layer

photon

KE

E_v

ϕ

E_f

valence
band

BE

core
levels
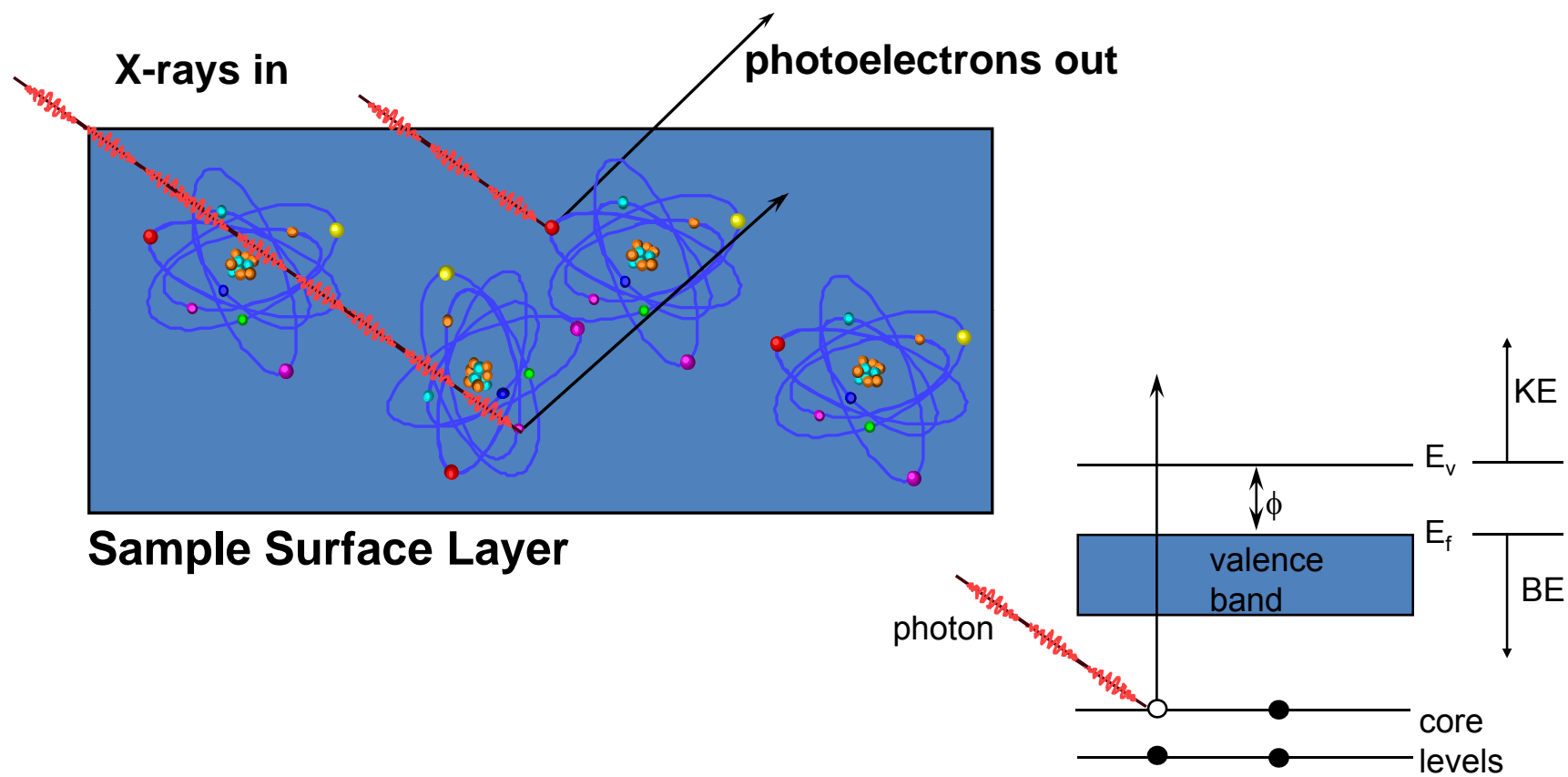
binding energy (eV) = photon energy - kinetic energy - work function
$$BE \text{ (eV)} = h\nu - KE - \phi$$

The Photoelectron Process

photoelectron

KE

E_v

ϕ

E_f

BE

2p
2s

1s

$KL_{2,3}L_{2,3}$
Auger electron

KE

E_v

ϕ

E_f

BE

2p — $L_{2,3}$
2s — L_1

1s — **K**
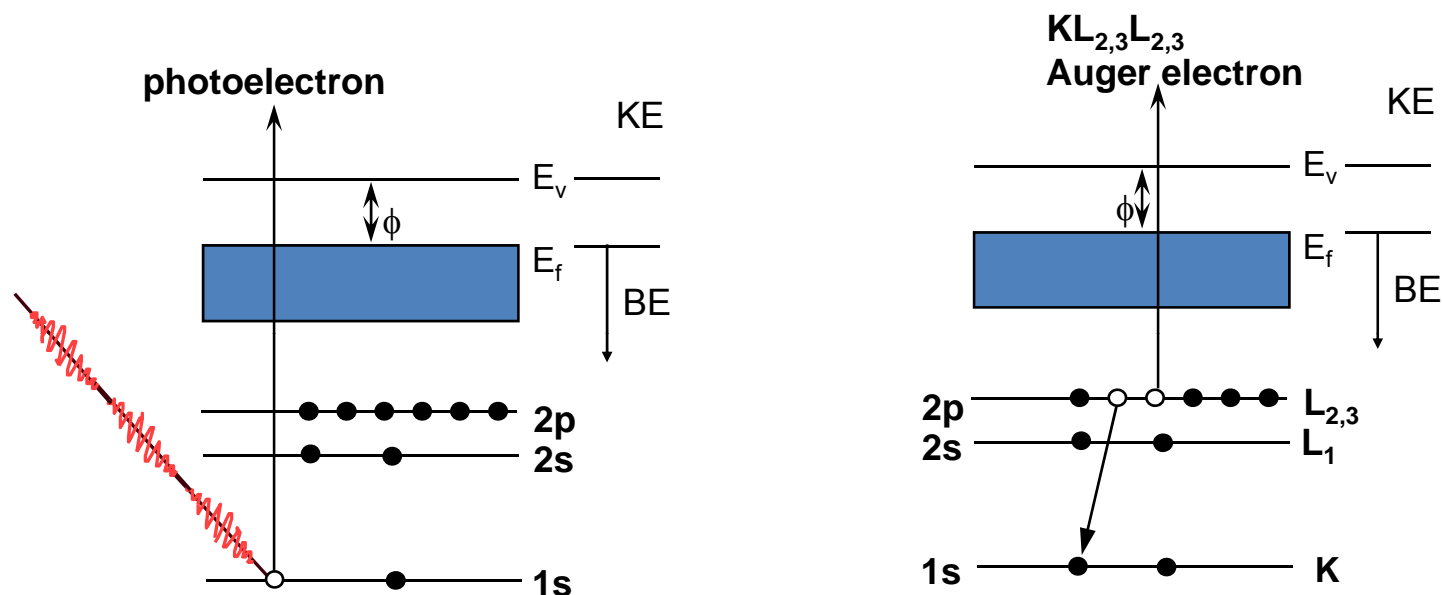
X-ray Photoemission is often described as a three-step process:
1) The photoelectric effect. The hole left behind can give rise to auger effect, which is visible even when the electron does not leave the material. In molecular solids phonons are excited in this step and may be visible as lines in the final electron energy. The inner photoeffect has to be dipole allowed.
2) Ballistic transport of half of the electrons to the surface. Some electrons are scattered.
3) Electrons escape from the material at the surface.

Relaxation process:
After ejection of the photoelectron relaxation of the excited ion may occur by ejection of an Auger , as electron as shown above. The competing emission of a fluorescent x-ray photon is a less likely event in this energy range.

Sample handling

- Do not use the plastic bag !
  - Contains Antistatic coating chemicals
- Do not touch with bare hand
- Do not use the antistatic finger cot (contains chemicals)
- Use aluminum foil (clean)
- Use tweezers (clean)
- Use a lint –free paper (clean room)
- Medicine container
- Kept in dry box (when needed)

- Do not do potting with epoxy*
- Do not gold coat the sample*
- May need to keep polymeric materials in a dry box of vacuum box, for degassing
- Down time due to degassing (Auger, ESCA, etc.)

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The Photoelectron Spectrum – Surveys/Wide Scans

Which elements are present and how much have we got?
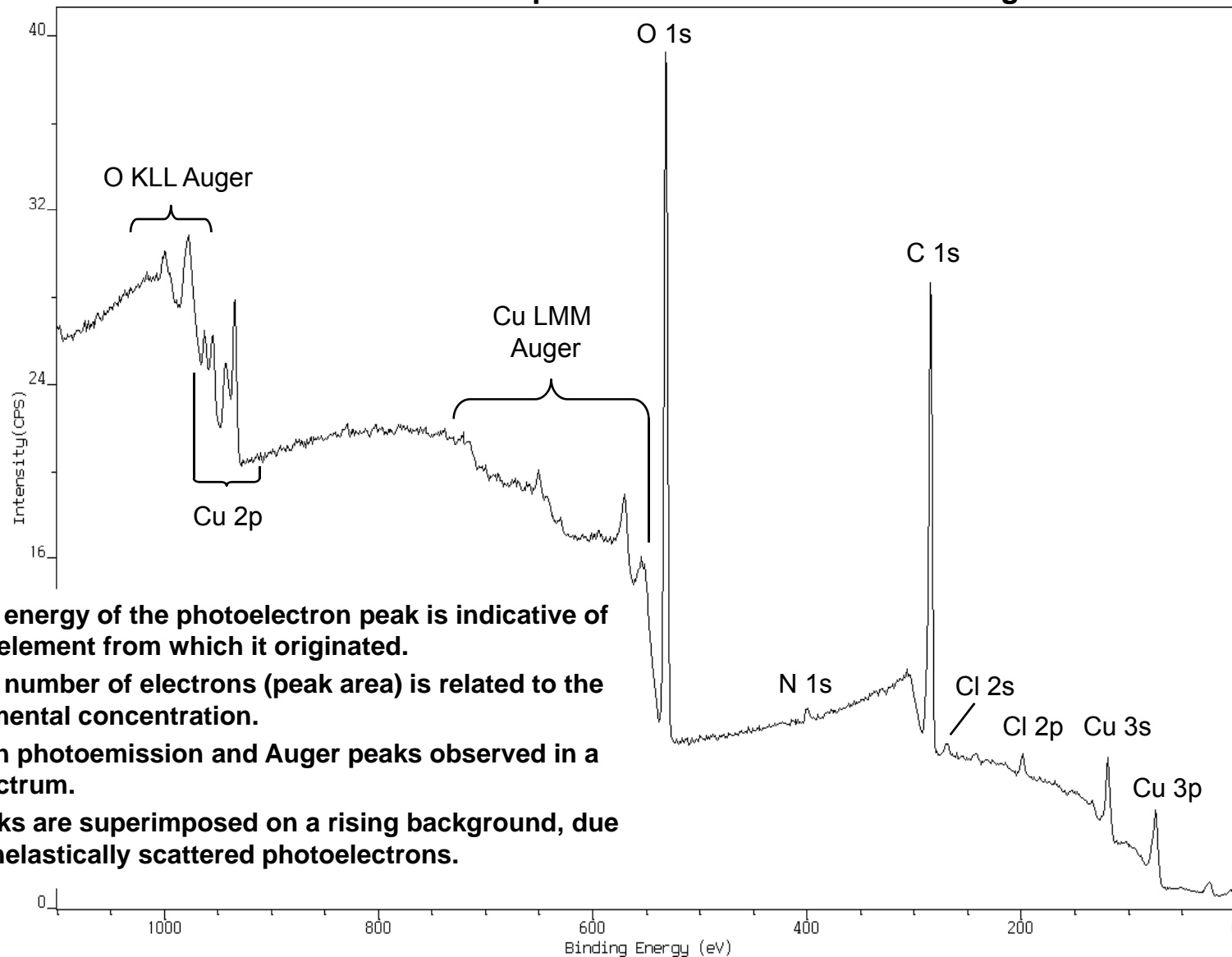
- The energy of the photoelectron peak is indicative of the element from which it originated.
- The number of electrons (peak area) is related to the elemental concentration.
- Both photoemission and Auger peaks observed in a spectrum.
- Peaks are superimposed on a rising background, due to inelastically scattered photoelectrons.

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The Photoelectron Spectrum – High Resolution

What chemical state are the elements in?
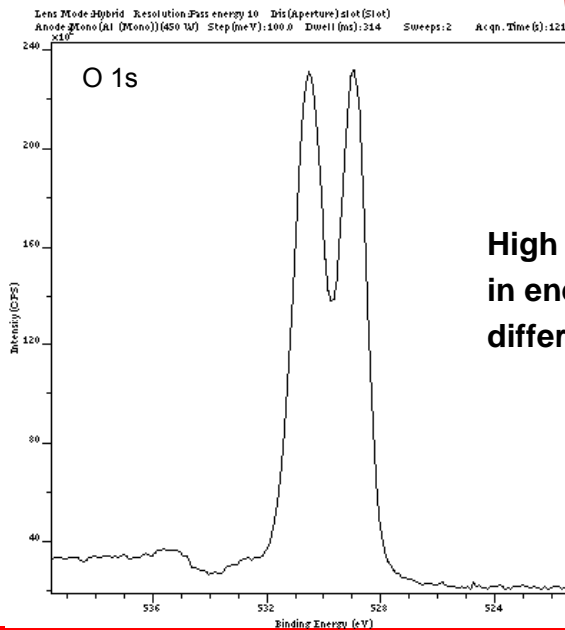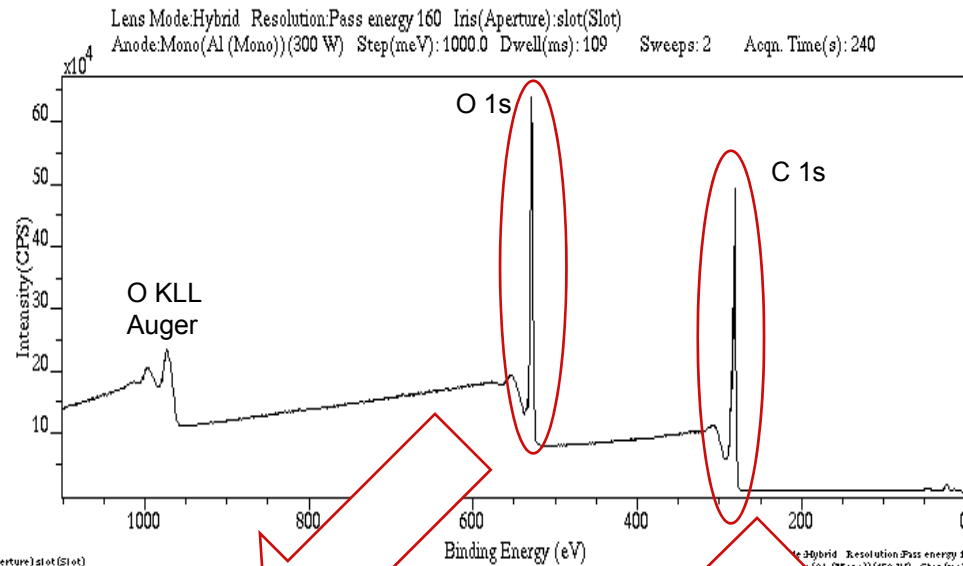
High resolution spectra show the subtle shifts in energy of photoelectrons originating form different chemical environments.

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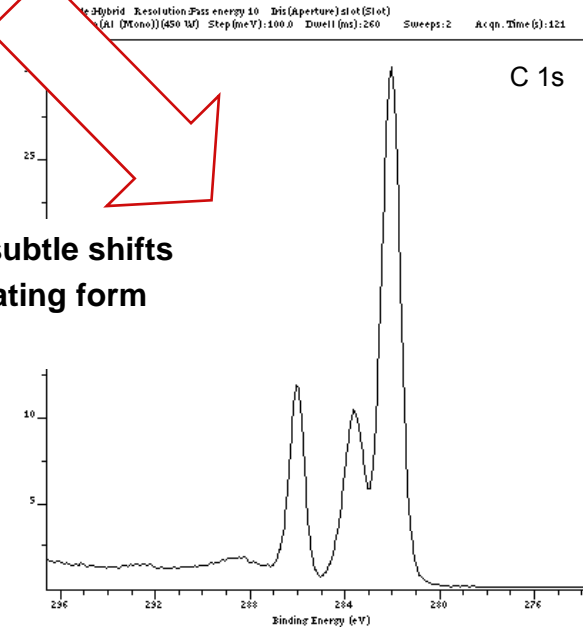
The Photoelectron Spectrum
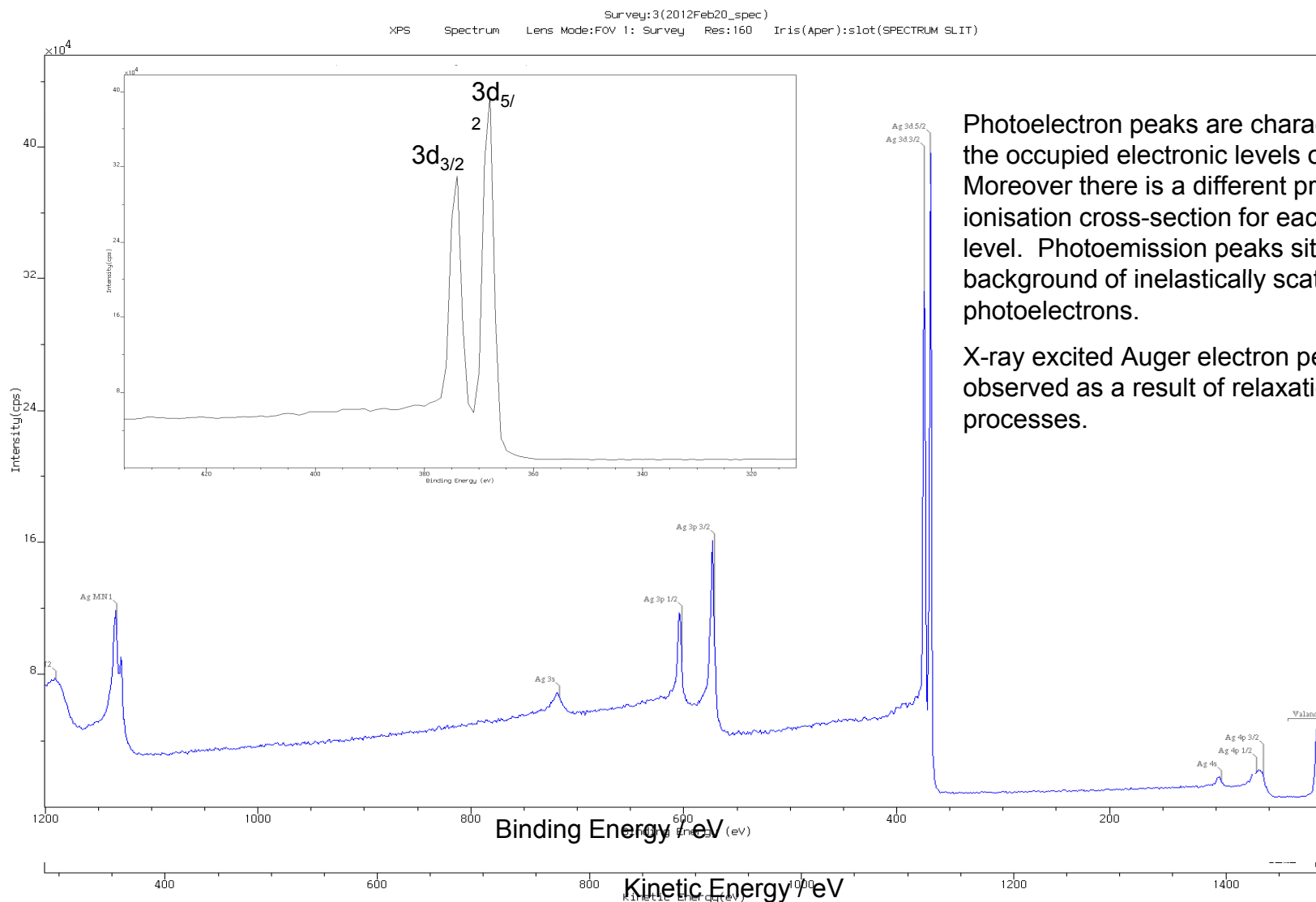
Photoelectron peaks are characteristic of the occupied electronic levels of the atom. Moreover there is a different probability or ionisation cross-section for each electronic level. Photoemission peaks sit on a background of inelastically scattered photoelectrons.

X-ray excited Auger electron peaks are also observed as a result of relaxation processes.

Spin-orbit splitting
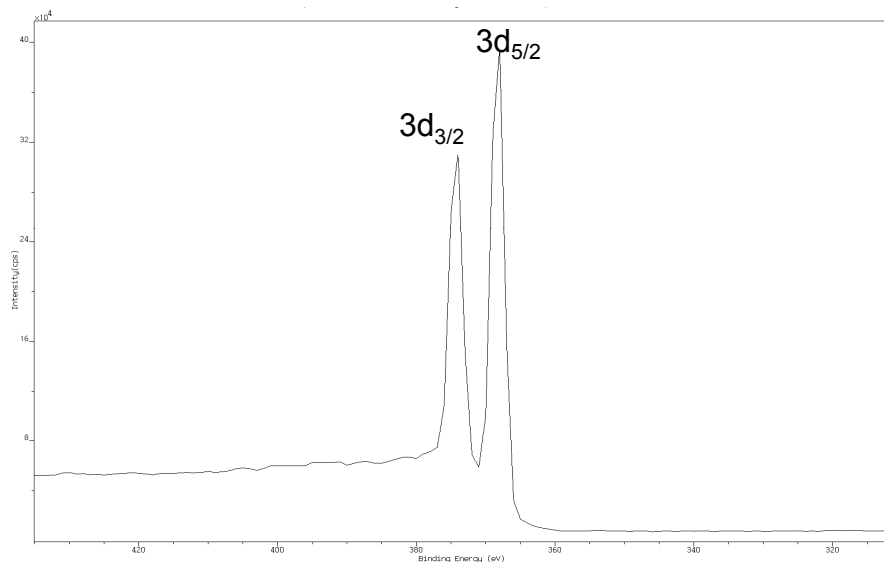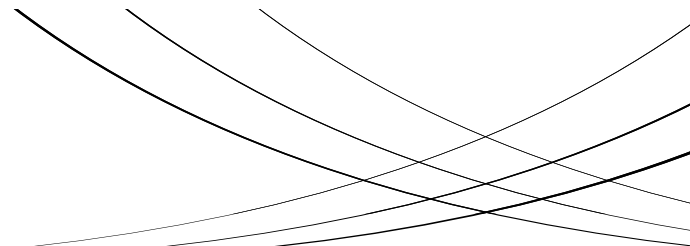
All photoemission peaks that originate from an orbital where $l > 0$ (p,d,f….) result doublets which arise due to spin-orbit coupling between the electronic spin ($\pm\frac{1}{2}$) and angular momenta.

$j = s + l$

Sub shell	j value	area ratio*
s	1/2	-
p	1/2, 3/2	1 : 2
d	3/2 , 5/2	2 : 3
f	5/2, 7/2	3 : 4

Defined by (2j+1)

The energy separation between spin-orbit doublets can vary from tenths of an electron volt to many tens of electron volts. For a given subshell, the separation will increase as the atomic number increases or increase as l decreases for a constant n. For example, for the Ag spectrum splitting of the 3p > 3d.
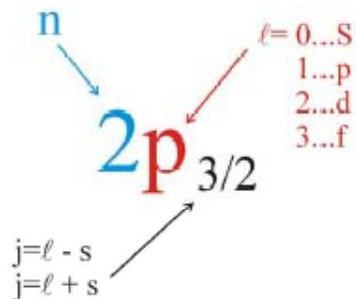
Spin-orbit splitting
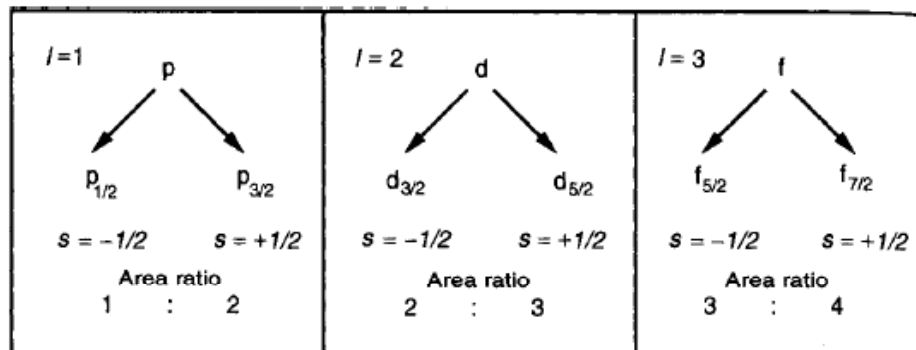
X-ray satellites and ghosts (1)

Magnesium or Aluminium anodes are typically chosen because of a dominant, strong emission line in the X-ray spectrum. X-rays with wavelengths related by integral multiples of the Aluminium $K\alpha$ X-ray line may be defracted using a quartz crystal to produce monochromatic X-ray sources. One of the advantages of using monochromatic X-rays is that the distribution of the photon energies used in the analysis is narrow compared to the non-monochromated (achromatic) X-ray line and therefore improves the resolution of the photoelectric peaks in the XPS spectrum. A further consequence of monochromating the X-rays is that minor X-ray emission lines in the X-ray spectrum are removed from the photoelectron excitation mechanism. If unmonochromated, these minor X-ray lines produce additional photoelectric peaks in the XPS spectrum and these appear at kinetic energies characteristic of the energy separation between the primary X-ray emission lines. Therefore, these satellite lines are only observed when using non-monochromated X-ray sources..

	$\alpha_{1,2}$	α_3	α_4	α_5	α_6	β
Mg radiation / eV	0	8.4	10.1	17.6	20.6	48.7
Relative height	100	8.0	4.1	0.6	0.5	0.5
Al radiation / eV						9.7
Relative height						.6
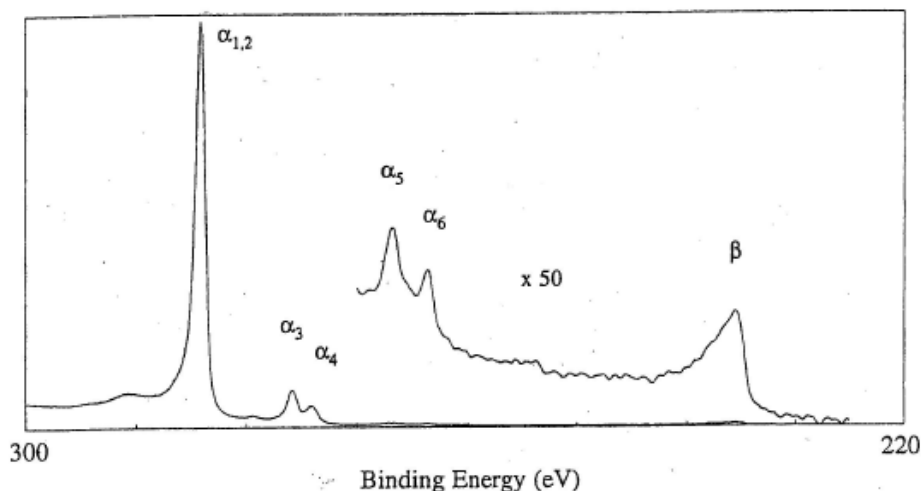
Non-monochromated Mg excited C 1s spectrum of graphite

It is possible that x-rays from a different x-ray anode than that being used can impinge on the sample, resulting in low intensity spectral peaks at positions characteristic of this excitation source superimposed on that of the anticipated spectrum. These photoemission peaks may arise from Mg impurity in the Al anode, or vice versa, copper breakthrough from the anode base, oxidation of the anode or generation of c-rays from the Al foil window. Whilst not common these minor lines can be significant in trying to assign photoemission peaks to specific elemental core levels.

The separation of the peaks will be characteristic of the energy between the x-ray sources and is defined in the table below :

Contaminating Radiation	Anode Material	
	Mg	Al
O (Kα)	728.7	961.7
Cu (Lα)	323.9	556.9
Mg (Kα)	-	233.0
Al (Kα)	-233.0	-

Shake-up satellites

Despite the simplicity of the photoelectric process outline in the previous slides, not every process results in the formation of an ion in the ground state. There is a finite probability that the ion will be left in an excited state, a few eV above the ground state. In such a case the KE of the emitted photoelectron is reduced, with the energy difference corresponding to the difference in energy between the ground state and the excited state. This will result in a satellite peak a few eV lower in KE (higher in binding energy) than the main core level peak. A good example of this is the shake-up satellite involving the energy of the $\pi - \pi^*$ transition for C 1s.

C 1s:1(Top_PET)
Lens Mode:Hybrid   Resolution:Pass energy 10   Iris(Aperture):slot(Slot)
Anode:Mono(Al (Mono))(450 W)   Step(meV): 100.0   Dwell(ms): 260   Sweeps: 2   Acquisition Time(s): 121

C 1s spectrum of PET

Shake-up satellites
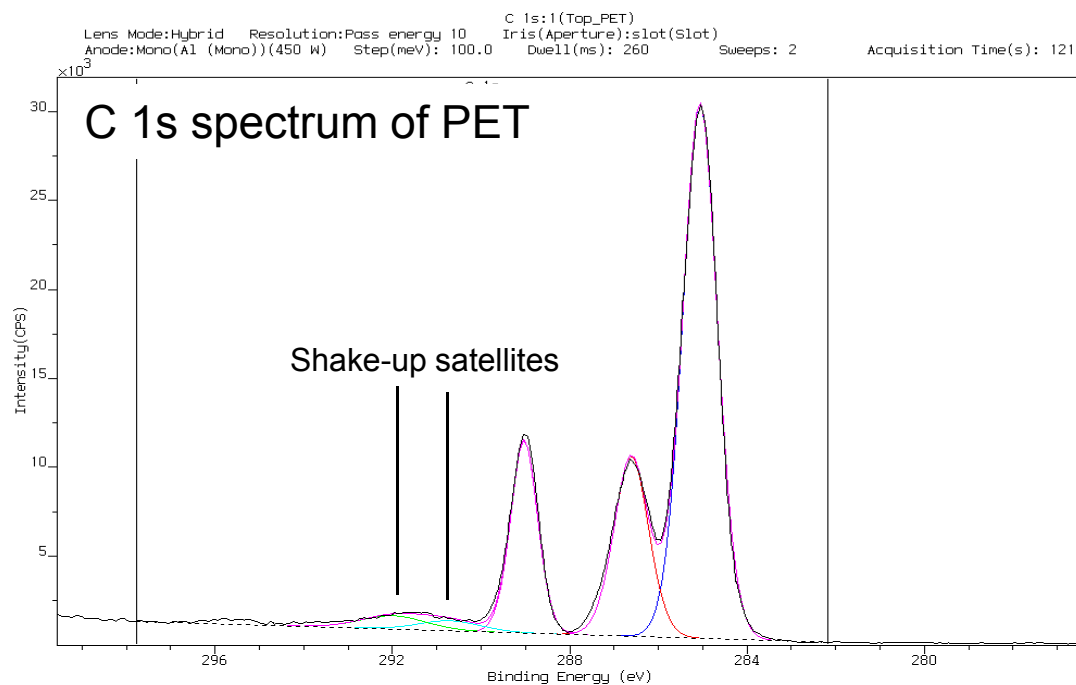
Energy Loss structure (plasmons)

In some cases there is the possibility of the loss of a specific (quantised) amount of energy due to interaction of the photoelectron with other electrons inGro the surface region of the sample. Such a process produces distinct and rather sharp features at 20 – 25 eV higher BE (lower KE). This effect is most apparent for metallic samples, as shown in the loss structure for clean Al metal. The energy loss due to the conduction electrons occurs in well defined quanta characteristic of the specific metal and can provide valuable information on the conduction band structure. These plasmons arise from group oscillations of the conduction electrons.

Plasmon lines are especially prominent in group Ia and IIa spectra.
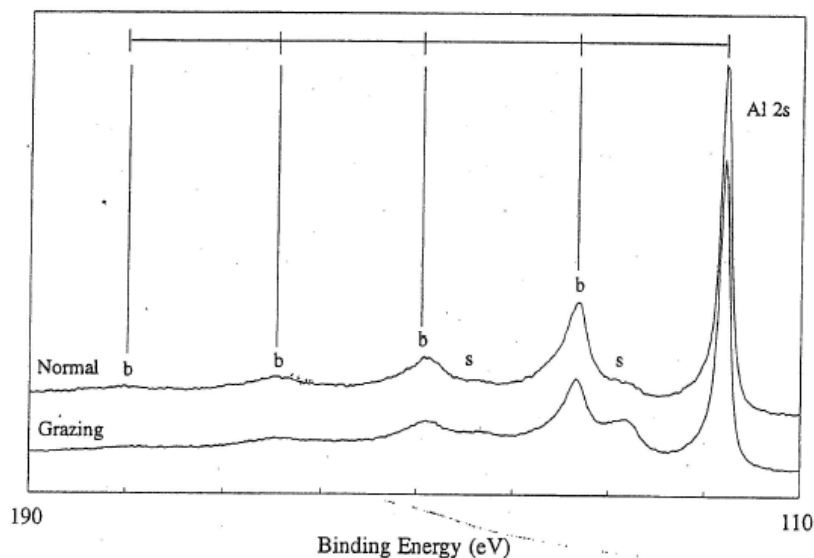
Taken from Handbook of XPS 2nd Edition J.F. Molder et al.

Figure 12. Surface (s) and bulk (b) plasmon lines associated with the Al 2s at normal and grazing take-off angles.

Valence Band (VB) spectra

The photoemission lines of low intensity near the Fermi level, or 0eV BE, are routinely referred to as valence band spectra. These lines are produced by photoelectron emission from molecular orbials and from solid state energy bands and are the electrons that are most weakly bound to the atom in question. A metallic sample is differentiated from a insulating samples by the presence of a relatively high number of electrons at the Fermi level. In contrast a non-conducting sample will be characterised by absence of electrons at the Fermi level.

A further useful application of the VB spectrum is to distinguish between materials where the core level XPS si the same with respect to BE position and peak shape. In many cases the VB spectrum for very similar materials can be quite different and used as a 'fingerprint' for a specific material. The classic example is the C 1s of polethylene and poly propylene which are indistinguishable from each other, whereas the VB are very distinct for each polymer.
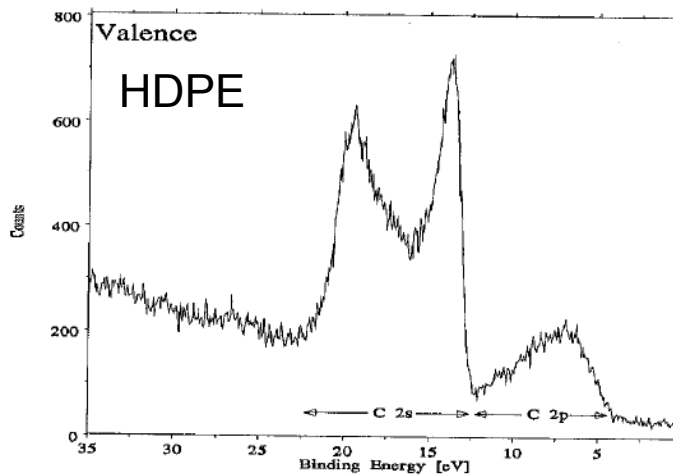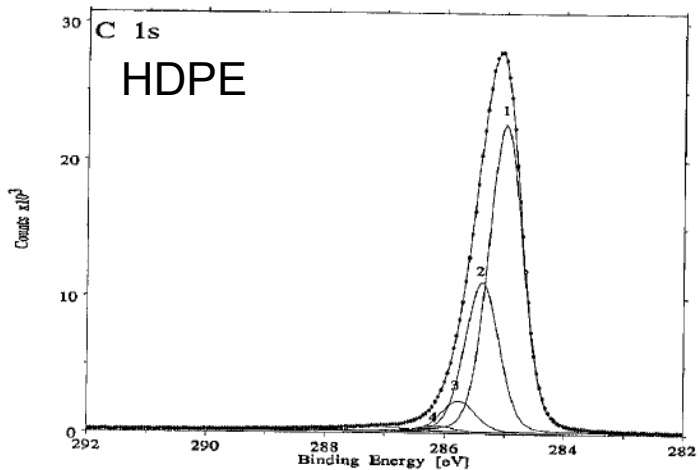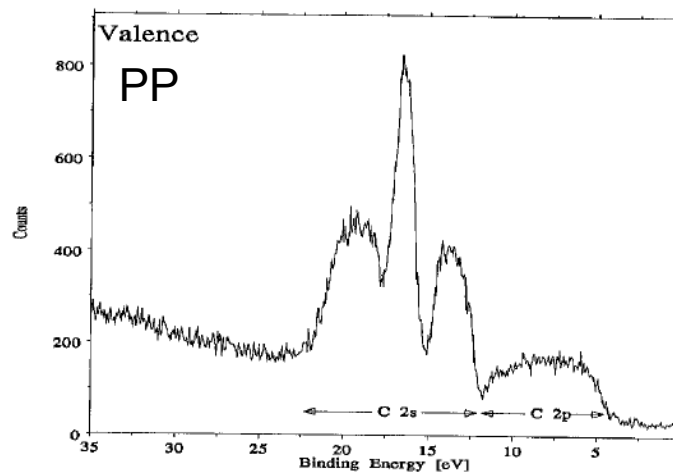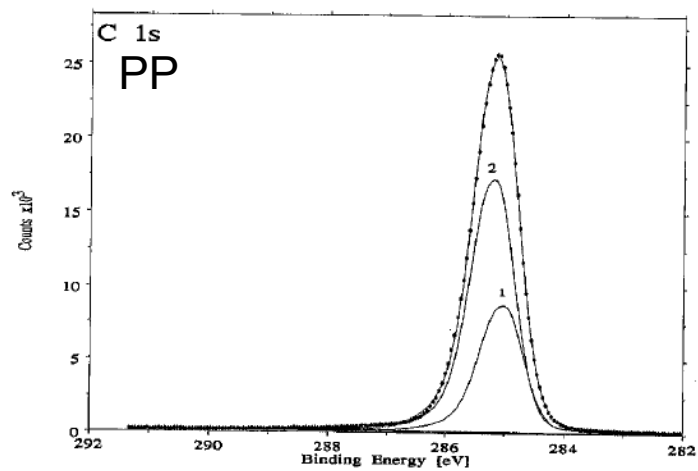
High Resolution Spectroscopy – 'Fingerprints'

- Three isomers of PBMA
- Monochromatic X-rays
- Identical C1s core level
- Valence band data
    - 'fingerprint' polymers
    - 5 minute acquisition
   - 20eV pass energy

Spectral Background

Photoemission peaks sit on a background of inelastically scattered photoelectrons. For an XPS spectrum excited using a monochromatic x-ray source the background is significantly lower than that for a non-monochromated x-ray source.
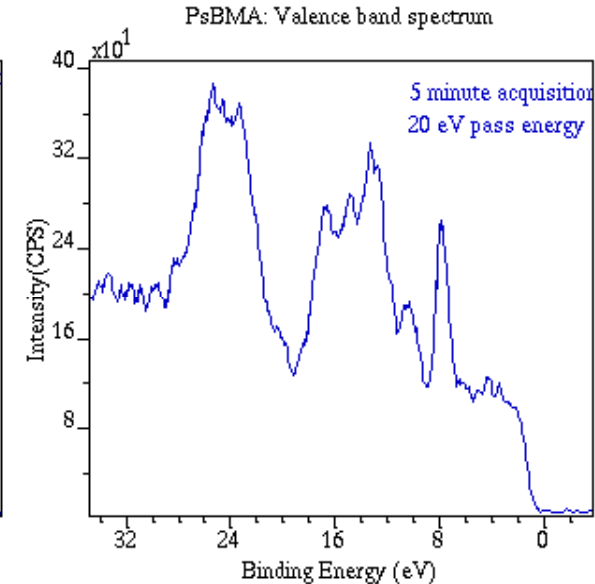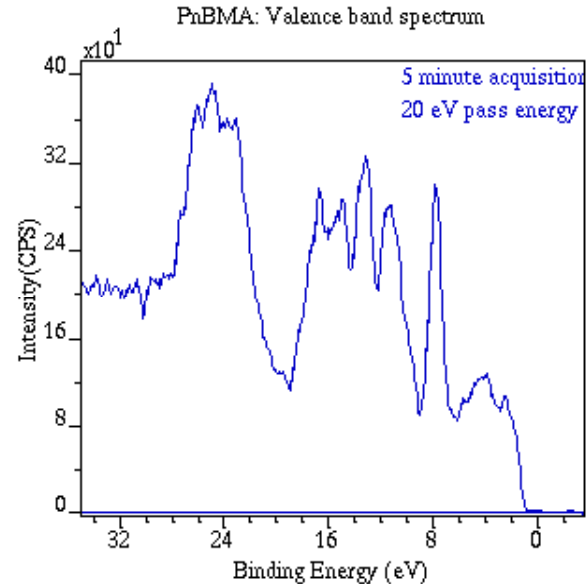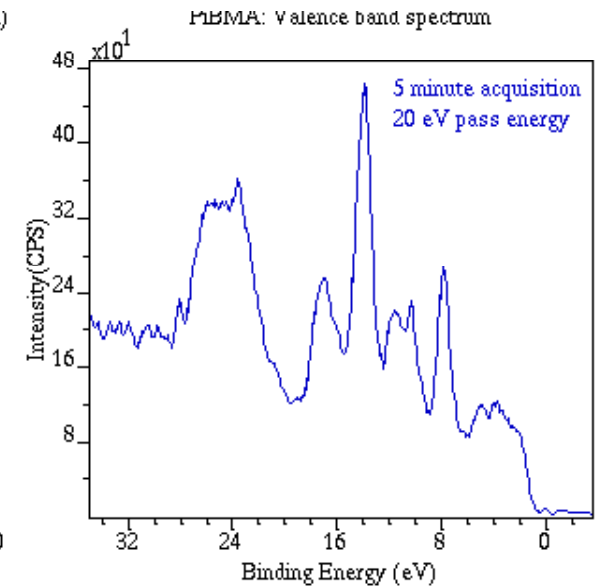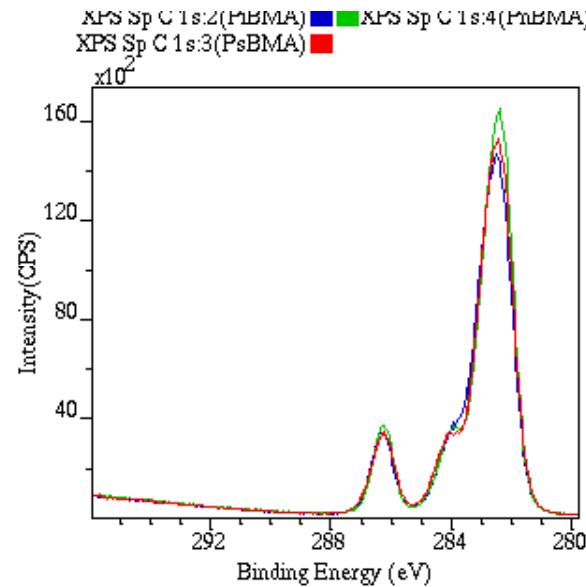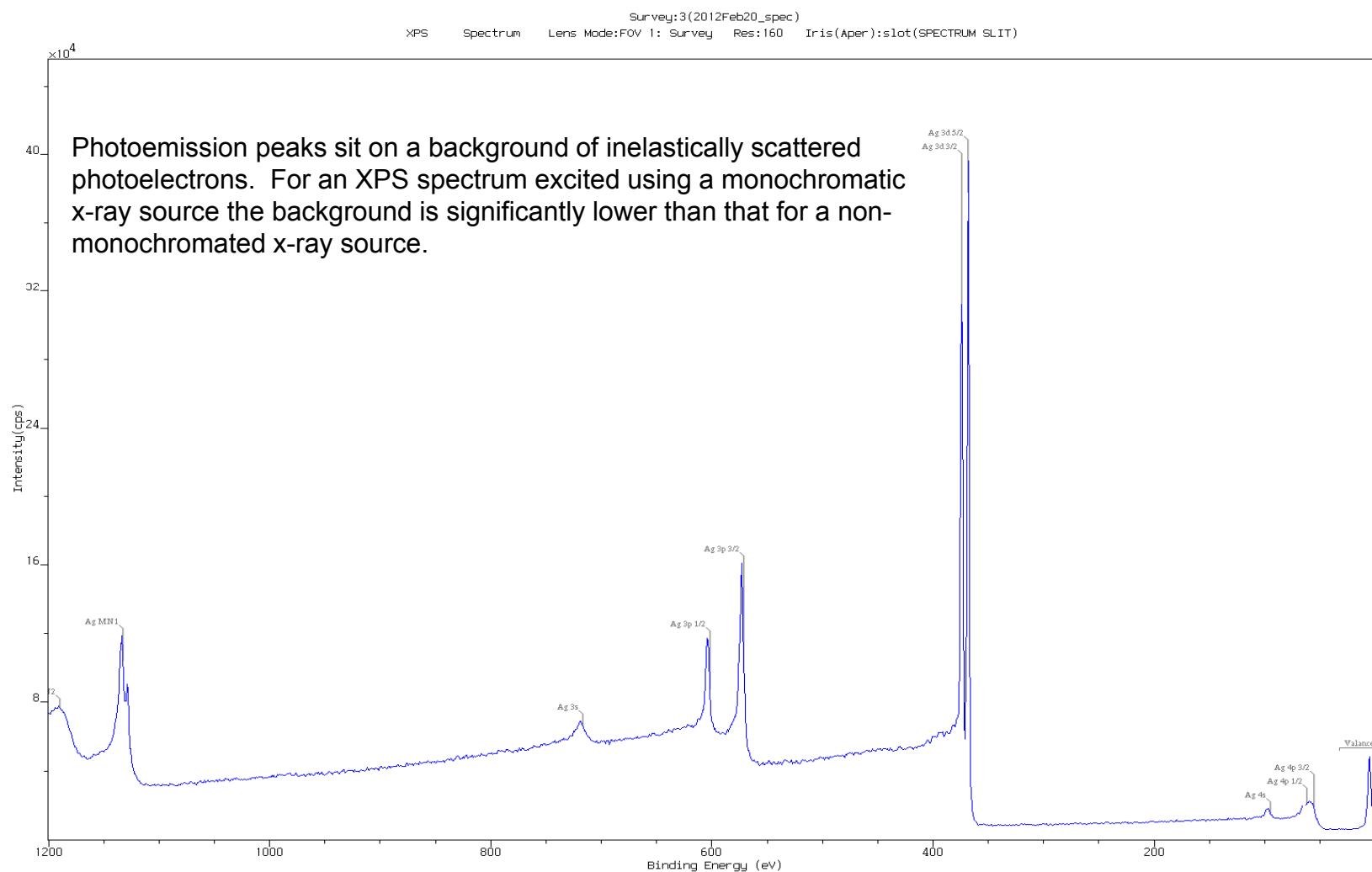
Monochromated vs non-monochromated X-ray source

- X-rays generated by accelerating high energy electrons onto an anode. The core holes created decay by emission of X-rays.

- Commonly used X-ray sources

anode material	energy (eV)	Width (eV)
Mg	1253.6	0.7
Al	1486.6	0.85

X-ray Intensity as a Function of Energy
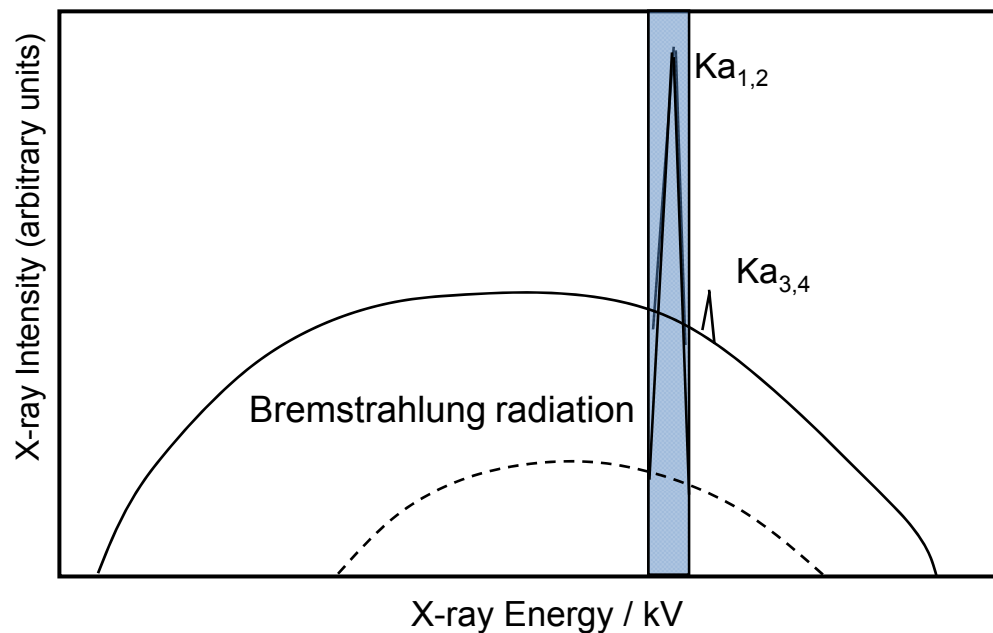
- Use of a monochromator prevents electrons, Bremsstrahlung, satellite X-ray lines and heat radiation striking the sample.

- The monochromator also decreases the energy spread of the X-rays.

Monochromated vs non-monochromated X-ray source
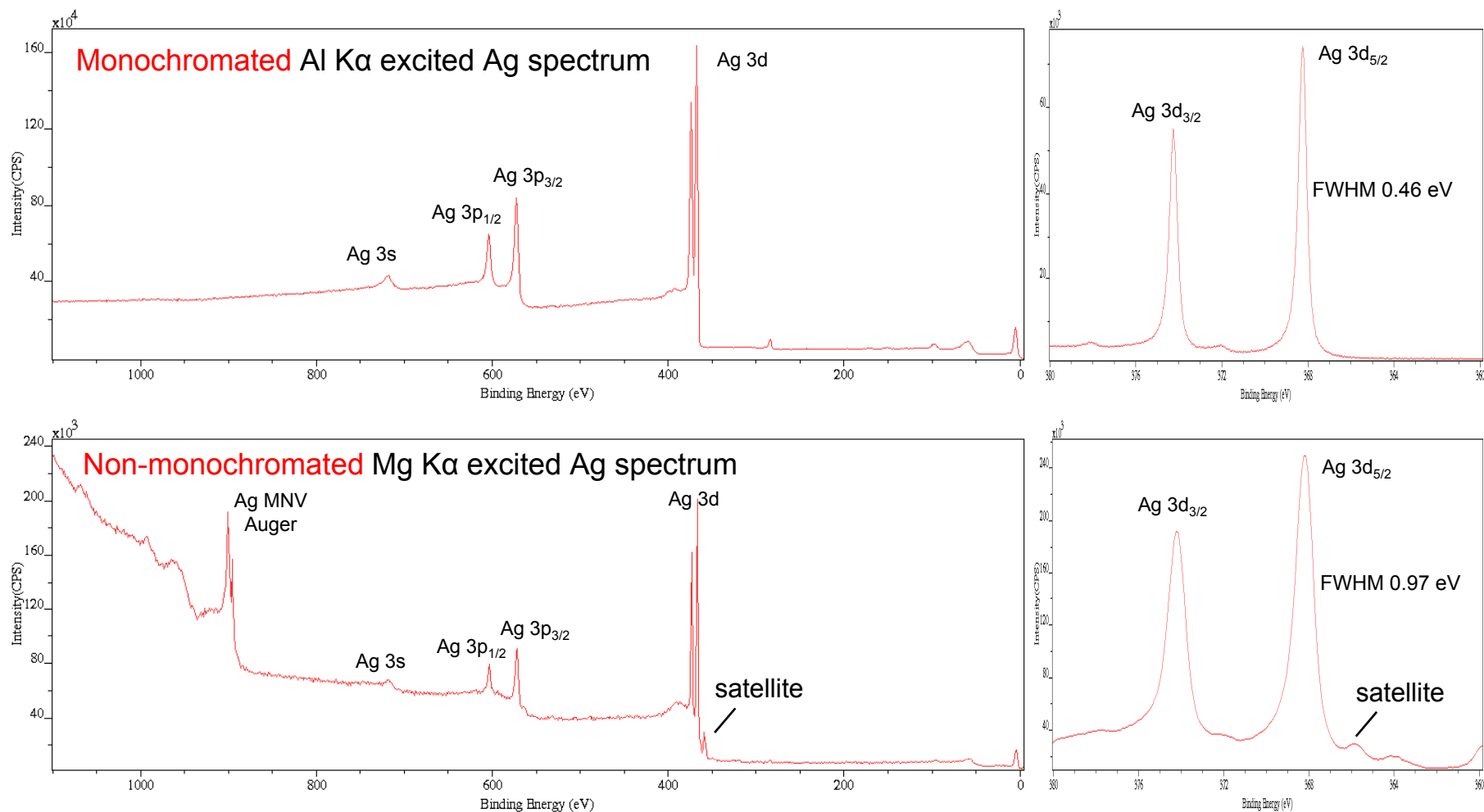
Things to note: loss of rising background, narrower peaks, loss of satellite peaks, movement of Auger peaks

What information do we get from XPS?

- **Surface sensitivity** - photoelectron signal from first 1-10 layers of atoms and molecules.
- **Identification** of all elements (except H & He) at concentrations >0.1atomic%*.
- **Quantitative** determination of the elemental composition.
- Information about the **chemical state** (molecular environment) of the element.
- **Non-destructive** analysis, including depth profiles, from the top 10 nm.
- Destructive **depth profiles** of inorganic materials for 100s of nm.
- **Lateral variations** in surface composition at 15µm resolution.
- **'Finger printing'** of materials using valance band.

- *Sensitivity - a sample with a surface of size 1 cm^2 - this will have ca. 10^{15} atoms in the surface layer. In order to detect the presence of impurity atoms present at the 1% level, a technique must be sensitive to ca. 10^{13} atoms.   Contrast this with a spectroscopic technique used to analyse a 1 cm^3 bulk liquid sample i.e. a sample of ca. 10^{22} molecules. The detection of 10^{13} molecules in this sample would require 1 ppb (one *part-per-billion*) sensitivity - very few techniques can provide anything like this level of sensitivity.

Surface Sensitivity of XPS

λ_i = inelastic mean free path of an electron in a solid.

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. So, the intensity I_s of the same electron
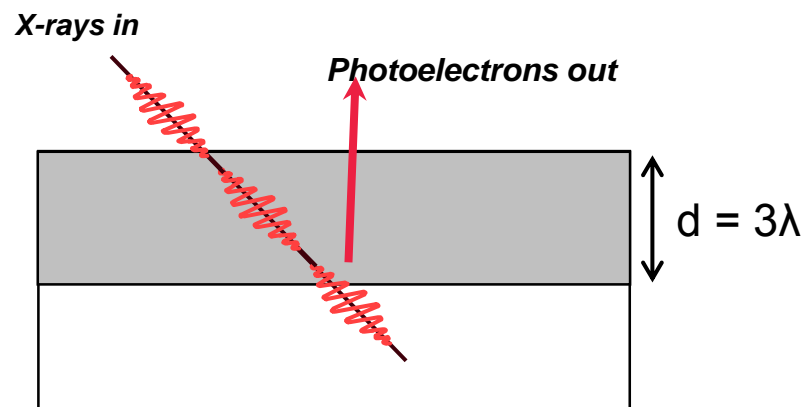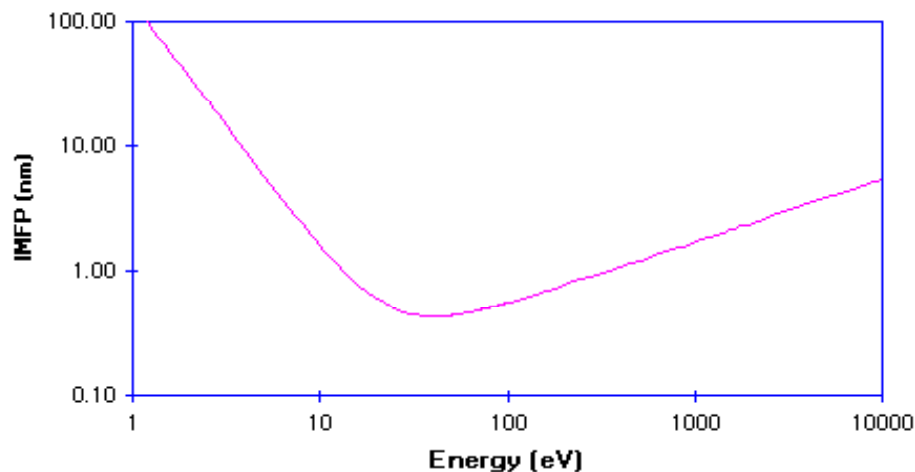
as it reaches the surface is given by

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

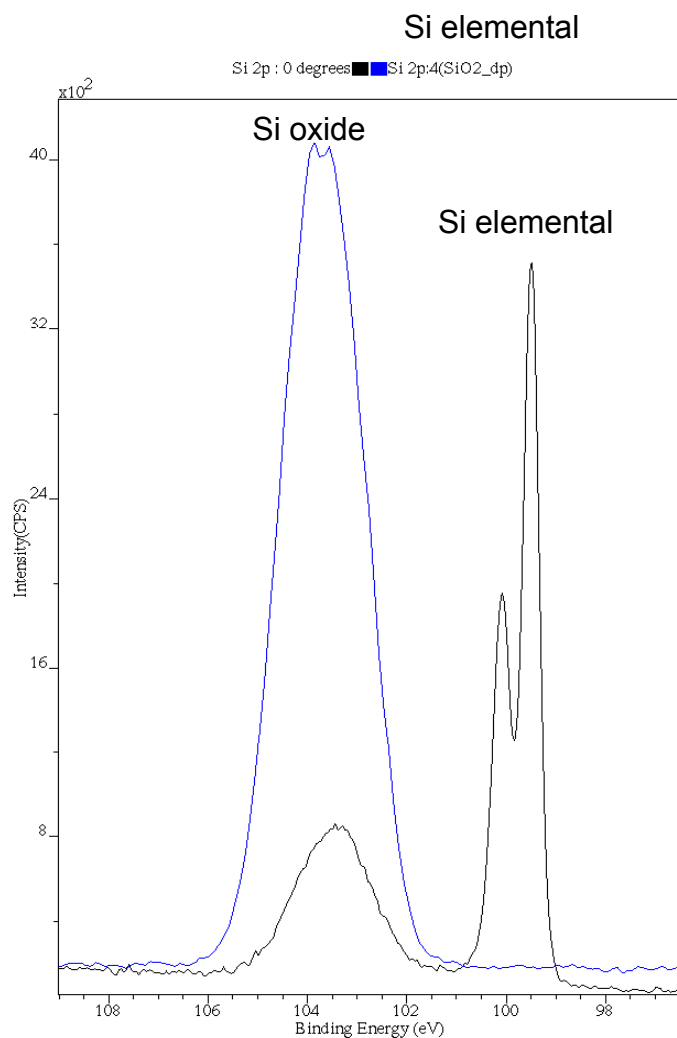With a path length of one λ, 63% of all electrons are scattered

X-rays in

I_s

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

$d = 3\lambda$

I_o
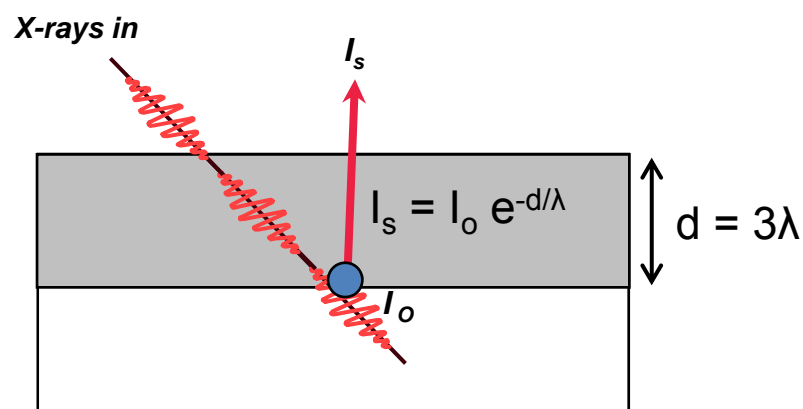
Surface Sensitivity of XPS

- Penetration depth of the X-ray radiation is 10^2-10^3 nm.

- However, the surface sensitivity of XPS arises from the short distance the photoelectrons can travel in the solid before suffering inelastic scattering.

- The average distance from the surface a photoelectron can travel without energy loss is defined as the inelastic mean free pathlength (IMFP), λ.

- Sampling depth, d, defined as the average distance from the surface for which 95% of photoelectrons are detected, d = 3λ.

XPS Spectra Showing the Chemical State of Si

Si elemental

Si 2p : 0 degrees ■ ■ Si 2p:4(SiO2_dp)

Si oxide

Si elemental

x10^2

Intensity(CPS)

40

32

24

16

8

108   106   104   102   100   98

Binding Energy (eV)

Two samples with different SiO_2 film thicknesses on Si substrate.

-note large chemical shift between elemental Si and silicon dioxide peaks.

d   d   Si oxide

Si elemental

Chemical State Information

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

Valence electron, low binding energy

Core level electron, high binding energy

- The variation of binding energy of a specific photoemission peak provides information on the chemical state of the atom or ion.

Chemical State Information

Typical binding energies for C 1s photoemission peaks from organic materials

	functional group	binding energy (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

Typical chemical shifts for O 1s photoemission peaks from organic materials

	functional group	binding energy (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

Quantitative Surface Analysis of Poly(ethylene terephthalate) - PET Large Area Survey
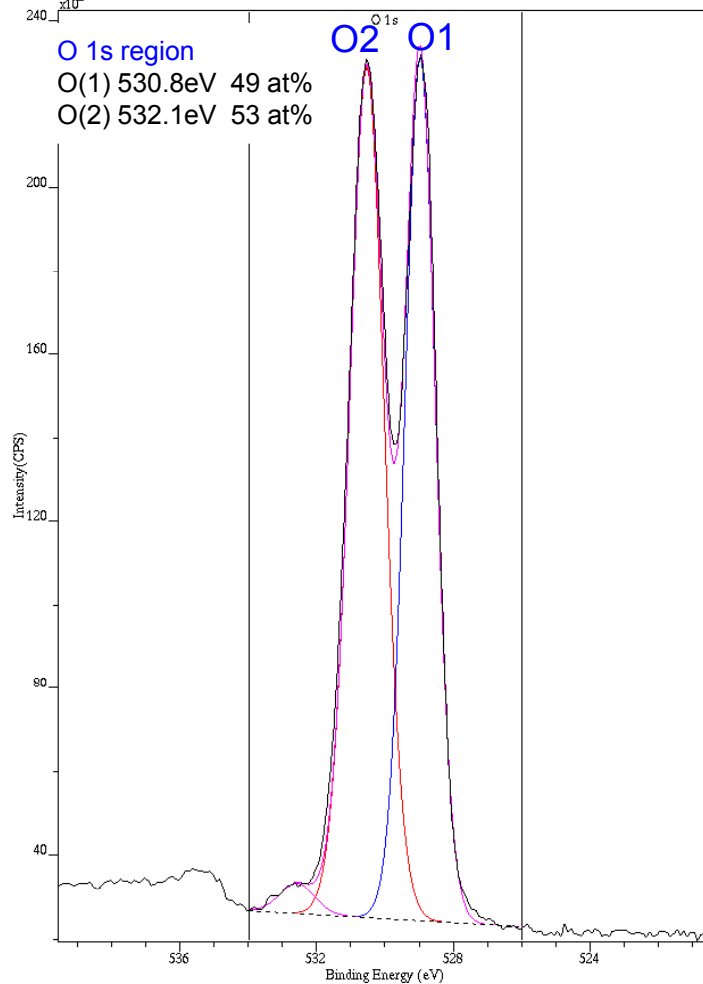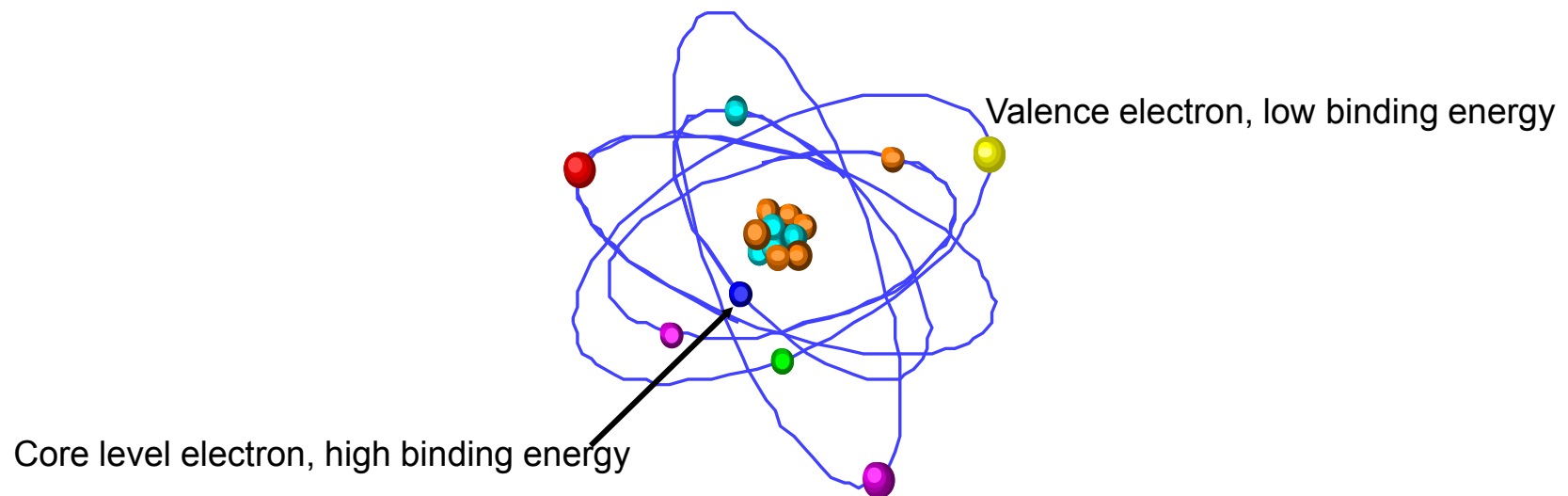

Lens Mode:Hybrid   Resolution:Pass energy 160   Iris(Aperture):slot(Slot)
Anode:Mono(Al (Mono))(300 W)   Step(meV): 1000.0   Dwell(ms): 109   Sweeps: 2   Acqn. Time(s): 240

Peak	Position BE (eV)	FWHM (eV)	Raw Area (CPS)	RSF	Atomic Mass	Atomic Conc %	Mass Conc %
C 1s	282.000	3.181	1988710.0	0.278	12.011	74.54	68.73
O 1s	530.000	3.623	2089951.0	0.780	15.999	25.46	31.27
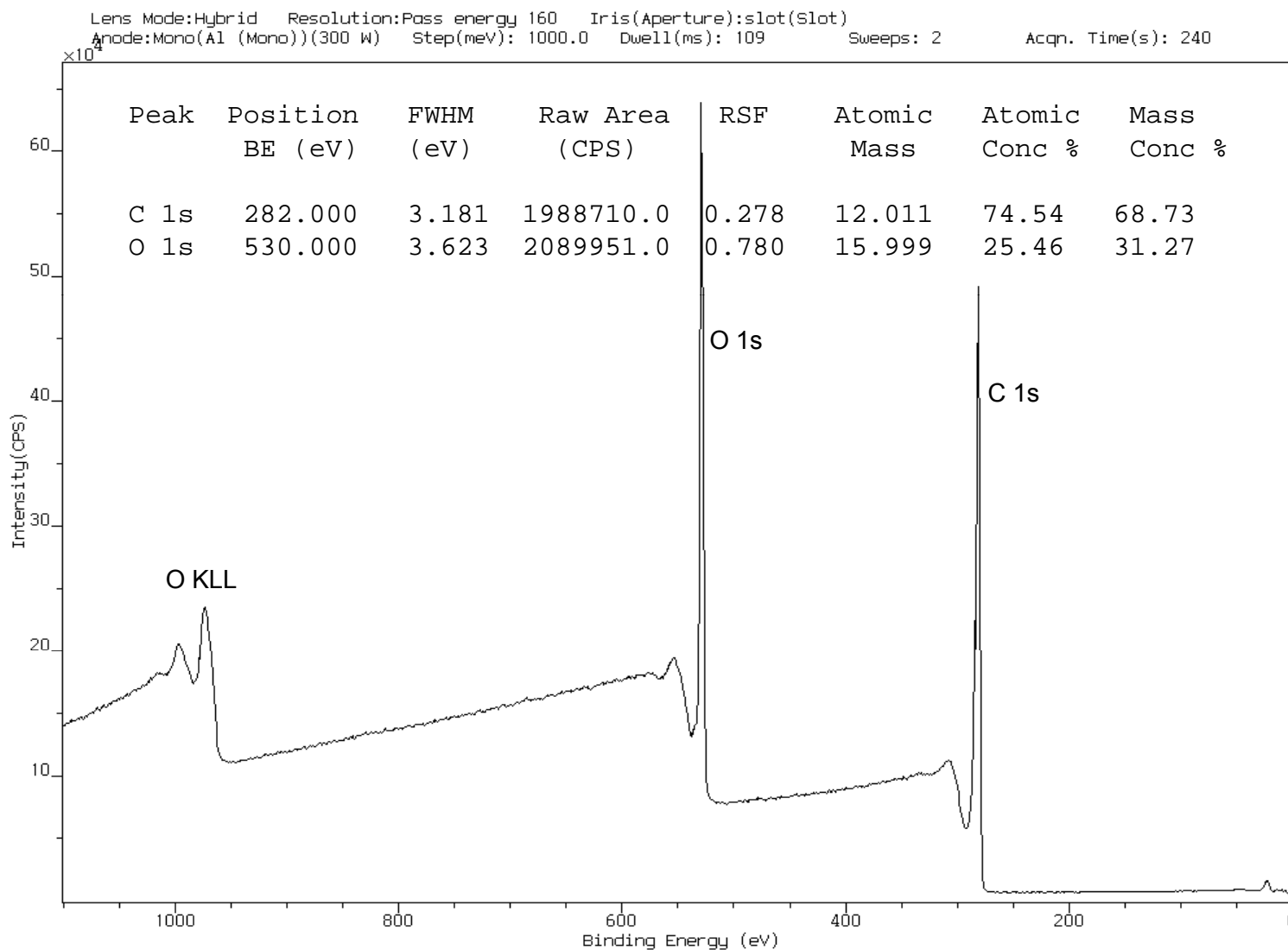
Neutralisation of Insulating samples - specifications

XPS performance on insulators for the Ultra^{HSA} is guaranteed by specification defined using a polymer. The standard used is PET (polyethylene terephthalate) which has the chemical structure shown. The specifications are defined as the cps from the CC,CH component at 285eV and the FWHM of the ester component (C-C(=O)-O-) at *ca.*289 eV.

C 1s:1(Top_PET)
Lens Mode:Hybrid   Resolution:Pass energy 10   Iris(Aperture):slot(Slot)
Anode:Mono(Al (Mono))(450 W)   Step(meV): 100.0   Dwell(ms): 260   Sweeps: 2   Acquisition Time(s): 121

Typical performance of a spectrometer for 700x300um analysis area

Sensitivity of CC,CH component (cps)

FWHM of ester peak (eV)
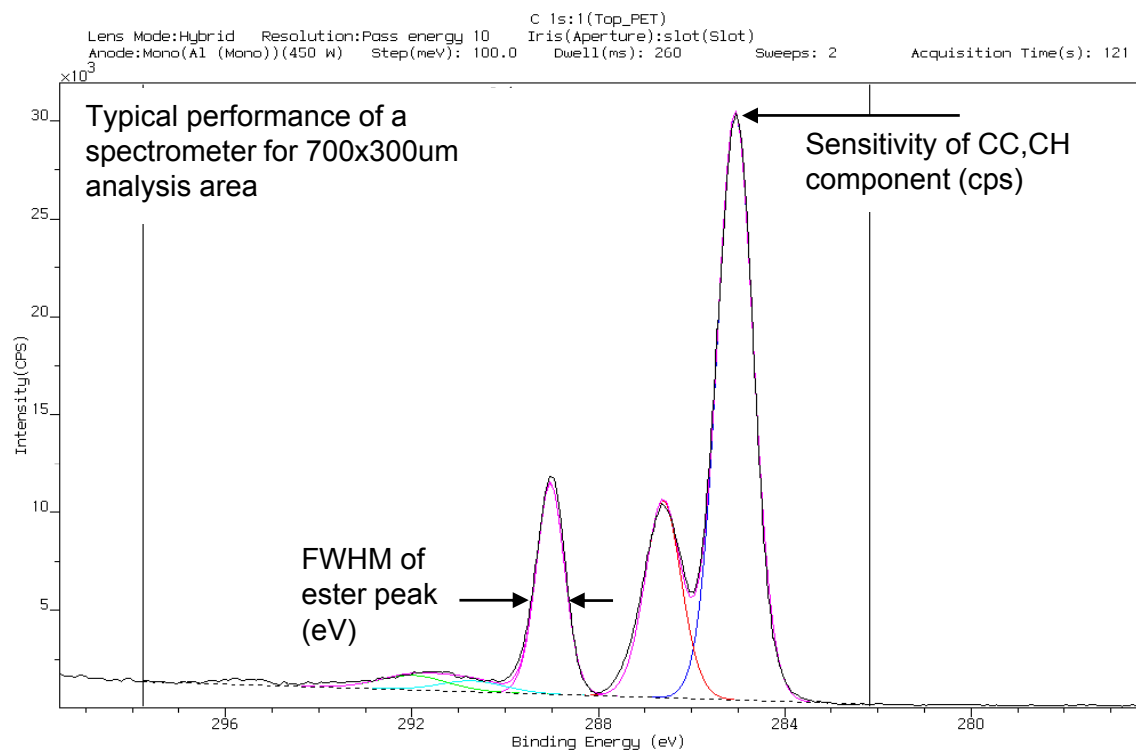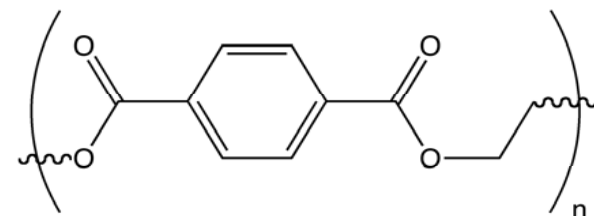
res^n \ area	700x300um	110um
0.68eV	12,000	2,000
1.0eV	100,000	10,000
1.3eV	150,000	15,000

Quantitative Surface Analysis of Poly(ethylene tetraphthalate) - PET
Chemical State Information
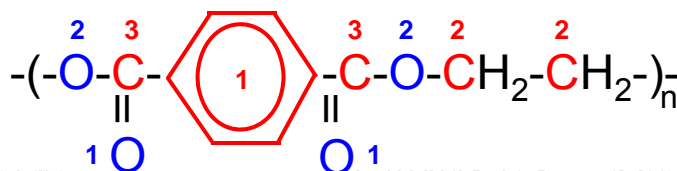
$$-(-\overset{2}{O}-\overset{3}{C}-\underset{1}{\bigcirc}-\overset{3}{C}-\overset{2}{O}-\overset{2}{CH_2}-\overset{2}{CH_2}-)_n$$

with $\overset{1}{O}$ (double bonded) on left C and O ^{1} on right C

C 1s region

C(1) 285.0eV 61 at%
C(2) 286.5eV 21 at%
C(3) 289.2eV 18 at%

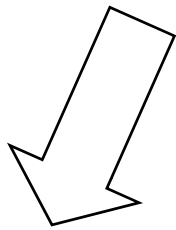**O 1s region**

O(1) 530.8eV 49 at%
O(2) 532.1eV 53 at%

Lens Mode:Hybrid Resolution:Pass energy 10 Iris(Aperture):slot(Slot)
Anode:Mono(Al (Mono))(450 W) Step(meV):100.0 Dwell(ms): 260 Sweeps: 2 Acqn. Time(s):121
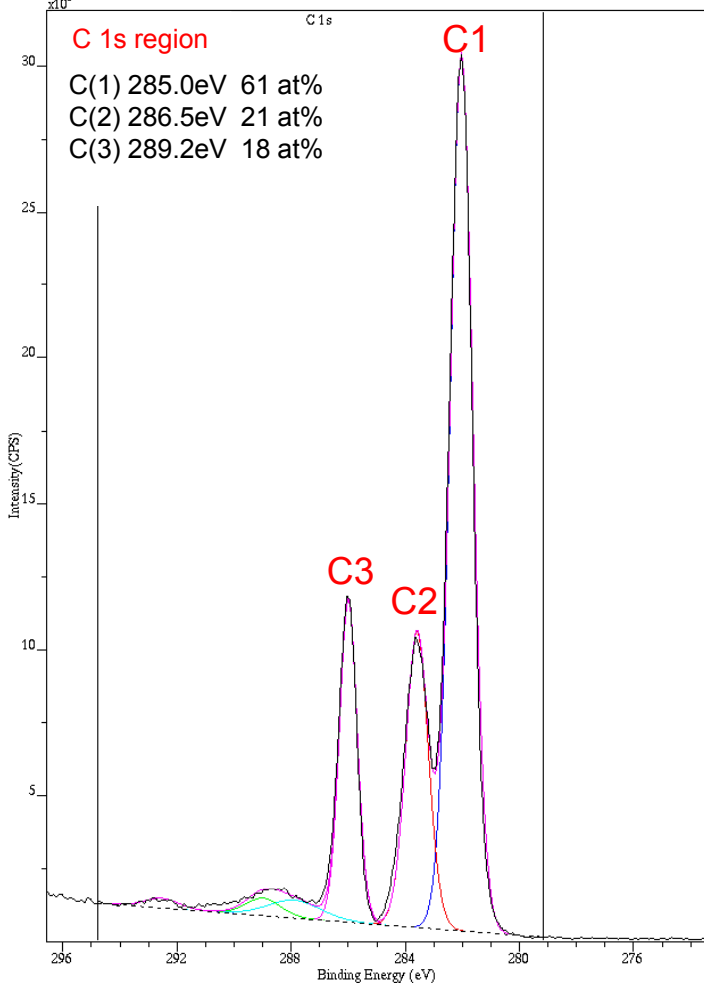
Lens Mode:Hybrid Resolution:Pass energy 10 Iris(Aperture):slot(Slot)
Anode:Mono(Al (Mono))(450 W) Step(meV):100.0 Dwell(ms): 314 Sweeps: 2 Acqn. Time(s):121

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Chemical State Information

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

Valence electron, low binding energy

Core level electron, high binding energy

- The variation of binding energy of a specific photoemission peak provides information on the chemical state of the atom or ion.

Chemical State Information

- Typical binding energies for C 1s photoemission peaks from organic materials

- functional group   binding energy (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	-CH2CF2-	290.6
3F bound to a carbon	-CF3	293-294

- Typical chemical shifts for O 1s photoemission peaks from organic materials

- functional group   binding energy (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

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Quantitative Surface Analysis of Poly(ethylene tetraphthalate) - PET

Large Area Survey

Lens Mode:Hybrid   Resolution:Pass energy 160   Iris(Aperture):slot(Slot)
Anode:Mono(Al (Mono))(300 W)   Step(meV): 1000.0   Dwell(ms): 109   Sweeps: 2   Acqn. Time(s): 240

Peak	Position BE (eV)	FWHM (eV)	Raw Area (CPS)	RSF	Atomic Mass	Atomic Conc %	Mass Conc %
C 1s	282.000	3.181	1988710.0	0.278	12.011	74.54	68.73
O 1s	530.000	3.623	2089951.0	0.780	15.999	25.46	31.27

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Beyond Large Area Spectroscopy

<10 nm

thin film　　　　　thicker layer or multilayers　　　　heterogeneous surface
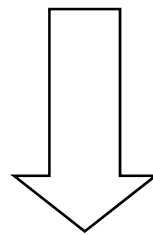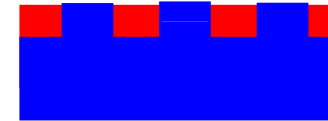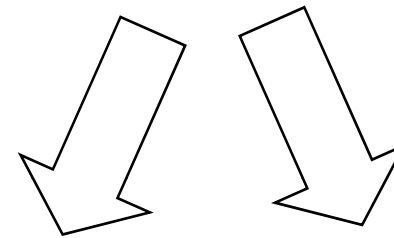
angle resolved XPS　　　　　　depth profile　　　parallel imaging　selected area spectroscopy

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Angular Dependence of XPS

photoelectrons

X-rays

d

photoelectrons

X-rays

d

d ~ 8-10 nm
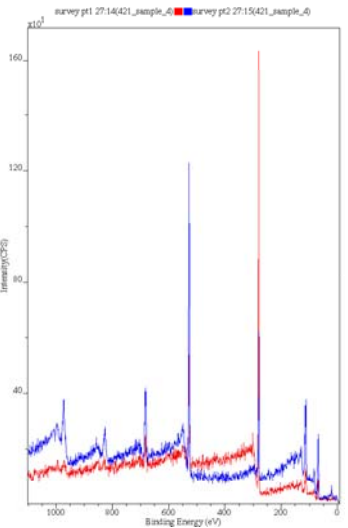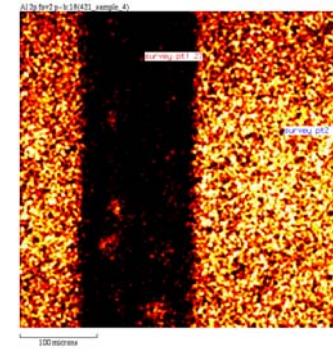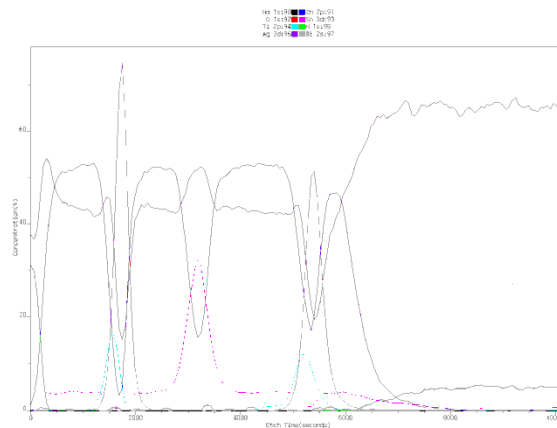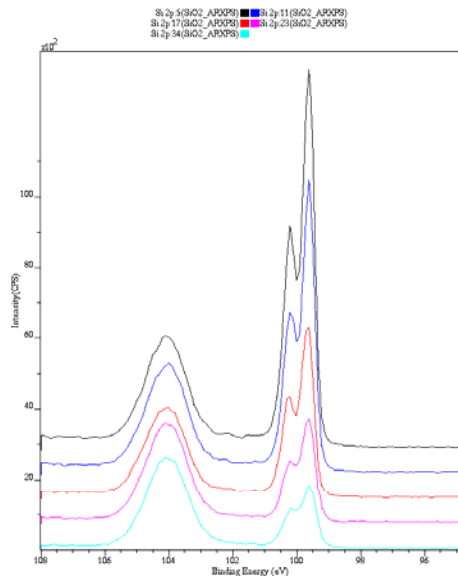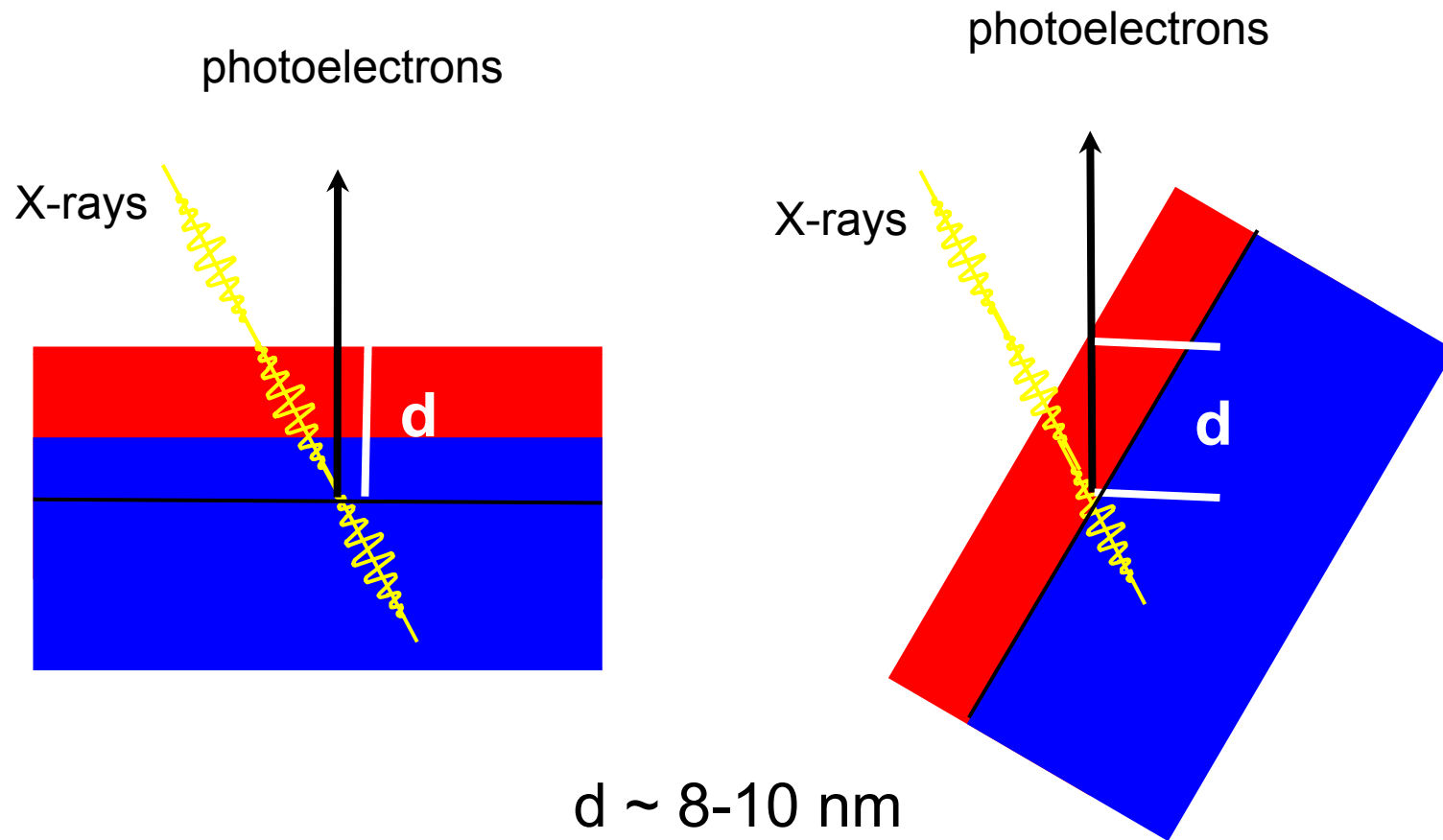
Angular Dependence of XPS - SiO$_2$ on Si wafer
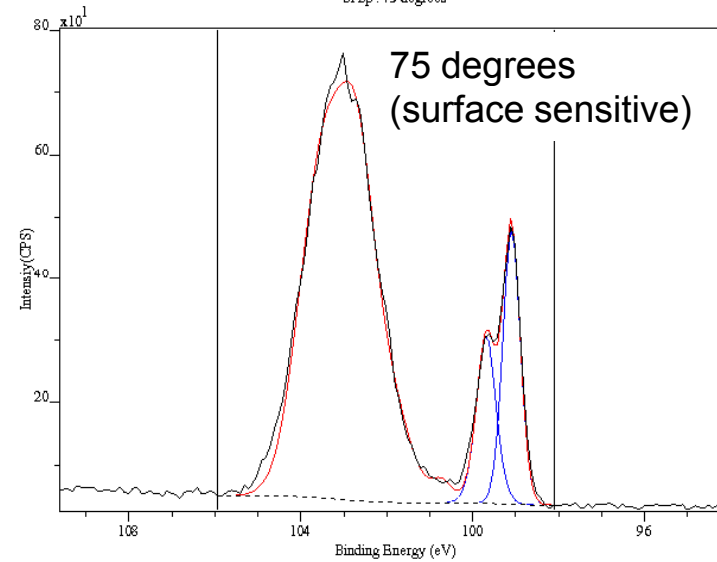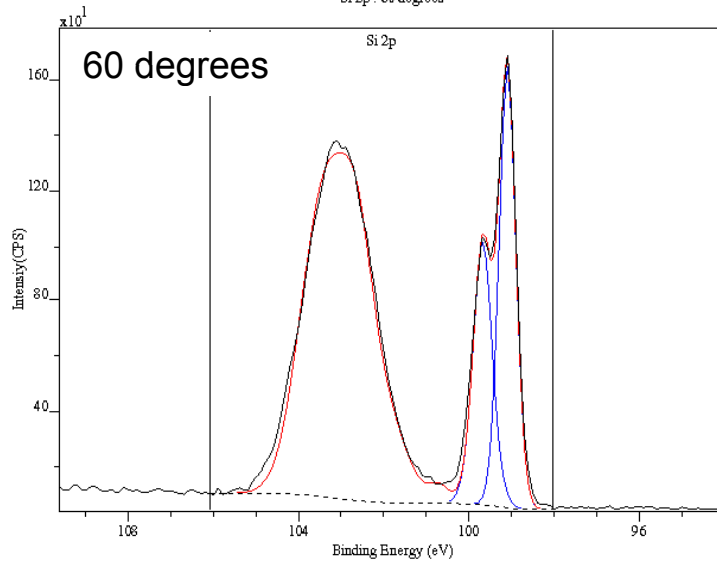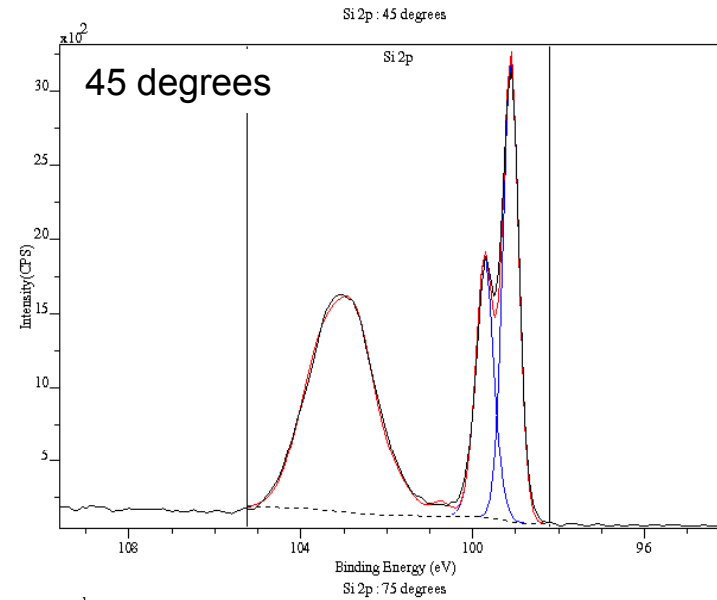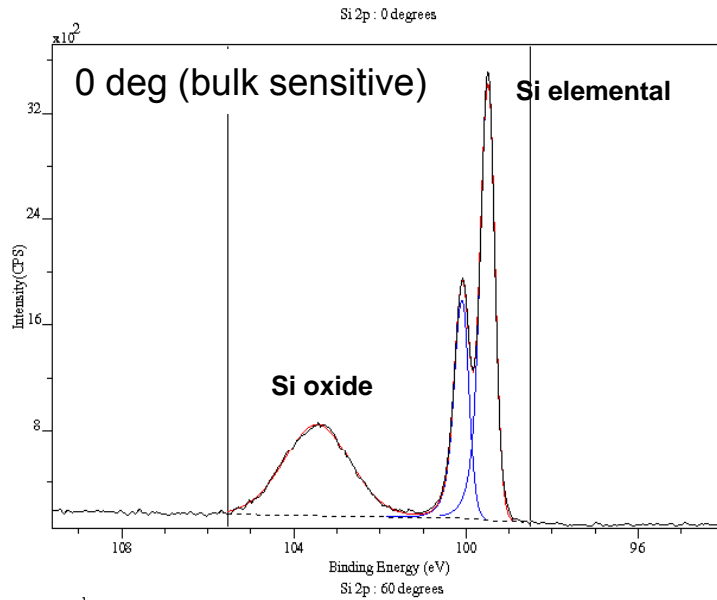
Non-destructive & destructive depth profile

Non-destructive

- By rotating the sample about it's axis, the sampling depth can be changed.

- Collecting data at different angles, will provide a non-destructive depth profile.

- This is limited to film thicknesses less than the sampling depth (~100 Å).
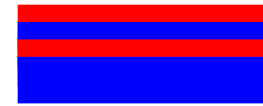
Destructive

- Destructive depth profile can be achieved by Ar+ bombardment of the sample to remove surface atoms, followed by data acquisition.

- When the etch / spectrum cycle is repeated a destructive depth profile of several 1000's Å through the sample may be acquired.
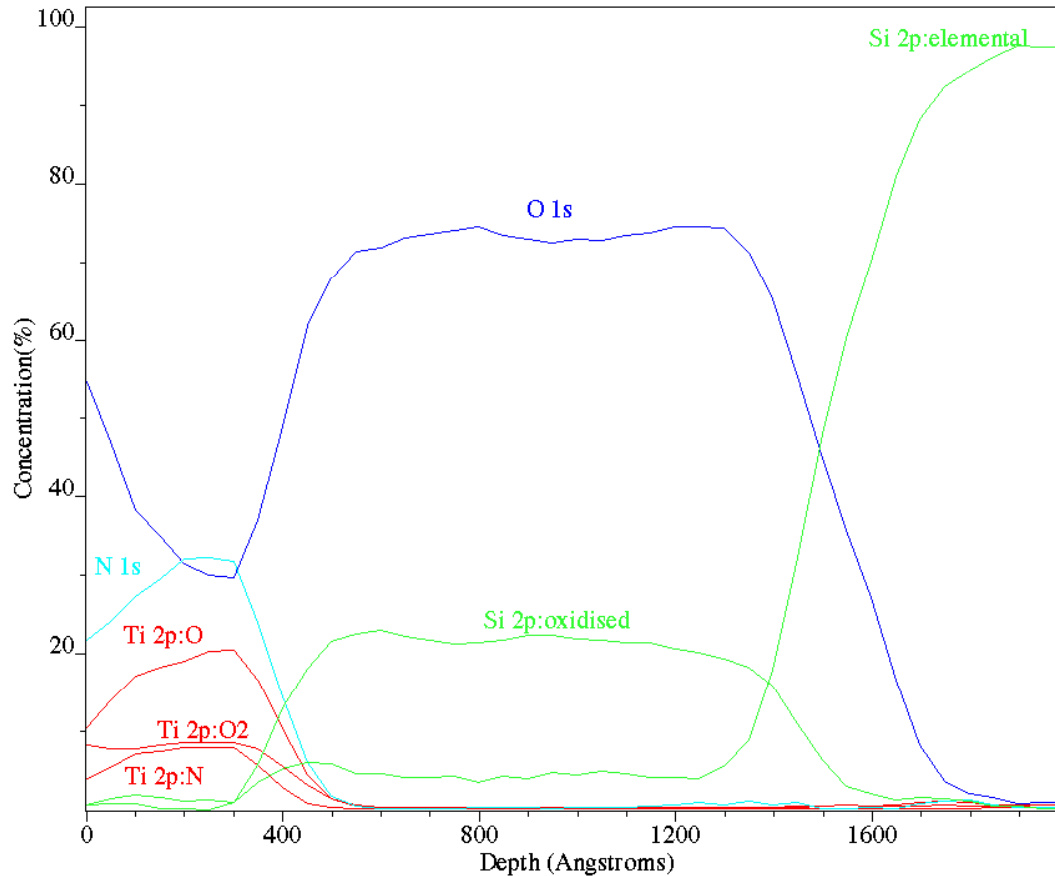
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Depth Profile through a TiN/SiO$_2$ thin film on Si
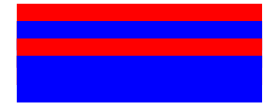
- Thin layer coatings increasingly used in industry to improve surface properties.

- Depth profiling combined with XPS allows valuable film thickness and chemical state information to be determined.
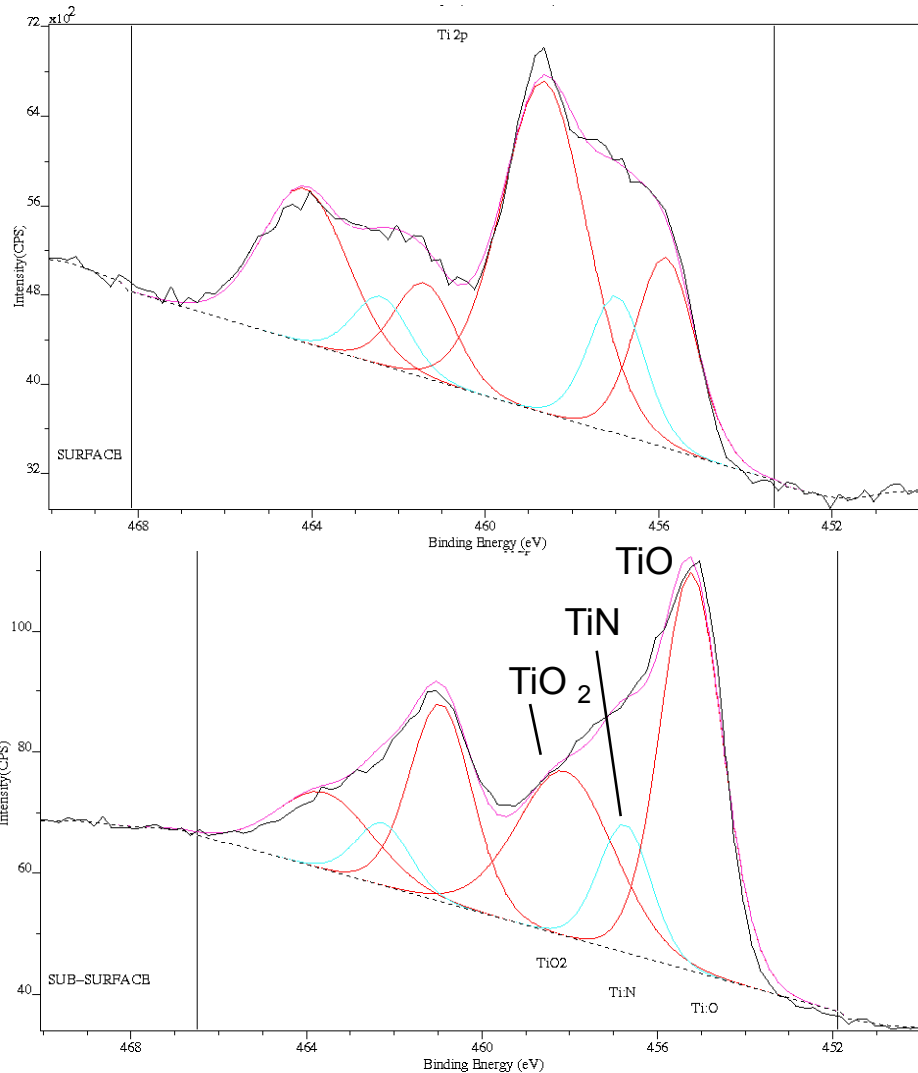
TiN

SiO$_2$

Si substrate
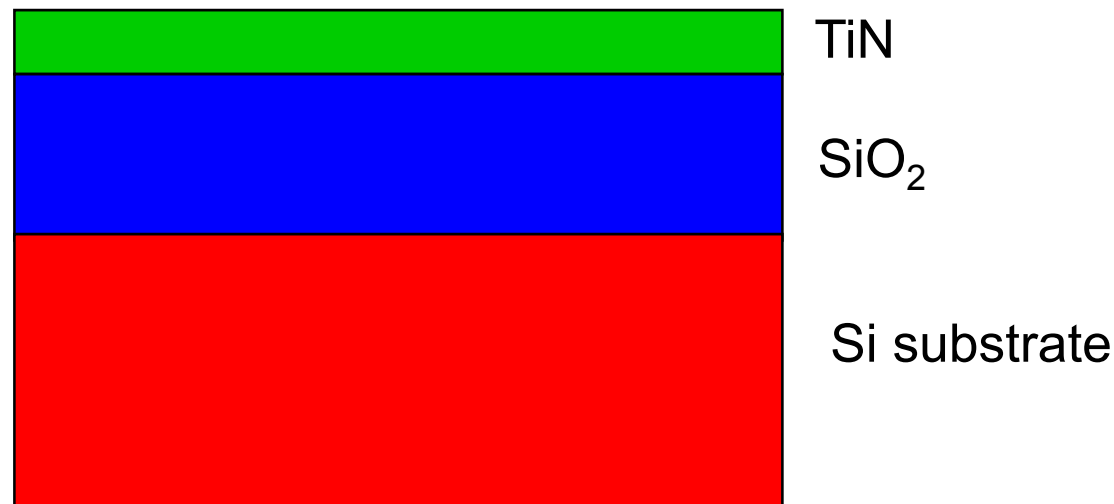
Depth Profile through a TiN/SiO$_2$ thin film on Si

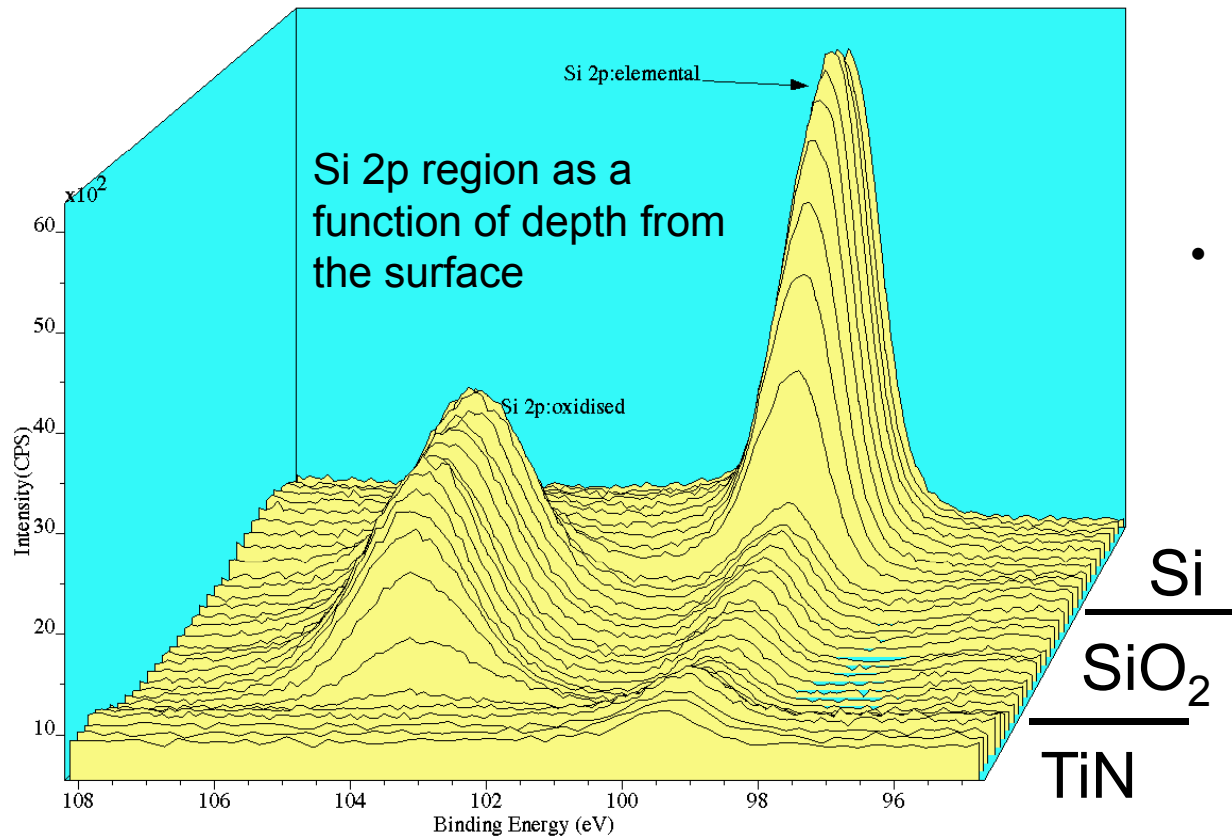- Full chemical state concentration depth profile through TiN film allowing determination of film thickness.

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Depth Profile through a TiN/SiO$_2$ thin film on Si

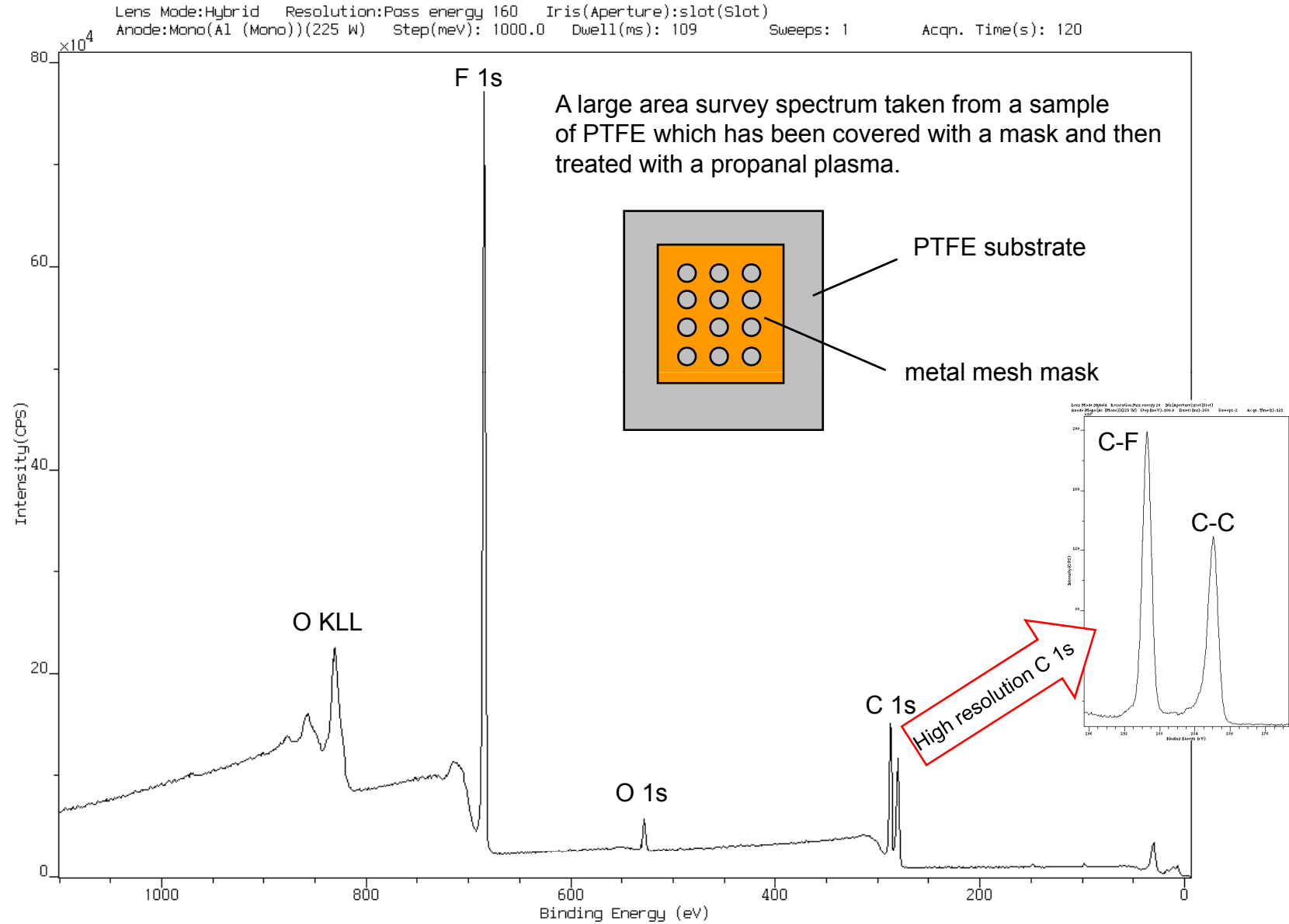High resolution of the Ti region indicates that Ti is also present as TiO$_x$ in the TiN layer.

TiO$_x$ persists through the entire TiN layer, as shown in the Ti 3d region recorded from the subsurface.

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Depth Profile through a TiN/SiO$_2$ thin film on Si

Si 2p region as a function of depth from the surface

- Si 2p region shows chemical environment of the Si atoms.

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Parallel Imaging

Lens Mode:Hybrid   Resolution:Pass energy 160   Iris(Aperture):slot(Slot)
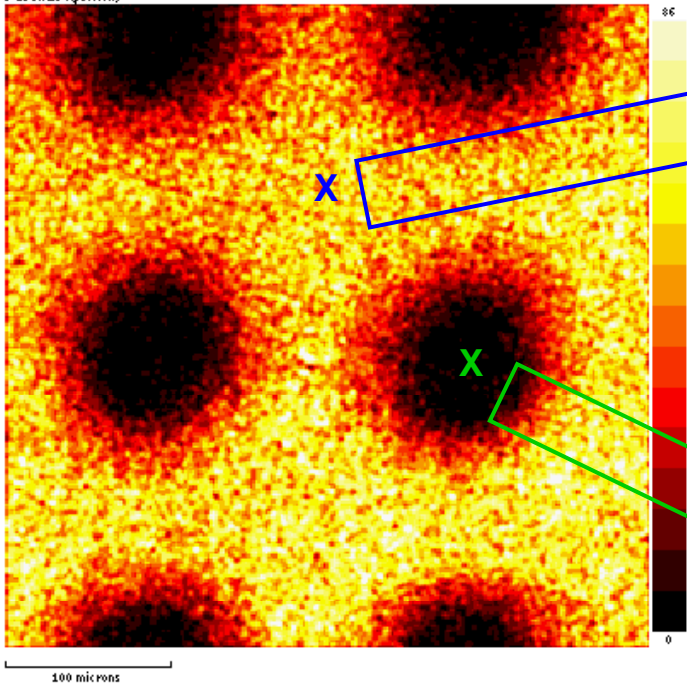Anode:Mono(Al (Mono))(225 W)   Step(meV): 1000.0   Dwell(ms): 109   Sweeps: 1   Acqn. Time(s): 120

A large area survey spectrum taken from a sample of PTFE which has been covered with a mask and then treated with a propanal plasma.

PTFE substrate

metal mesh mask

F 1s

O KLL

C 1s

O 1s

High resolution C 1s

C-F

C-C

Intensity(CPS)

Binding Energy (eV)

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Parallel Imaging
elemental & chemical state imaging

Lens Mode:Hybrid   Resolution:Pass energy 160   Iris(Aperture):slot(Slot)
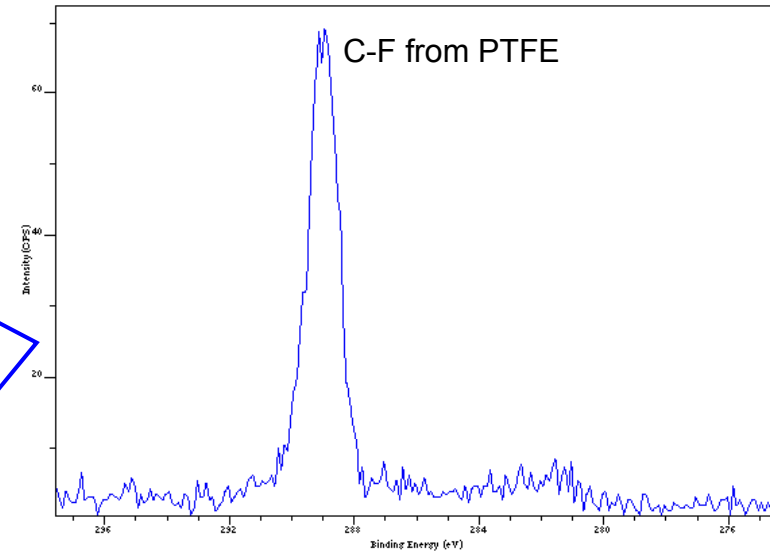Anode:Mono(Al (Mono))(225 W)   Step(meV): 1000.0   Dwell(ms): 109   Sweeps: 1   Acqn. Time(s): 120

•Parallel XPS images taken at energies corresponding to the peaks shown.
•Each image is ~400x400µm
•Acquisition time per image = 120s

F 1s

C-F

O 1s

C-C

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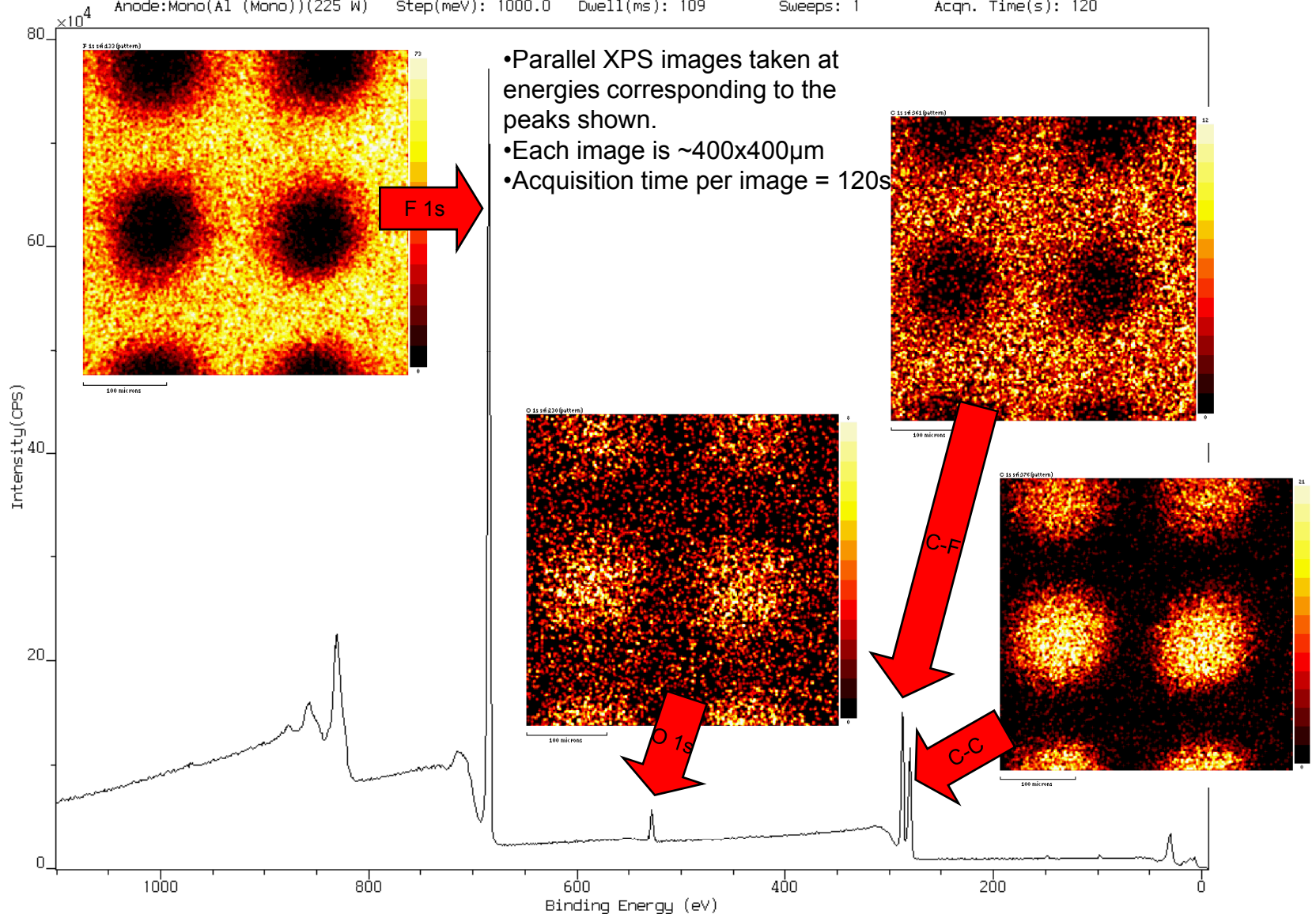
Selected Area Spectroscopy

27 µm selected area C 1s spectra acquired from the positions shown.

C-F from PTFE

C-C from propanal
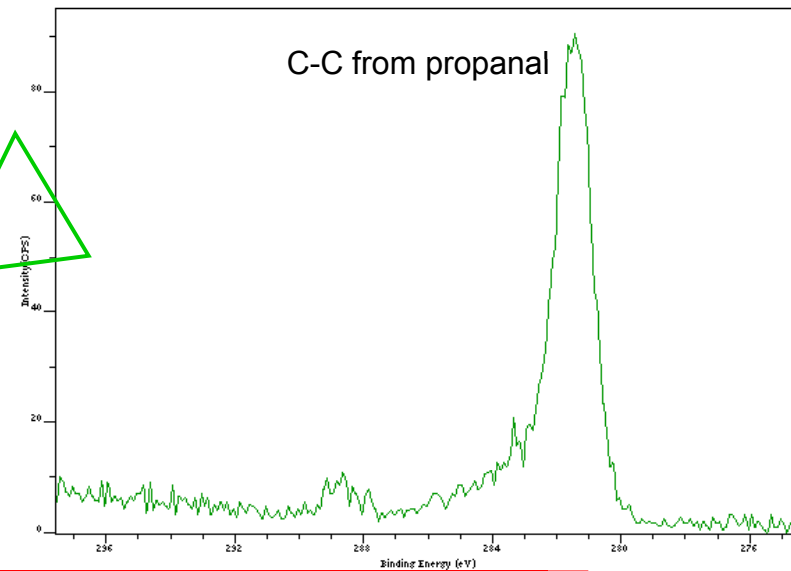
## Basic Concepts in Surface Imaging & Selected Area Spectroscopy (I)

- There are essentially two approaches to generating a spatially resolved photoelectron map of a surface.
    - scanning of the focussed X-ray (electron) probe or analysis area across the surface.
    - Use of an array detector and parallel imaging.

- Mapping with a focussed (incident) probe

Photoelectrons analysed

Focussed X-rays

Sampled region
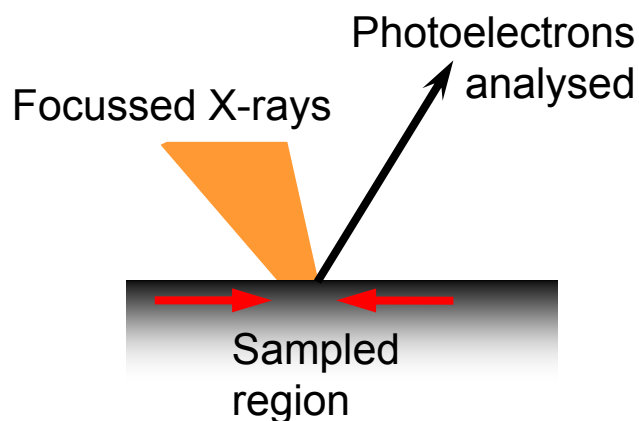
Spatial resolution of this mode depends on the degree of focussing of the incident probe - charged particles (e.g. electrons & ions) are easily focused, neutral particles (e.g. x-ray photons) are not readily focussed.

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Basic Concepts in Surface Imaging & Selected Area Spectroscopy (II)

- Mapping with a focussed (collected) probe

Analysed photoelectrons

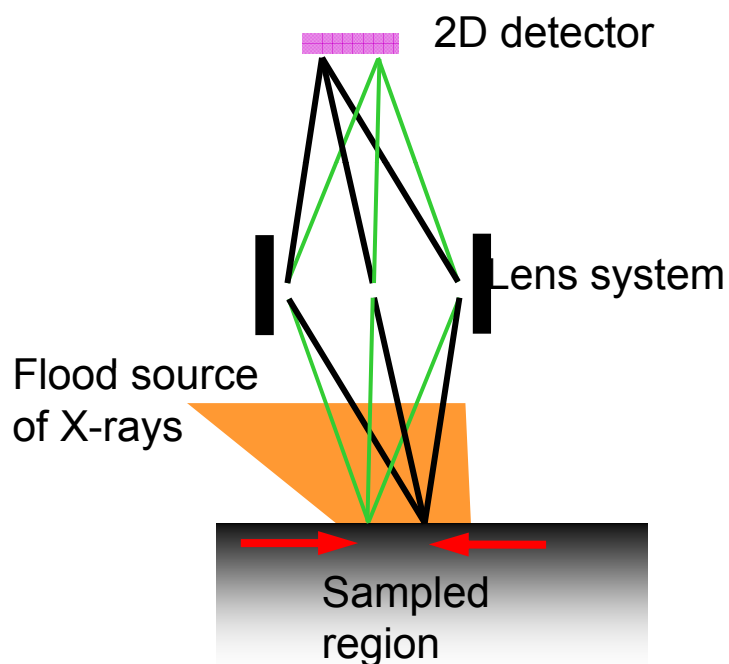Lens system

Flood source of X-rays

Sampled region
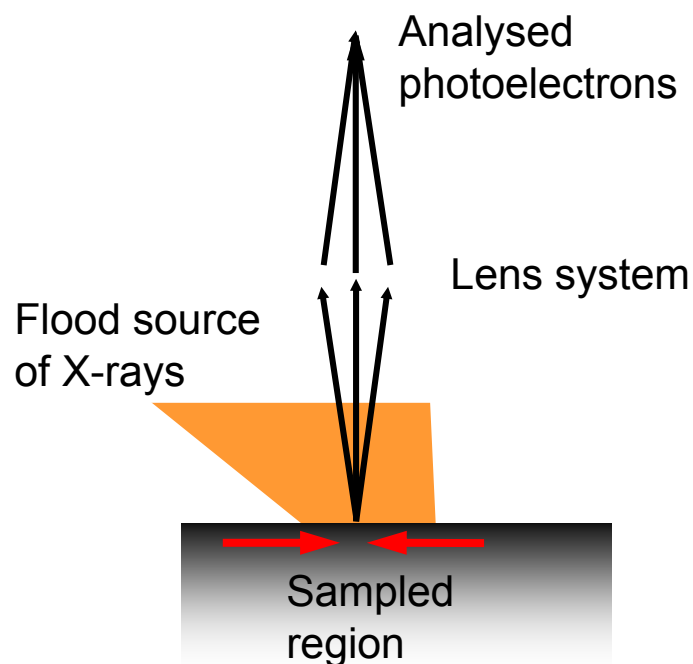
Alternative approach where large area of the sample is illuminated with X-rays but signal is only collected from a small area of the sample.

In principle this is an easy approach, using an appropriate lens system to collect as much signal as possible and focus it onto the detector.

In order to generate an image of the surface it is necessary to either scan the sample position under the detection system or make use of additional scanning plates in the electron-optical focusing lens.

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Basic Concepts in Surface Imaging & Selected Area Spectroscopy (III)

- Imaging with a linear or 2-dimensional detector

2D detector

Lens system

Flood source
of X-rays

Sampled
region

Second approach to obtaining a surface image involves using a large X-ray illumination area and a 2-dimensional detector. The relative positions of the emitted photoelectrons are maintained as they are transmitted through the lens system and focused at the detector.

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Points to Note

1.