

# K-Alpha

**ThermoFisher**  
S C I E N T I F I C

*The world leader in serving science*

Introduction to Surface  
Analysis XPS and AES

Tim Carney

# What do we mean by surface analysis?

*Space is big. You just won't believe how vastly, hugely, mind-bogglingly big it is. I mean, you may think it's a long way down the road to the chemist, but that's just peanuts to space'.*

- The Hitchhikers Guide to the Galaxy on Space and how big it is by Douglas Adams

- Surface analysis is almost exactly the opposite....

*'Surface analysis is small. You just won't believe how infinitesimal minuscule, mind-bogglingly small it is. I mean you may think a surface finish of 1 micron is small but that's just peanuts to surface analysis, I mean listen....'*

# What do we mean by a surface?

A surface means different things to different people

- **Astronomers** - light years for galaxy  
10's km for the sun's surface
- **Seismologist** - km's - m's for earth crust
- **Builders** - m's - mm's for surface finish
- **Engineers** - mm's to  $\mu\text{m}$ 's for surface finish
- **Semiconductors** (and surface analysts)  
 $\mu\text{m}$ 's to nm's

## So what do these units mean?

- $1 \text{ m} = 1000 \text{ mm} = 10^3 \text{ mm}$
- $1 \text{ m} = 1\,000\,000 \text{ }\mu\text{m} = 10^6 \text{ }\mu\text{m}$
- $1 \text{ m} = 1\,000\,000\,000 \text{ nm} = 10^9 \text{ nm}$
  
- Roughly 1 atomic layer is 0.1 nm  
The unit sometimes used is Å (Angstrom) which is  $10^{-10} \text{ m}$
  
- So how thick is a surface analyst?
  
- Generally they are interested in the 0.1 nm to 1  $\mu\text{m}$  range

## What do these units mean?

distance East Grinstead  
to central London = 50km

thickness of human hair  
=  $100\mu\text{m}$  (radius =  $50\mu\text{m}$ )

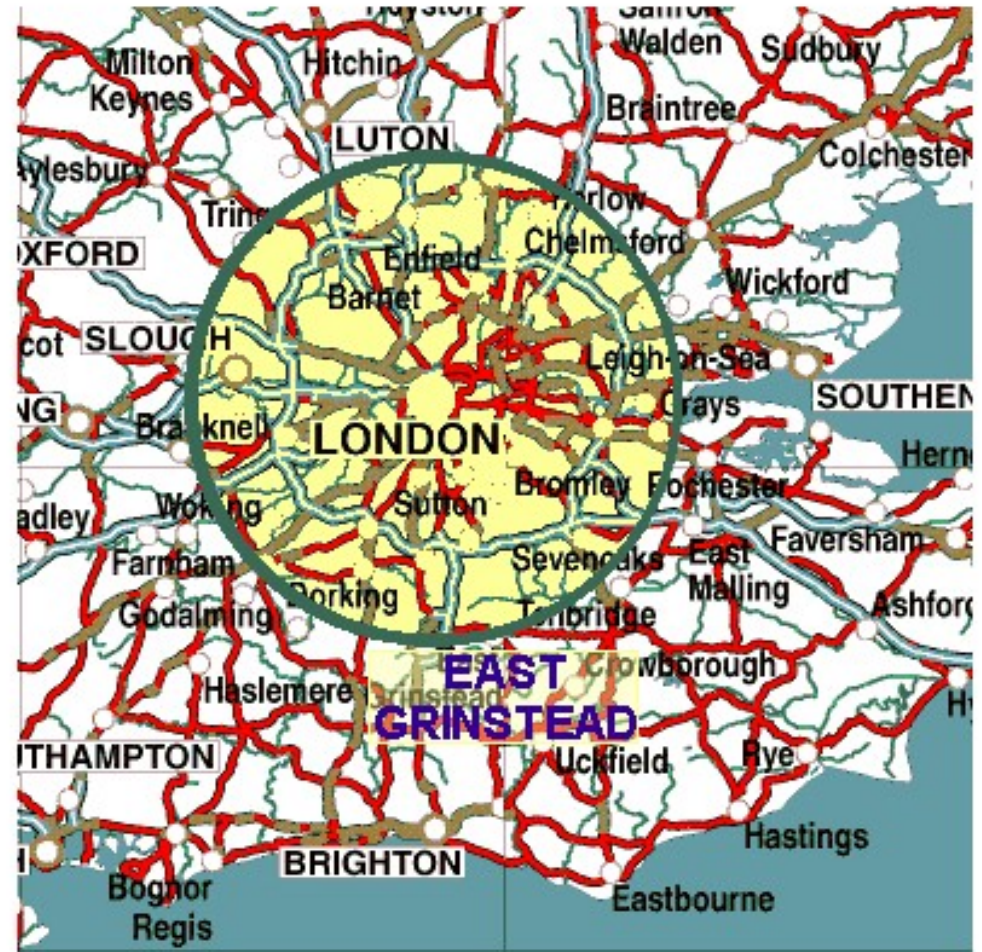
on this scale

50km =  $50\mu\text{m}$

1km =  $1\mu\text{m}$  (TVGS to The Star)

1m = 1nm

10m = 10nm (across this room)



# Why are we interested in the surface?

*God made solids, but surfaces were the work of the Devil'*

Wolfgang Pauli 1900-58

- Lots of interesting things happen at the surface (HONEST!)
  - The surface is the interface between something solid and the atmosphere
  - The chemistry of the surface maybe DIFFERENT from that of the bulk
- We talk of surface analysis but that is only a subset of what we really do

- The **surface** is the interface between something solid and an atmosphere
- An **interface** is what happens between two materials (e.g. paint sticking to a surface)
- **Thin films** are something which is thin (of the order of atomic sizes) which requires 'surface analysis' techniques to see it

**Slide 6**

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**t1**

tim.carney; 02-04-2007

# Why are we interested in the surface?

- Simple Example
- Problem: Cannot 'glue' two pieces of aluminium together
- Aluminium is a reactive metal



## Bulk analysis (1 $\mu$ m)

0.5at% Oxygen  
99.5at% Aluminium

Bulk analysis does not tell us if something is preventing bonding  
– Oxygen from oxide layer (2nm thick)

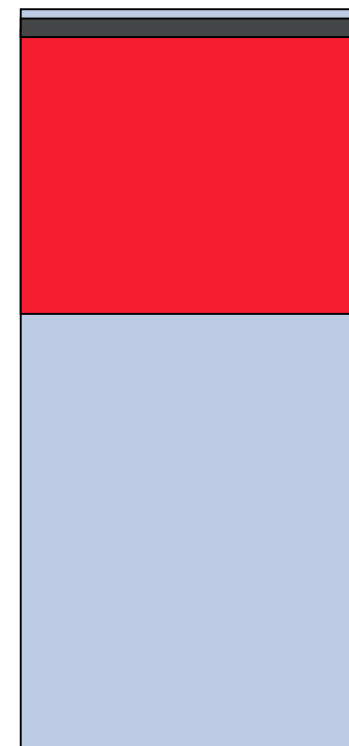
## Surface analysis (10nm)

45%at% Oxygen  
30at% Aluminium  
10at% Carbon

5at% Fluorine

Presence F preventing bonding?

Weakly bound carbon layer preventing bonding?





# Why the interest in surfaces?

Examples include:

- Catalysts - all reactions occur on the surface layer so why and how they work is important
- Polymer surfaces - how can the surface be modified so you can print on it?
- Polymers - how can the surface be modified so it becomes bio-inert?
- Corrosion - generally starts at the surface and works down
- Metal surfaces - how can they be cleaned using 'green' solvents so that paint sticks
- ditto to be glued together
- Control of thin layer thickness is critical in semiconductors
- Surface contaminates greatly effect the 'yield' of semiconductor devices from a wafer
- etc etc

# What do we want to know?

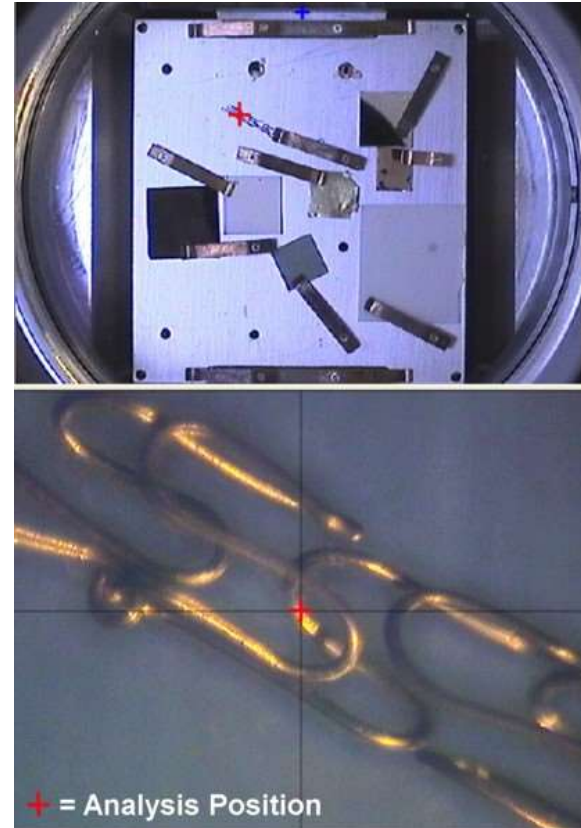
- Where is it?
  - Uniform on surface?, 'Black Bit?', 'White Bit?', etc
- What is it?
  - Carbon?, Aluminium?, Oxygen?, Elemental?, Compound? (oxide, carbonate)
- How much of it?
  - 15at% Carbon, 30at% Aluminium, 45at% Oxygen? or 30at% Carbon, 20at%Aluminium, 50at% Oxygen
- How thick is it?
  - 2nm thick  $\text{Al}_2\text{O}_3$  layer with very thin carbon layer on top or 2nm thick  $\text{Al}_2\text{O}_3+\text{AlCO}_3$  layer?

# Where is it?

Both Platter View and Live Reflex Optics view are always available

Platter View can be used to select the sample

Live Reflex View is used to select the analysis position on the sample

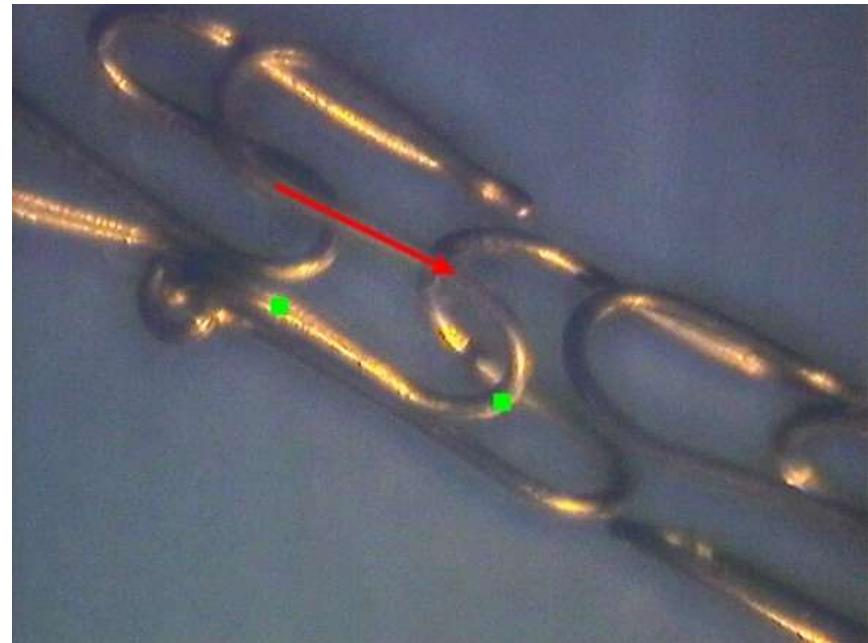


*Upper: Platter View showing whole sample plate  
Lower: Reflex Optics View of one of the samples  
(an arterial stent)*

*The analysis position is always shown on each image*

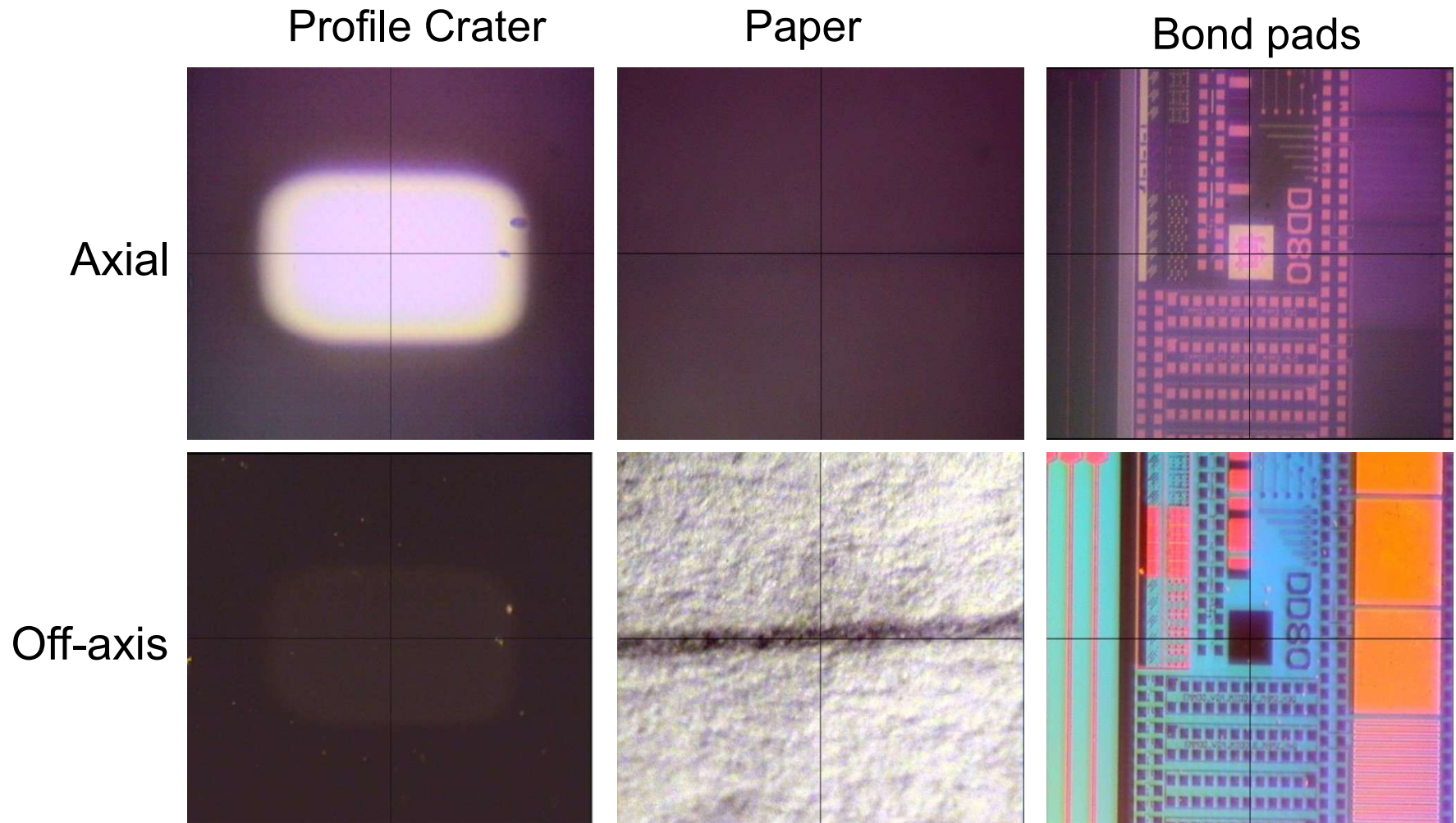
## Where is it?

- Reflex Optics provide accurate view of analysis position, co-axial with analysis lens
- High magnification image for accurate selection of small area analysis position
- To align a feature with the analysis position simply click on it
- Use Reflex Optics view to define positions for analysis
- Choice of co-axial or diffuse illumination



*Sample view using Reflex Optics*

# Illumination – where is it?

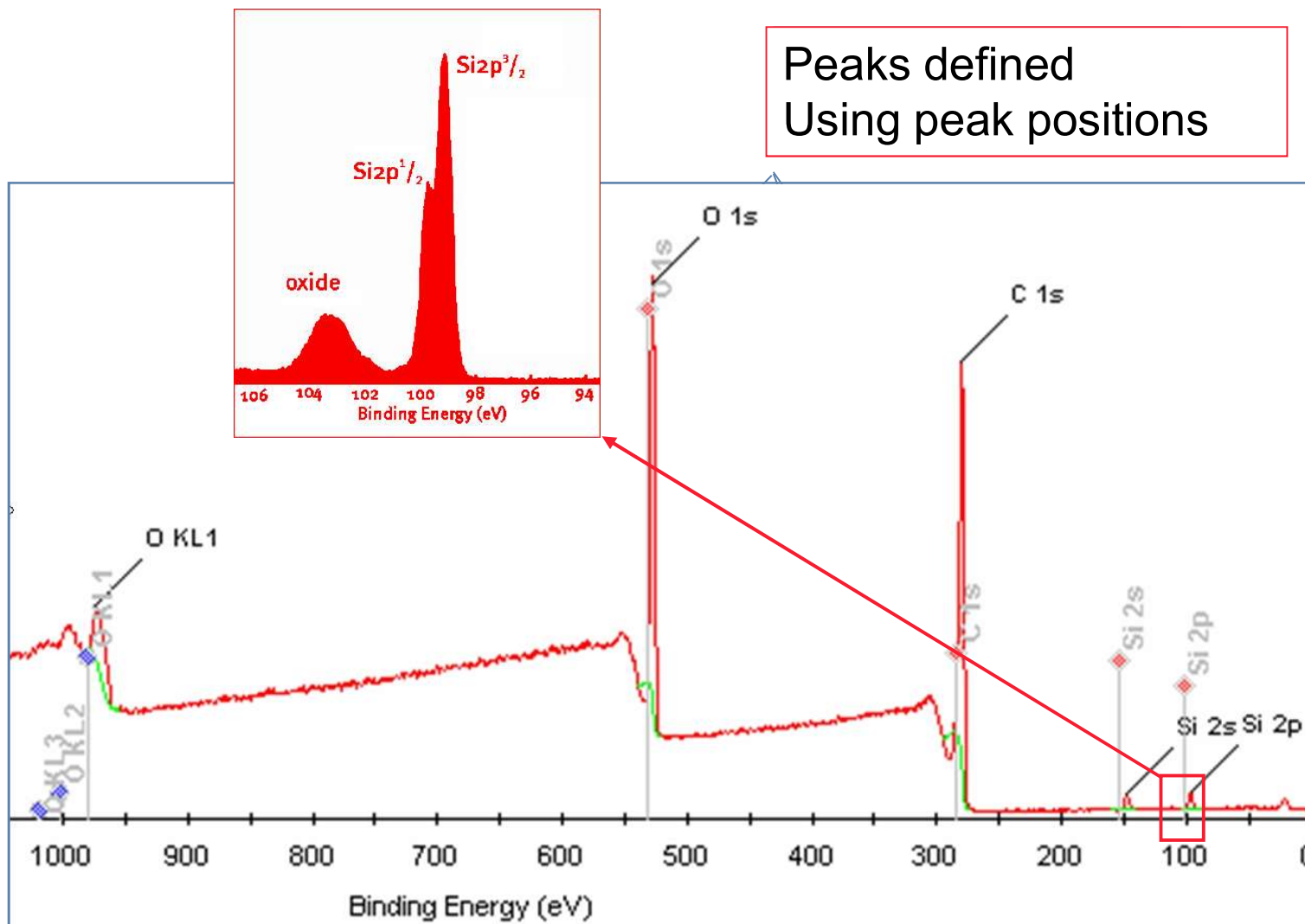


# What is it?

## Qualitative analysis from the SURFACE:

- X-ray Photoelectron Spectroscopy (XPS)

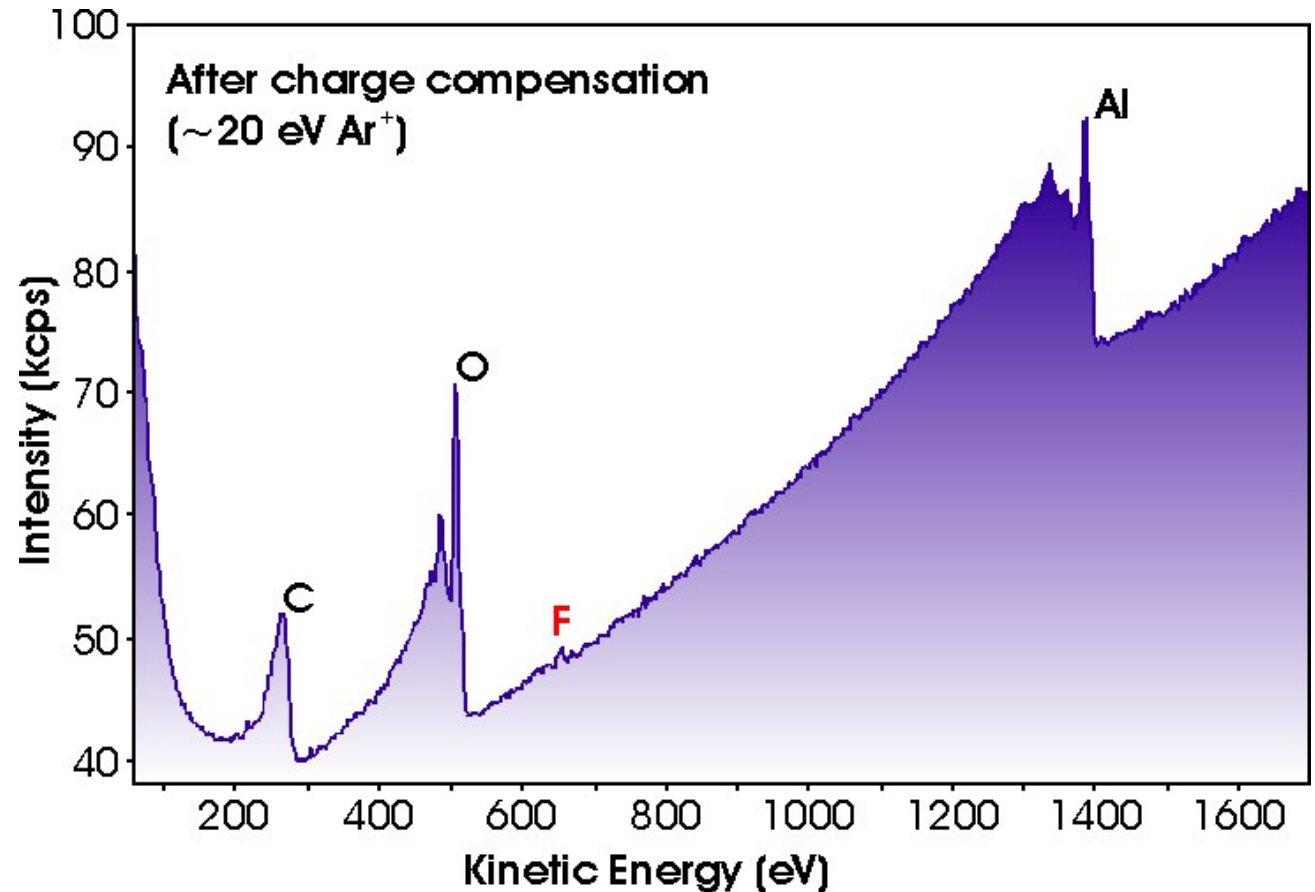
Chemical State Determination





# What is it?

- Auger Electron Spectroscopy (AES) also gives us this Chemical information from the SURFACE.
- Techniques such as EDX (Energy Dispersive X-ray Microanalysis) give us information from the 'Bulk' which maybe different to the surface



# Quantification

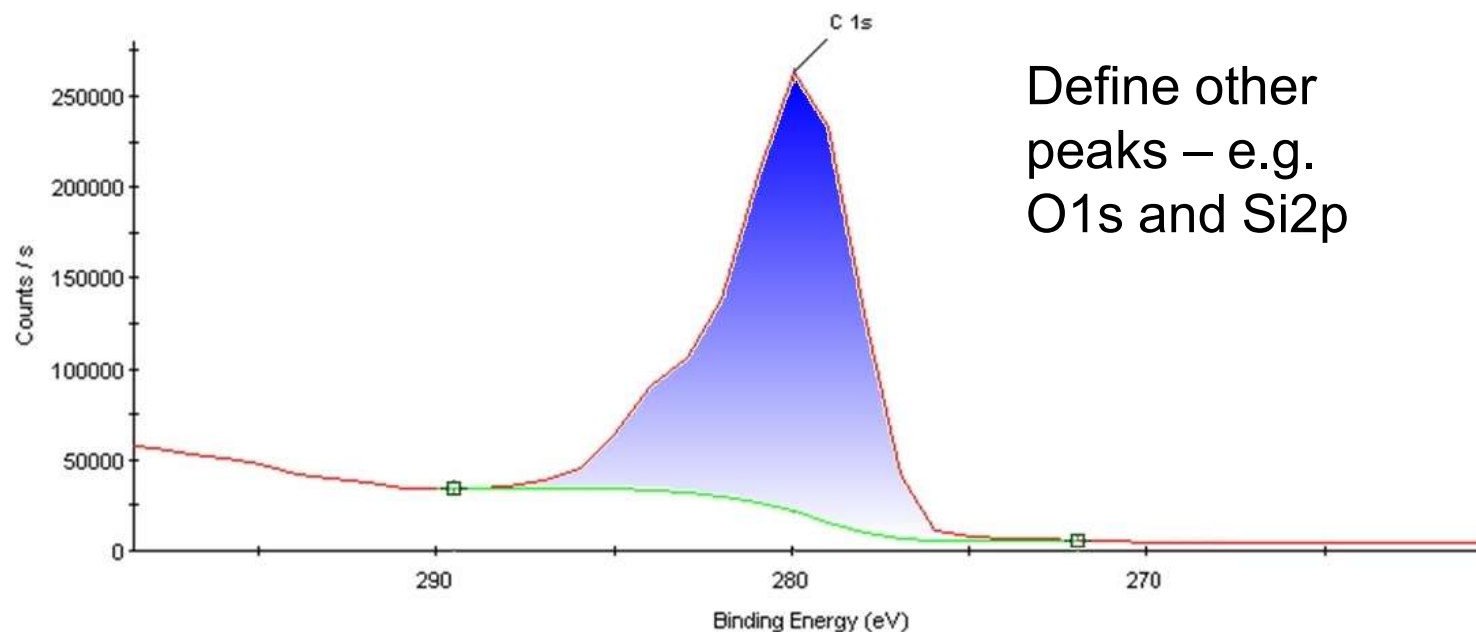
Both XPS and AES are quantitative

That is we get a number relating to how much is there

Quantification in this column

Name	Start BE	Centre BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N)	At. %	F	Q	SF
O 1s	533.55	527.97	519.96	244894	4.0262	1.0306	0.9365	25.7	<input type="checkbox"/>	<input checked="" type="checkbox"/>	2.93
C 1s	289.51	279.96	271.96	241532	3.8223	1.0891	2.6263	72.07	<input type="checkbox"/>	<input checked="" type="checkbox"/>	1
Si 2s	159.95	146.95	139.95	9119.9	3.7002	33691.	0.0814	2.24	<input type="checkbox"/>	<input checked="" type="checkbox"/>	0.955

SURVEY

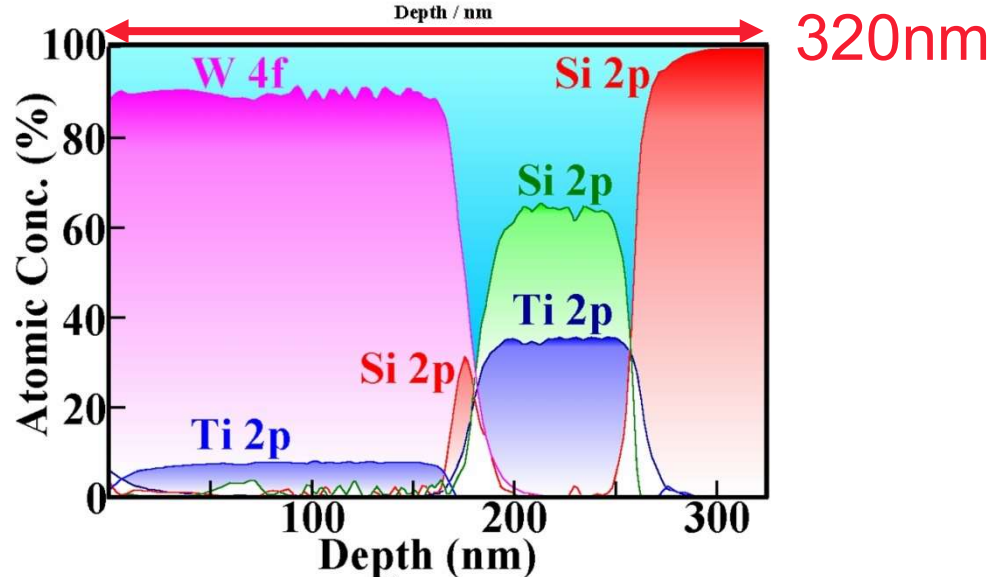
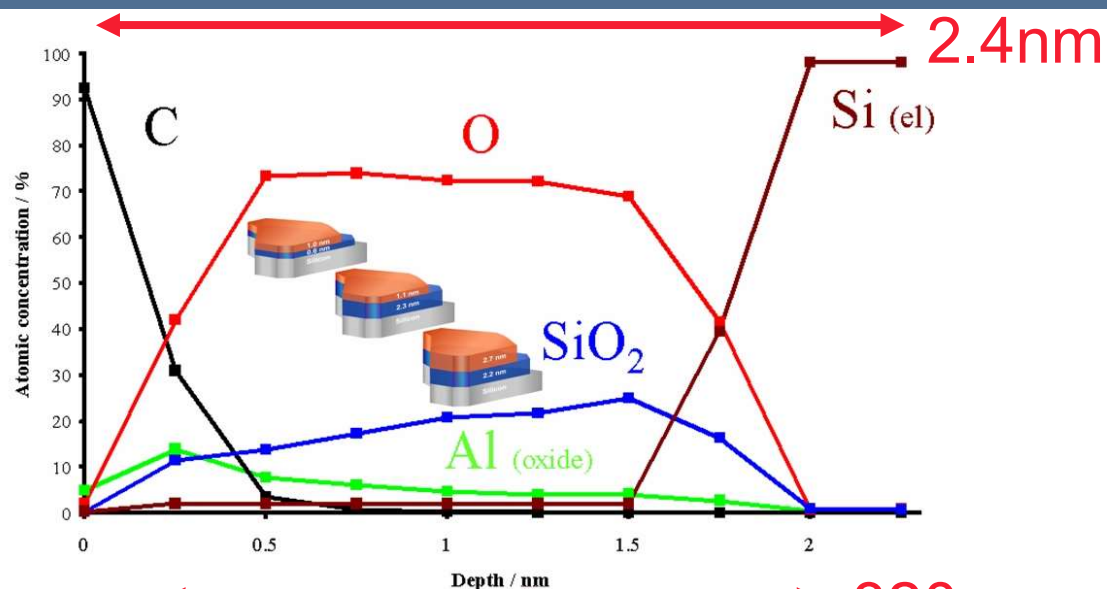


Define other peaks – e.g. O1s and Si2p



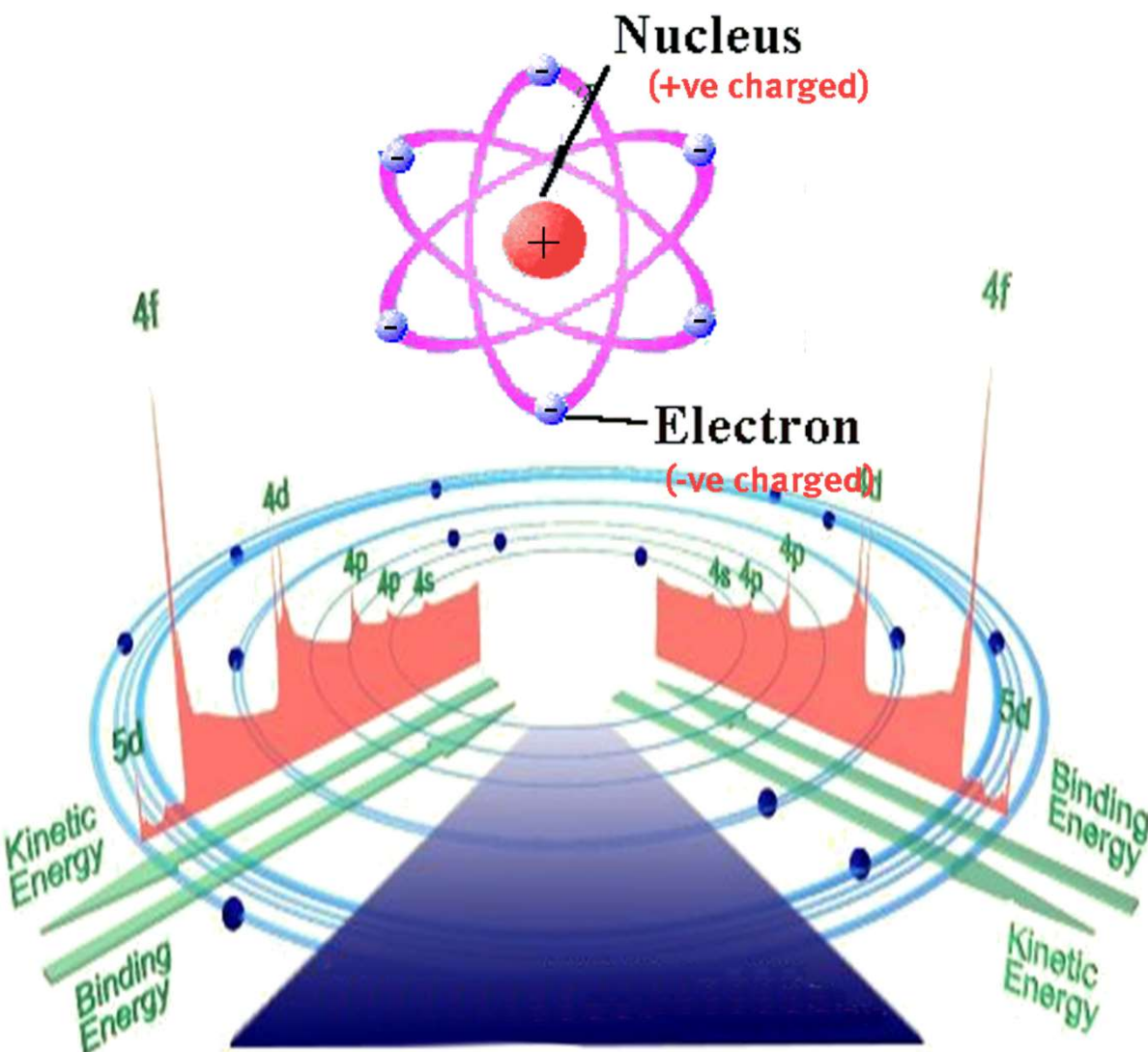
# How thick is it?

- XPS gives thickness information
- Non-destructive analysis by Angular Resolved Analysis (Theta Probe Family and ESCALAB)
- Ion Etch Depth Profiling using ion beam (all instruments)



# How do we get a spectrum?

- An atom consists of a positively charged nucleus and negatively charged electrons 'orbiting' around it
- These electrons are held in position by a 'binding energy' (opposites attract)
- Electrons are located in discrete 'shells' or orbitals (e.g. 4f, 4p, 4s), each of which have a specific binding energy



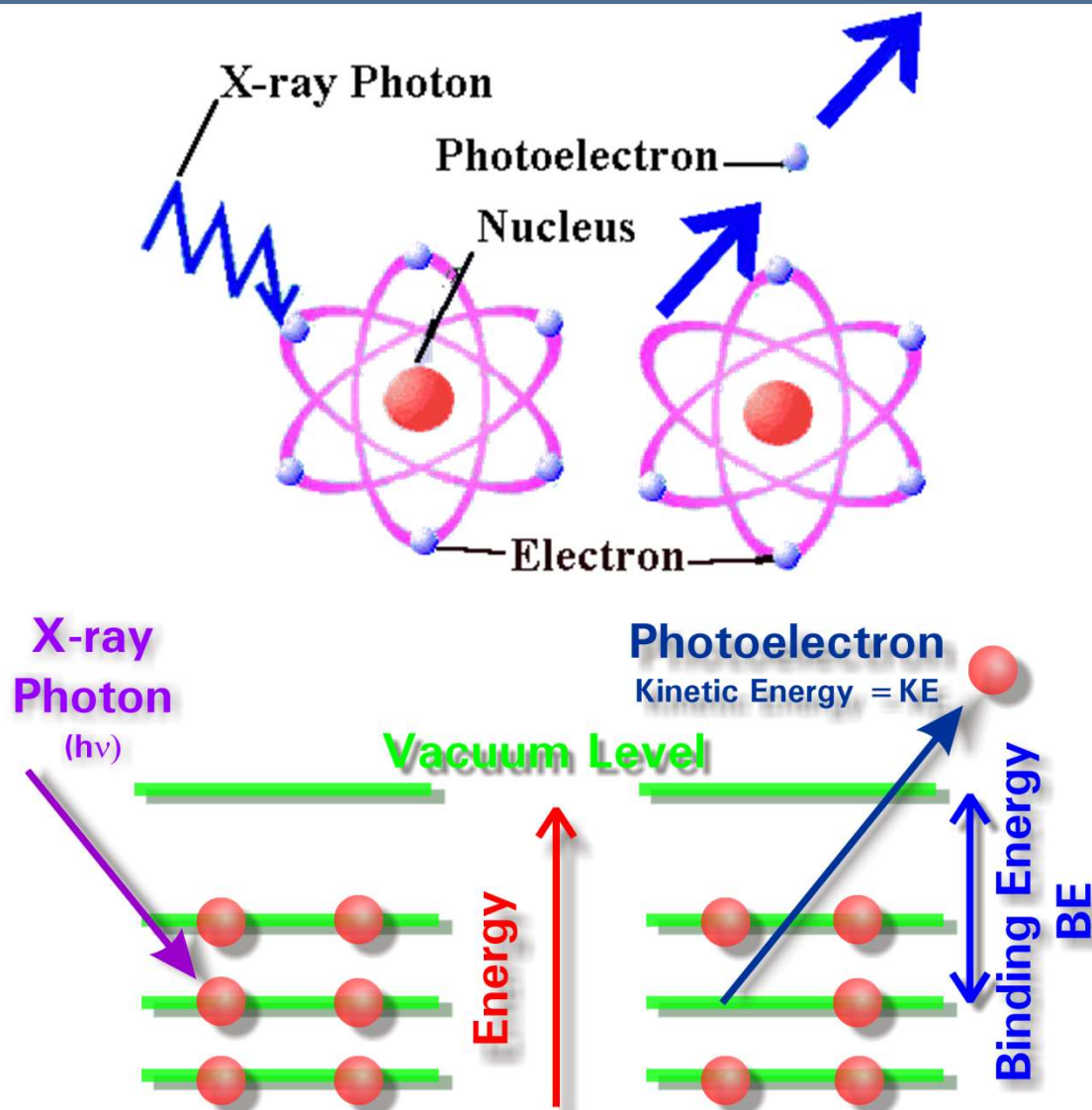
## How do we get a spectrum #2

### X-ray Photoelectrons

X-ray photon of energy  $h\nu$  'hits' the atom, and excites an electron (i.e. gives it more energy)

If this energy is greater than the Binding Energy (BE) (plus a bit) it is ejected from the atom with a Kinetic Energy (KE) equal to the photon energy ( $h\nu$ ) minus the binding energy (BE) minus a work function ( $\psi$ ).

This is the Photoelectron effect

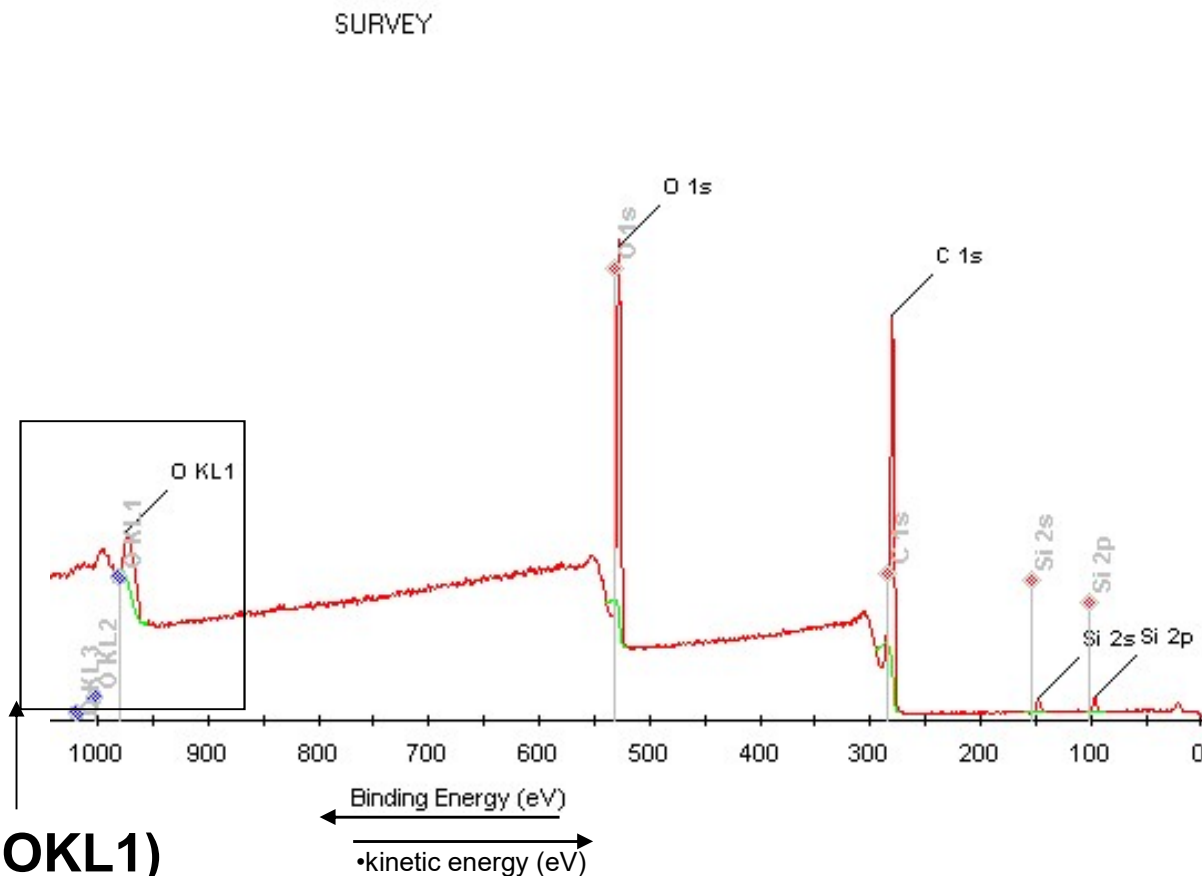


# Features on XPS Spectra

## X-ray Photoelectrons

The Si2p, Si2s, C1s and O1s peaks we see on the spectrum are at the energies of these photoelectrons.

However there are other peaks in this spectrum



## Auger Transition Peaks (OKL1)

These peaks are due to Auger transitions which are INDEPENDENT of the radiation used

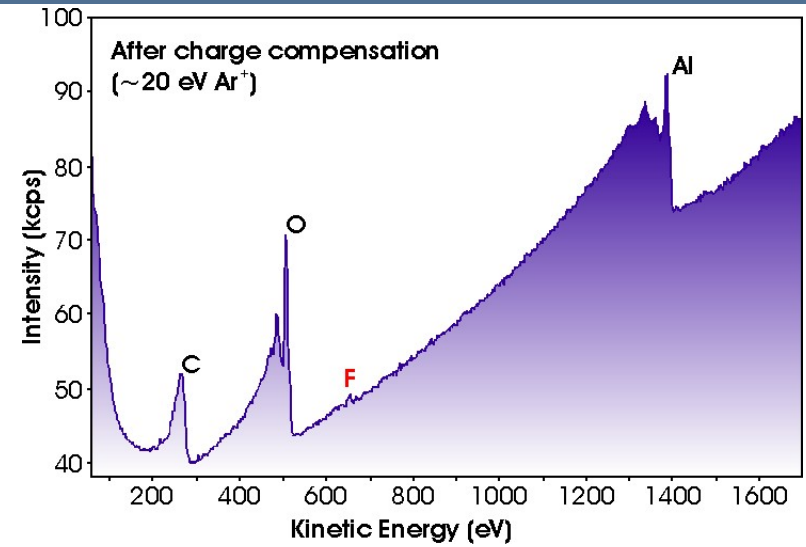
Hence you see them on 'XPS' spectra and 'AES' spectra  
(You do not see XPS peaks in AES spectra though!)

# Auger transitions

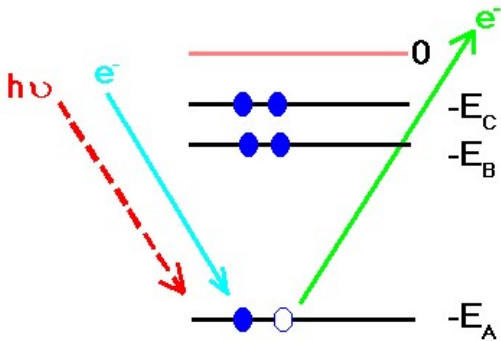
## Auger Transitions

Are produced from a relaxation effect (getting rid of too much energy in the atom after an electron has been ejected)

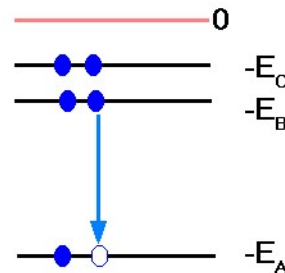
The energy of the emitted electron again is an indication of what element it has come from and its intensity how much of it is there



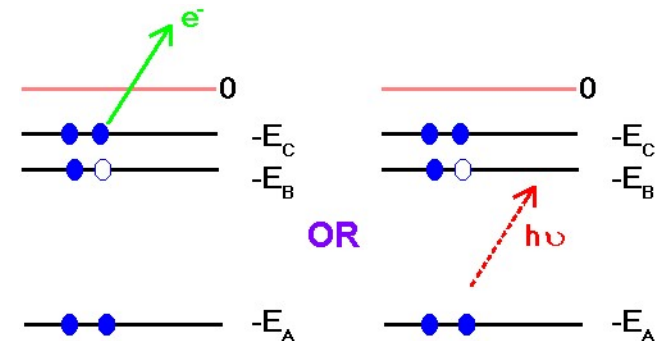
Ejection of core electron leaving unstable state



Electron drops down to fill empty position



Excess energy removed by ejection of Auger electron or X-ray



# Surface Analysis Instruments

So Surface Analysis Instruments detect two 'types' of electrons

Photoelectrons - Generated by X-ray interaction

Auger Electrons - Generated by both X-rays and electron beams

By analysing the energy and intensity of the peaks generated by these electrons in the spectrometers we can gain useful information about the sample surface

However these two types of electrons have particular characteristics which makes some information easier to obtain with one type compared to the other.



# Kinetic Energy and Binding Energy

## X-ray Photoelectron Spectroscopy The Equation

$$\blacksquare KE = h\nu - BE - \psi$$

Where:

KE = kinetic energy of photoelectron

This is what we measure with the spectrometer  
(in the range 0 to 1486 eV, which gives the surface sensitivity!)

$h\nu$  = Energy of X-ray photon

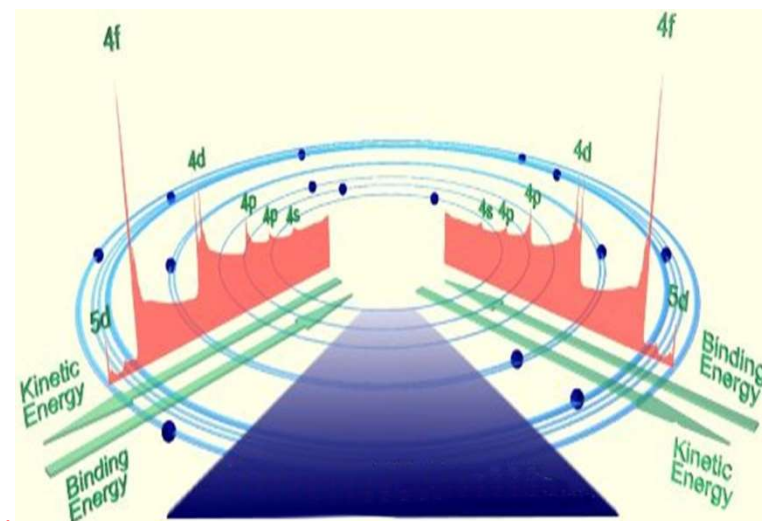
X-ray energy is known -  $AlK\alpha = 1486.6$  eV,  $MgK\alpha = 1253.6$  eV

BE = Binding energy of photoelectron

This is what we want to know – as it gives us Qualitative Chemical Information

$\psi$  = Work function

This allows for the electron to travel from the solid state to the vacuum state and is typically about 4.2 eV.  
It is calculated from a known standard(s) [e.g.  $Ag3d5 = 368.27$  eV binding energy]



## So why are XPS and AES surface sensitive?

The Kinetic energies of the electrons detected are in the range 0 to 1486 eV for XPS and up to 2500 eV for AES  
- These are LOW energy electrons!

**X-rays will penetrate to several microns into the material so the surface sensitivity is NOT (repeat NOT!) due to the X-ray source!  
(In a similar way AES is not due to the primary electron beam)**

Surface sensitivity is due to the probability that a low energy electron can escape from the material

This is referred to as the **Electron Mean Free Path (EMFP)**  
(or Inelastic Mean Free Path (IMFP) or  $\lambda$ )

Simply this is the distance that an electron will travel in a solid before it hits something



## Why is $\lambda$ important?

If an electron hits something else one of two things can happen

- 1: Nothing happens, well maybe the direction of the electron changes but its kinetic energy does NOT change  
This is referred to as **ELASTIC SCATTERING**
- 2: The electron loses some energy (and changes direction)  
This is referred to as **INELASTIC SCATTERING**

If an electron undergoes enough inelastic scattering events (i.e. it keeps losing energy) it **DOES NOT** escape from the surface and is not detected

The term  $\lambda$  gives us a handle on how far an electron will travel on average before such an event happens

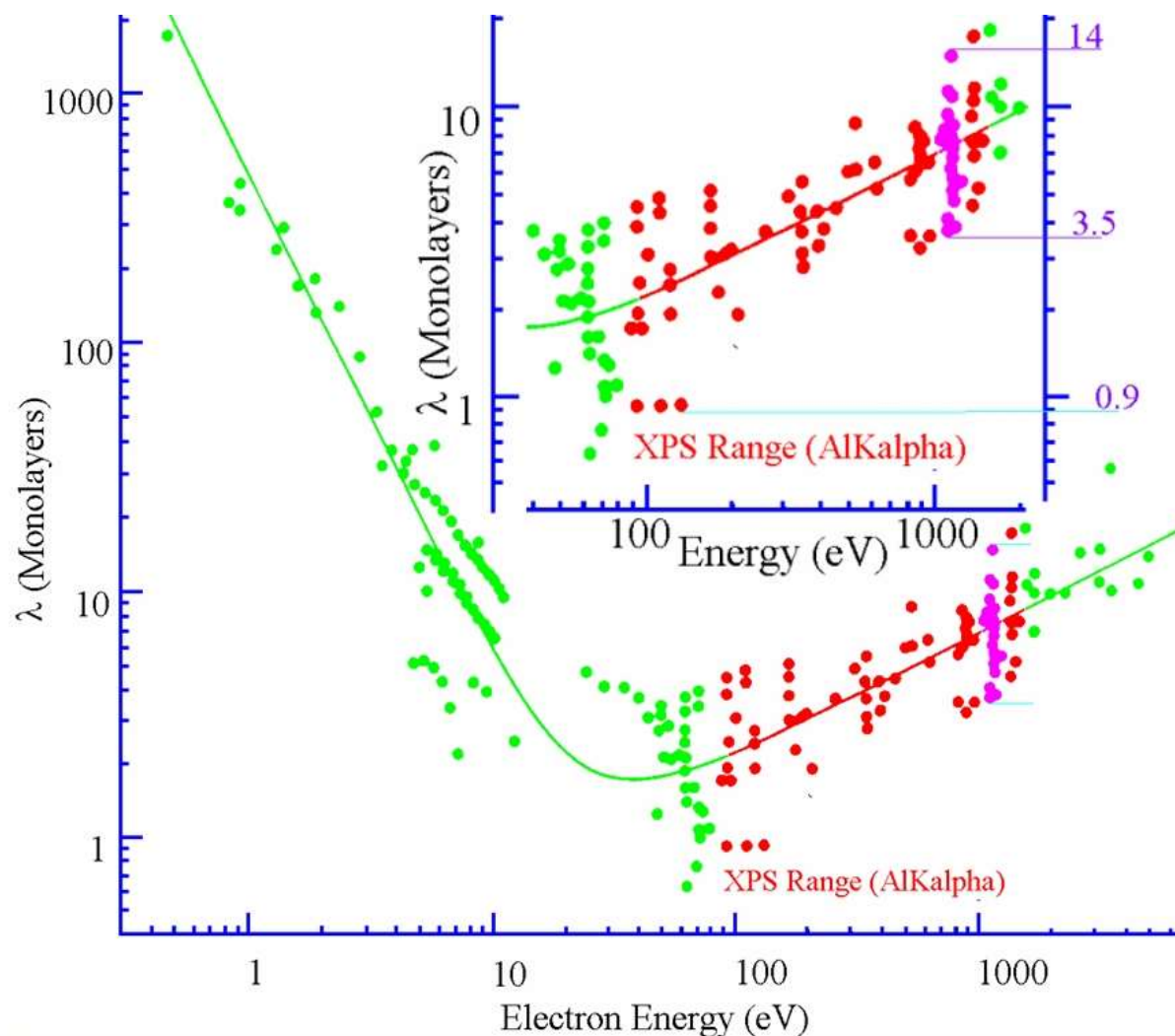
# How big is $\lambda$ ?

The value of  $\lambda$  depends on the energy of the electron and what material the electron is travelling through

Commonly approximated to  $KE^{0.6}$  from the universal curve shown

At one energy (approximately Si2p) the scatter from the universal line is about 3.5 to 14 monolayers (atoms)

which is about 2.2 to 3.3nm



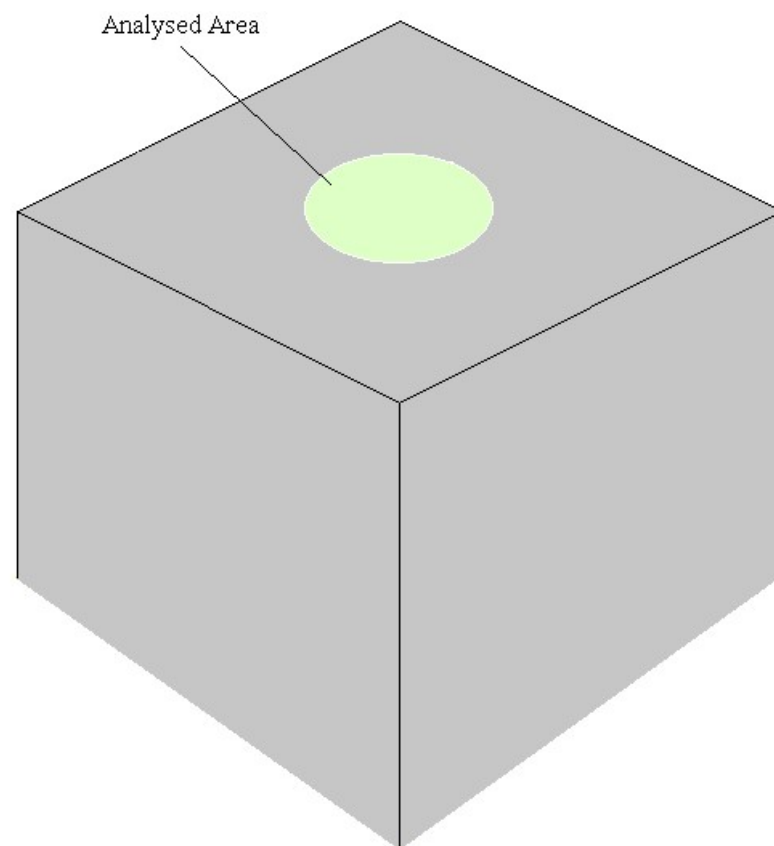
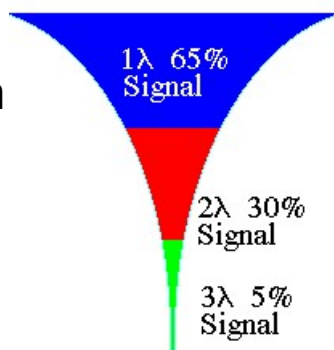
# How does $\lambda$ relate to depth of analysis?

$\lambda$  gives us an indication of far an electron will probably travel before it is inelastically scattered

Probability also determines if an electron will escape from a material

For any peak analysed the probability is that 65% of that signal has arrived from a depth equal to  $1\lambda$

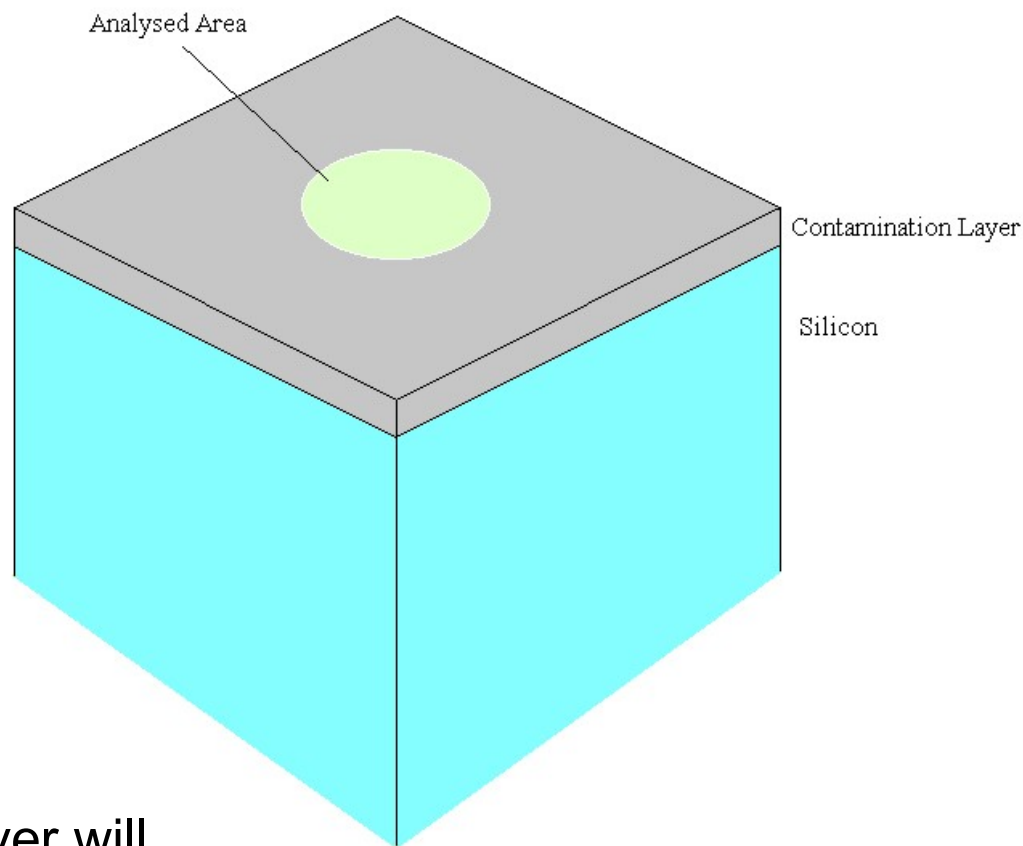
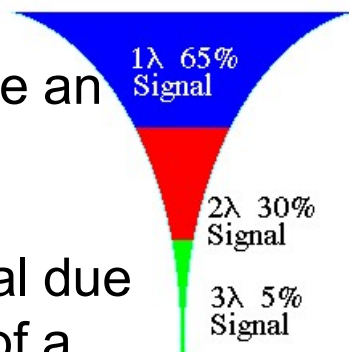
In a similar way 95% of the signal has arrived from a depth equal to  $2\lambda$  (65% + 30%)



# What happens when there is contamination?

Virtually ALL samples have contamination layers

This layer will have an enhanced signal compared to the underlying material due to the probability of a photoelectron emerging from the sample

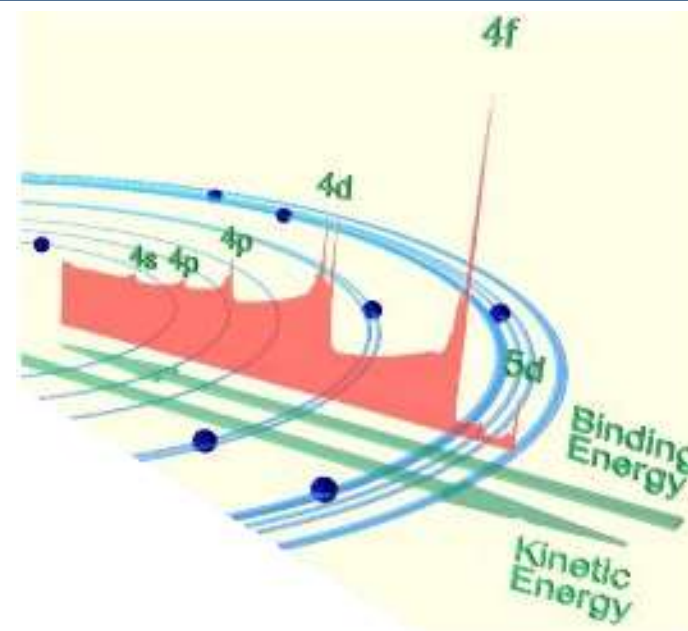


Thus even a thin contamination layer will have an enhanced signal

# Why the interest in Binding Energy?

Elements (C, O, N, Cu, Si etc) have electrons in discrete shells which have a particular binding energy

If we measure this binding energy we can then work out from which element it came from



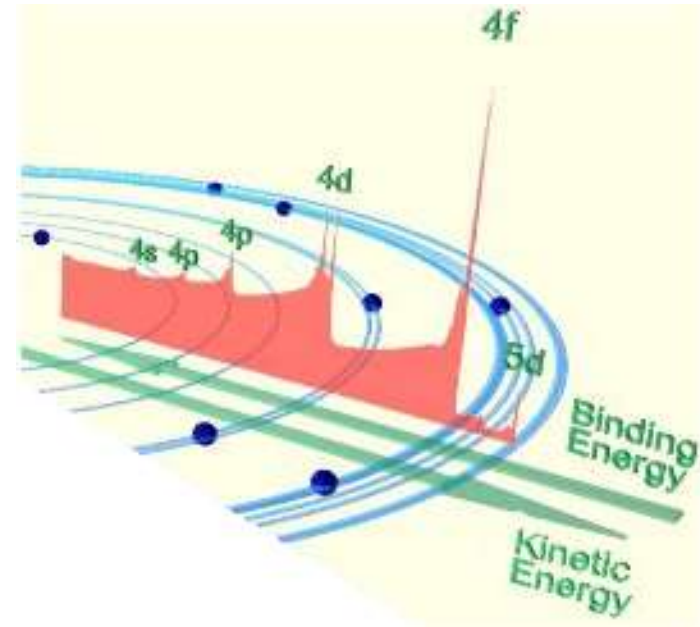
## Qualitative Analysis

# What's all this 1s, 2p, 3d,4f all about?

Each shell of electrons are given a notation:  
s, p, d and f  
as we go along the elements each shell is  
'filled' with electrons

There is a set order in which they are filled  
1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 5s, 4f,  
5p, 5d etc

Each shell can hold a set number of  
electrons  
2 in the s shell, 6 in the p shell  
10 in the d shell, 14 in the f shell

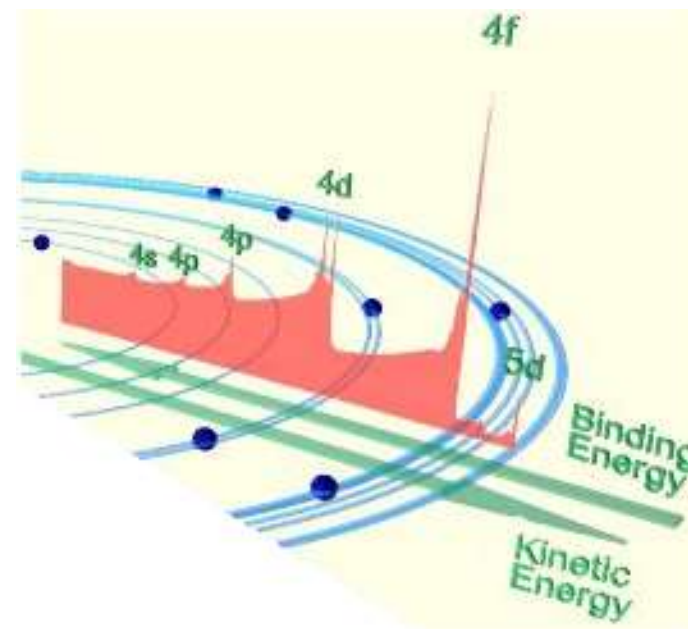


# What's all this 1s, 2p, 3d,4f all about?

For gold there are 79 electrons

1s=2	(2)	BE=80 725 eV
2s=2	(4)	BE= 14 353 eV
2p=6	(10)	BE= 11919 eV
3s=2	(12)	BE= 3425 eV
3p=6	(18)	BE= 2743 eV
3d=10	(28)	BE= 2206 eV

<u>4s=2</u>	<u>(30)</u>	<u>BE= 762 eV</u>
<u>4p=6</u>	<u>(36)</u>	<u>BE= 546 eV</u>
<u>4d=10</u>	<u>(46)</u>	<u>BE= 335 eV</u>
<u>5s=2</u>	<u>(48)</u>	<u>BE= 107 eV</u>
<u>4f=14</u>	<u>(62)</u>	<u>BE= 84 eV</u>
<u>5p=6</u>	<u>(68)</u>	<u>BE= 57 eV</u>
<u>5d=10</u>	<u>(78)</u>	<u>BE= VB region</u>
<u>6s=1</u>	<u>(79)</u>	<u>BE= VB region</u>



For gold only these shells can be excited  
by AlK $\alpha$  radiation

i.e. the binding energy of the Au3d  
(BE= 2206eV) electron is higher than the  
photon energy of the AlK $\alpha$  radiation  
(1486.6 eV)



# What's all this, $2p_{3/2}$ , $3d_{5/2}$ , $4f_{7/2}$ all about?

The p, d and f shells are actually two shells close together but at different binding energies

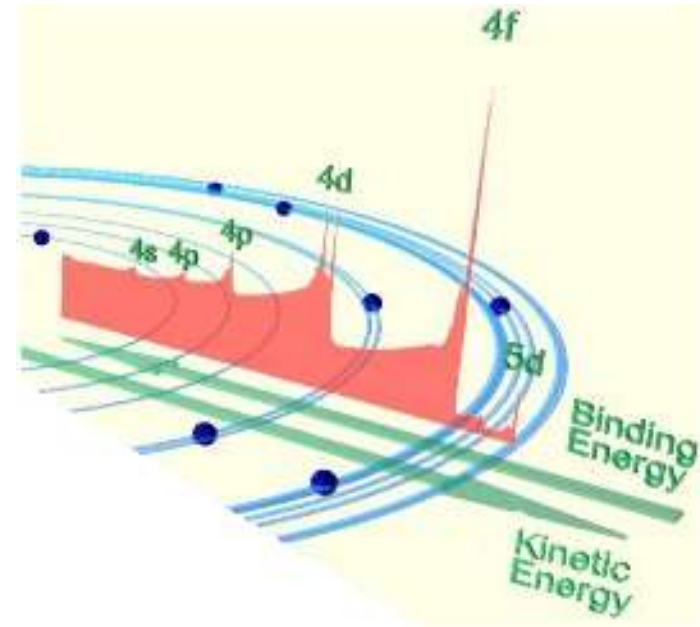
$p_{3/2}$  has 4 electrons,  $p_{1/2}$  has 2 electrons  
i.e. ratio 2:1

$d_{5/2}$  has 6 electrons,  $d_{3/2}$  has 4 electrons  
i.e. ratio 3:2

$f_{7/2}$  has 8 electrons,  $f_{5/2}$  has 6 electrons  
i.e. ratio 4:3

Having these ratios is useful as it helps in interpretation of spectra i.e. two peaks in an area ratio a certain distance apart

In some cases these shells are so close together that we cannot separate them as separate peaks





# So what is all this KLL, LMM all about ?

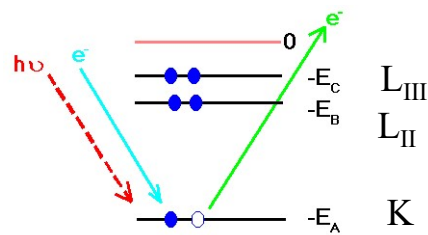
The Auger transition is named according to how the transition occurs

From before the shells are named 1s, 2s, 2p etc but also have different labelling system K, L<sub>I</sub>, L<sub>II</sub>, L<sub>III</sub> etc

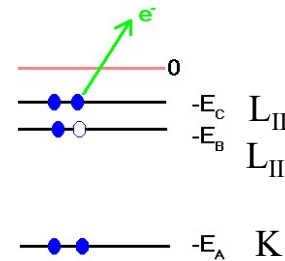
For some reason the Auger guys use this system to name their transitions

## Magnesium Electron binding energies

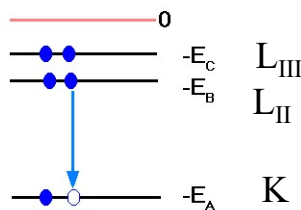
Orbital	eV	Label
1s	1303	K
2s	88.6	L <sub>I</sub>
2p <sub>1/2</sub>	49.6	L <sub>II</sub>
2p <sub>3/2</sub>	49.2	L <sub>III</sub>



The label of the primary ejected electron is used as the first character e.g. 'K'



The label of the Auger electron that is ejected is used as the third character e.g. 'L<sub>III</sub>' or just 'L'

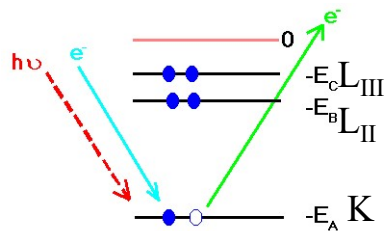


The label of the electron that drops down is used as the second character e.g. 'L<sub>II</sub>' or just 'L'

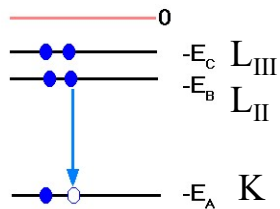
So this transition is 'KL<sub>II</sub>L<sub>III</sub>' or just 'KLL'

# Why is the Kinetic Energy in AES element specific?

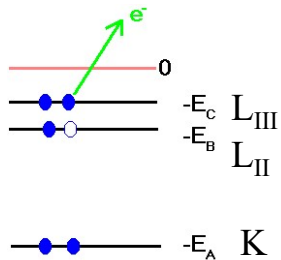
For Magnesium the KLL transition energy (i.e. the kinetic energy with which the Auger electron leaves the atom) can be calculated approximately from the Binding Energies of the shells which the electrons involved are situated\*



Primary ejected electron  
e.g. 'K' ( $E_A$ )  
Binding Energy = **1303 eV**



Electron that drops down  
e.g. 'LII' or just 'L' ( $E_B$ )  
Binding Energy = **50 eV**  
( $Z+1(Al)=74$  eV)



Auger electron that is  
ejected e.g. 'LIII' or just  
'L' ( $E_C$ )  
Binding Energy = **49 eV**  
( $Z+1(Al)=73$  eV)

\* An approximation to this is:

$$KE = E_A - \frac{1}{2}(E_{B(Z)} + E_{B(Z+1)}) - \frac{1}{2}(E_{C(Z)} + E_{C(Z+1)})$$

TM

$$1303 - \frac{1}{2}(50+74) - \frac{1}{2}(49+73) = 1303 - 62 - 61 = 1180 \text{ eV}$$

# So why is the knowledge useful?

- The full list of gold, chromium and magnesium orbitals are shown
- If peaks on the spectrum have *about* the same energies it is likely to contain that element!
- As before not all are accessible using  $AlK\alpha$  radiation

## Magnesium Electron binding energies

Orbital	eV	Label
1s	1303	K
2s	88.6	L <sub>I</sub>
2p <sub>1/2</sub>	49.6	L <sub>II</sub>
2p <sub>3/2</sub>	49.2	L <sub>III</sub>

## Chromium Electron Binding Energies

Orbital	eV	Label
1s	5989	K
2s	696	L <sub>I</sub>
2p <sub>1/2</sub>	583.8	L <sub>II</sub>
2p <sub>3/2</sub>	574.1	L <sub>III</sub>
3s	74.1	M <sub>I</sub>
3p <sub>1/2</sub>	42.2	M <sub>II</sub>
3p <sub>3/2</sub>	42.2	M <sub>III</sub>

## Gold Electron Binding Energies

Orbital	eV	Label
1s	80725	K
2s	14353	L <sub>I</sub>
2p <sub>1/2</sub>	13734	L <sub>II</sub>
2p <sub>3/2</sub>	11919	L <sub>III</sub>
3s	3425	M <sub>I</sub>
3p <sub>1/2</sub>	3148	M <sub>II</sub>
3p <sub>3/2</sub>	2743	M <sub>III</sub>
3d <sub>3/2</sub>	2291	M <sub>IV</sub>
3d <sub>5/2</sub>	2206	M <sub>V</sub>
4s	762.1	N <sub>I</sub>
4p <sub>1/2</sub>	642.7	N <sub>II</sub>
4p <sub>3/2</sub>	546.3	N <sub>III</sub>
4d <sub>3/2</sub>	353.2	N <sub>IV</sub>
4d <sub>5/2</sub>	335.1	N <sub>V</sub>
4f <sub>5/2</sub>	87.6	N <sub>VI</sub>
4f <sub>7/2</sub>	83.9	N <sub>VII</sub>
5s	107.2	O <sub>I</sub>
5p <sub>1/2</sub>	74.2	O <sub>II</sub>
5p <sub>3/2</sub>	57.2	O <sub>III</sub>

## You said *about* ...

- *If peaks on the spectrum have about the same energies it is likely to contain that element!*
- But the actual energy depends on which chemical state the atom is in
- **THIS IS KNOWN AS CHEMICAL SHIFT** and is key to why we use XPS

### Gold Electron Binding Energies

Orbital	eV	Label
1s	80725	K
2s	14353	L <sub>I</sub>
2p <sub>1/2</sub>	13734	L <sub>II</sub>
2p <sub>3/2</sub>	11919	L <sub>III</sub>
3s	3425	M <sub>I</sub>
3p <sub>1/2</sub>	3148	M <sub>II</sub>
3p <sub>3/2</sub>	2743	M <sub>III</sub>
3d <sub>3/2</sub>	2291	M <sub>IV</sub>
3d <sub>5/2</sub>	2206	M <sub>V</sub>
4s	762.1	N <sub>I</sub>
4p <sub>1/2</sub>	642.7	N <sub>II</sub>
4p <sub>3/2</sub>	546.3	N <sub>III</sub>
4d <sub>3/2</sub>	353.2	N <sub>IV</sub>
4d <sub>5/2</sub>	335.1	N <sub>V</sub>
4f <sub>5/2</sub>	87.6	N <sub>VI</sub>
4f <sub>7/2</sub>	83.9	N <sub>VII</sub>
5s	107.2	O <sub>I</sub>
5p <sub>1/2</sub>	74.2	O <sub>II</sub>
5p <sub>3/2</sub>	57.2	O <sub>III</sub>

# What is Chemical State?

- Chemical state describes in what form an element is bonded to another element.

For example

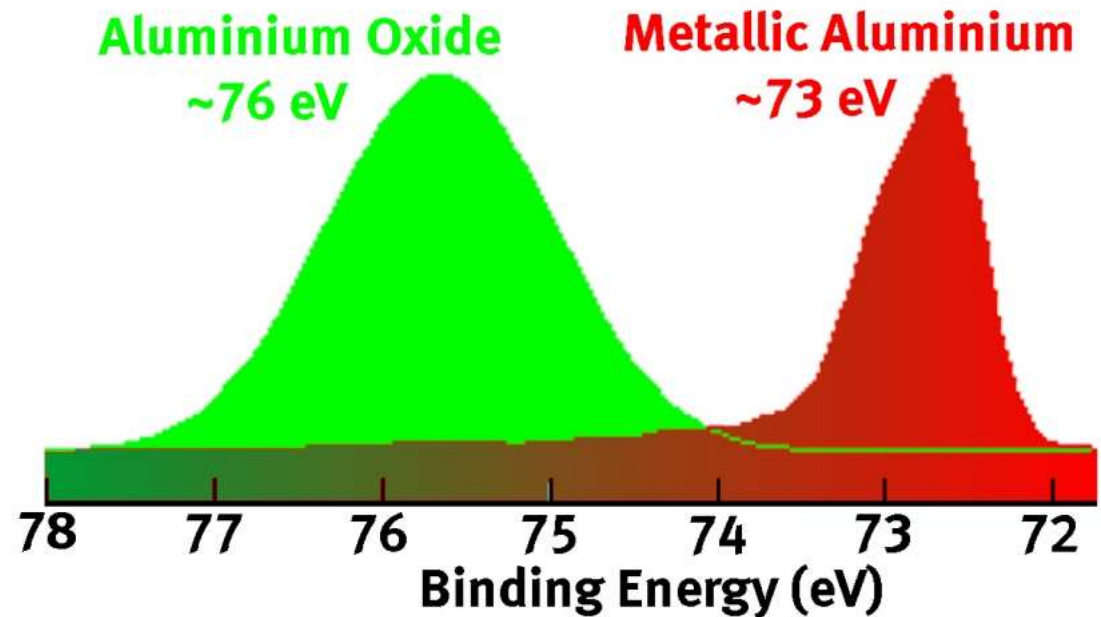
**Elemental aluminium**  
(aluminium bonded to itself)

or

**Aluminium oxide**  
(aluminium bonded to oxygen)

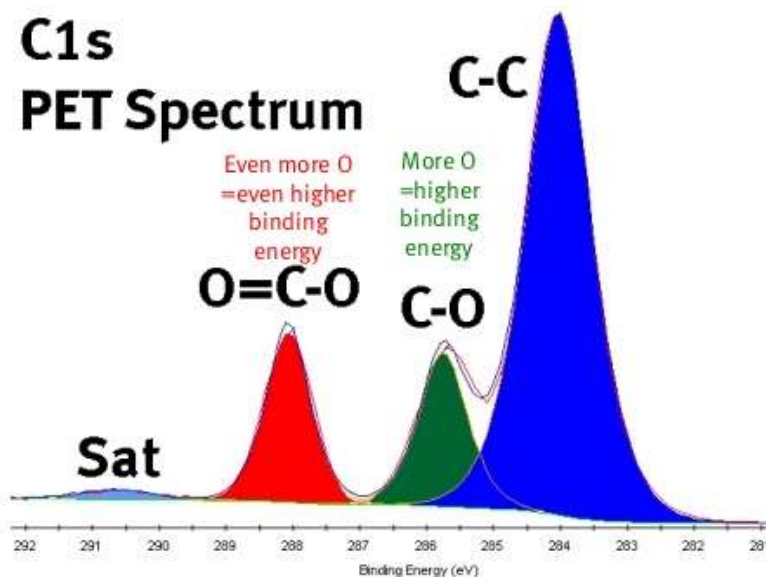
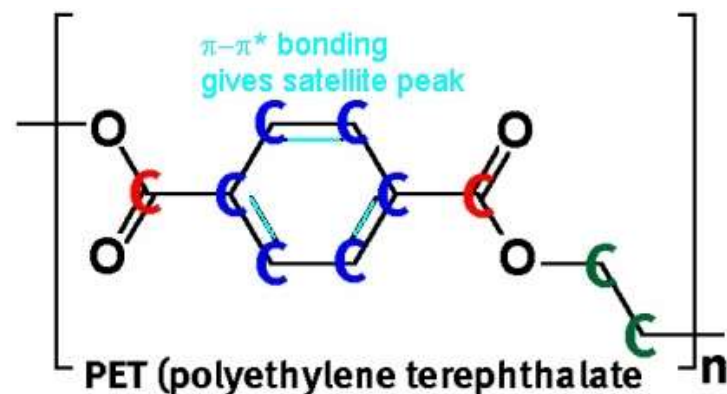
The amount of chemical shift depends on what the element is bonded to and on what type of bond

## Al2p Region



# Why do we see a Chemical Shift?

- In one word 'Complex!' but...
- Oxygen (O) attracts electrons to itself (electronegativity)
- If a carbon (C) atom is bonded to oxygen it will 'lose' some of its electrons to the oxygen and become more 'positively' charged
- As it becomes more positive, the electrons will have a higher 'binding' energy
- If the number of oxygen atoms (and the type of bond) increases this positive charge and hence the binding energy increases





# Peak resolution

- To see good chemical state information we need to be able to see or resolve the peaks

Resolution is measured by the full width at half maximum (FWHM)

- There are several factors that effect this:

## Instrumental factors -

Size of hemisphere, slit widths, detector type and pass energy

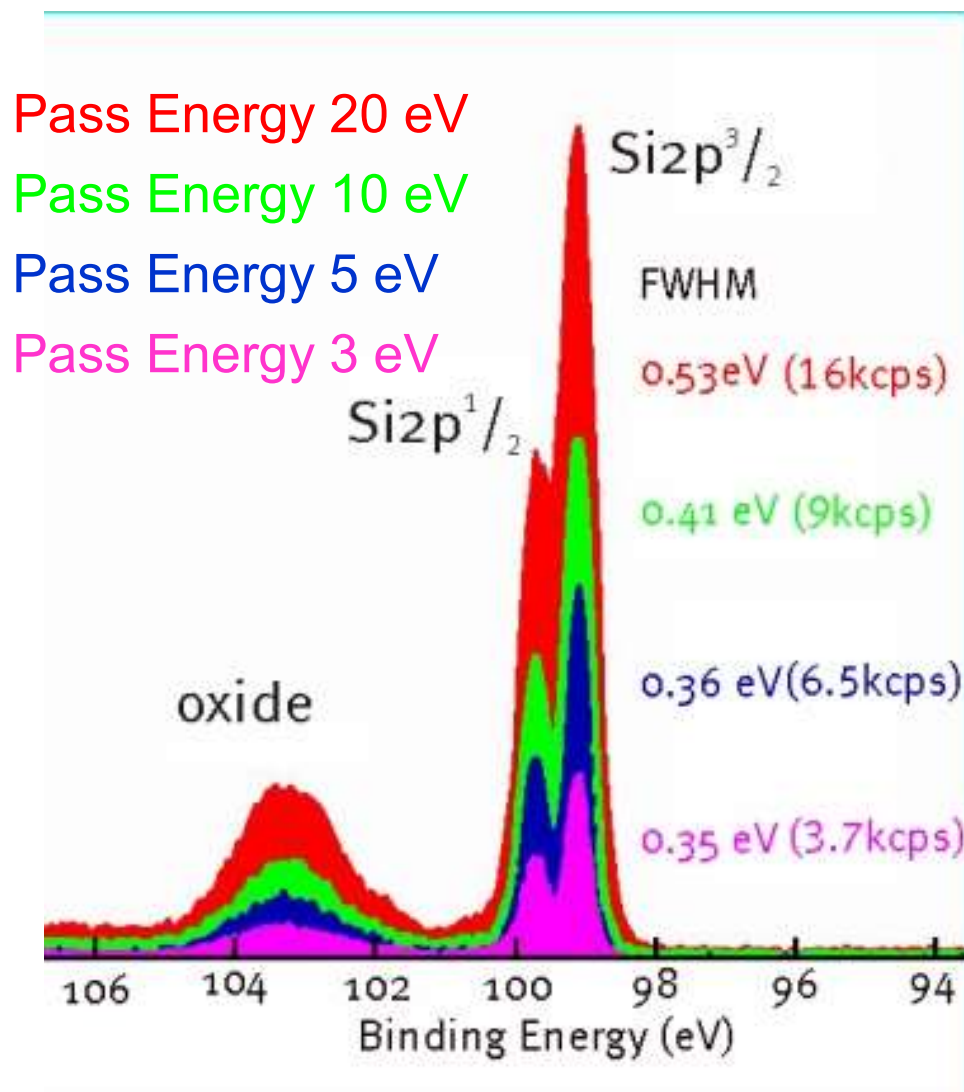
## Source factors -

Monochromator or twin anode X-ray source

## Intrinsic factors -

The natural width of the peak\*

\* We can not do much about this!



# Pass Energy and peak resolution/sensitivity

In XPS it is common to use different spectrometer resolutions (Pass Energies)

Increasing the spectrometer resolution by decreasing the pass energy enables peaks to be resolved (seen), hence determine chemical state

However this is at the loss of sensitivity (counts per second)

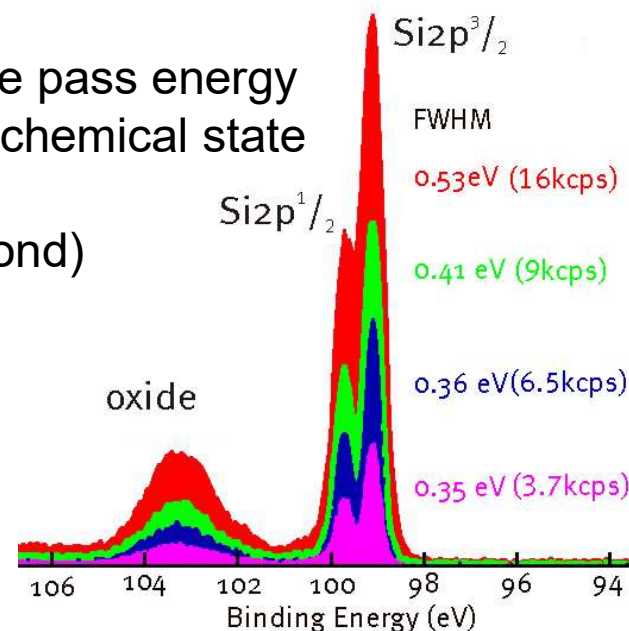
Decreasing the pass energy will not continually improve spectral resolution

The width of a peak ( $\Delta E$ ) is determined by:

$$\Delta E = \sqrt{(\Delta E_{\text{int}}^2 + \Delta E_{\text{source}}^2 + \Delta E_{\text{inst}}^2)}$$

As  $\Delta E_{\text{inst}}^2$  is decreased by reducing the pass energy the other terms  $\Delta E_{\text{int}}^2 + \Delta E_{\text{source}}^2$  become more important

We cannot change  $\Delta E_{\text{int}}^2$  but we can change  $\Delta E_{\text{source}}^2$  by changing the source e.g. twin anode to monochromators



Where:

$\Delta E_{\text{int}}^2$  is the square of the intrinsic (or natural) line width

$\Delta E_{\text{source}}^2$  is the square of the source line width

$\Delta E_{\text{inst}}^2$  is the square of instrumental factors



## So why use a monochromator?

The natural line width  $\Delta E_{\text{source}}$  of the standard anodes

- $\Delta E_{\text{source}} = 0.75 \text{ eV MgK}\alpha$
- $\Delta E_{\text{source}} = 0.85 \text{ eV AlK}\alpha$
- $\Delta E_{\text{source}} = 0.3 \text{ eV AlK}\alpha \text{ (mono)}$

So from:

$$\Delta E = \sqrt{(\Delta E_{\text{int}}^2 + \Delta E_{\text{source}}^2 + \Delta E_{\text{inst}}^2)}$$

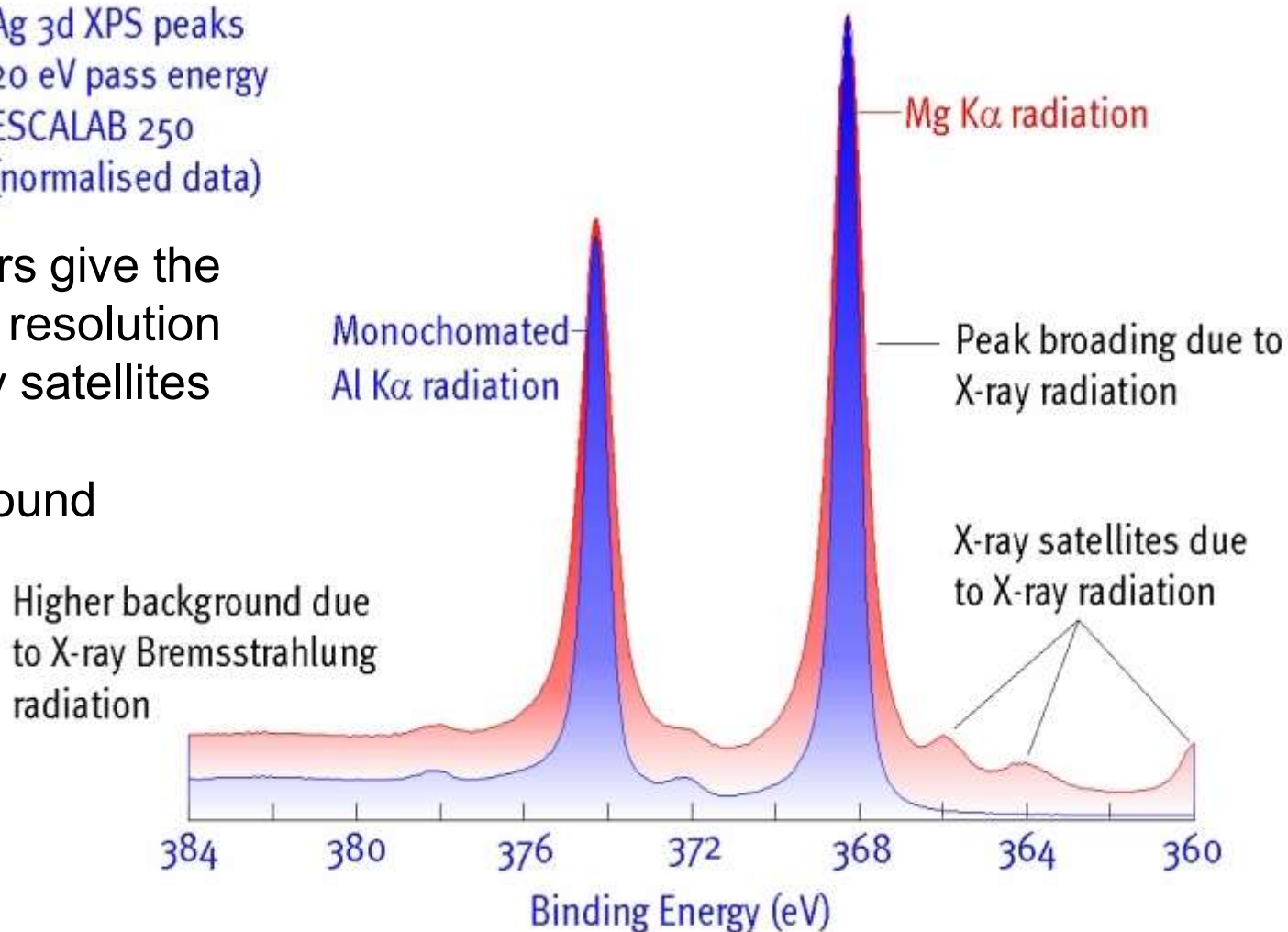
It would be expected that the XPS peak width measured under the same conditions would be narrower with a Mg source compared with an Al source and would be narrower still with a monochromated source

Also monochromators have other advantages such as can be focused to small spots (30 $\mu\text{m}$  to 400 $\mu\text{m}$ ), reduction in background levels and removal of satellite features.

# So why use a monochromator?

Ag 3d XPS peaks  
20 eV pass energy  
ESCALAB 250  
(normalised data)

- Monochromators give the highest spectral resolution
- Removes X-ray satellites from spectrum
- Lowers background



# Quantification

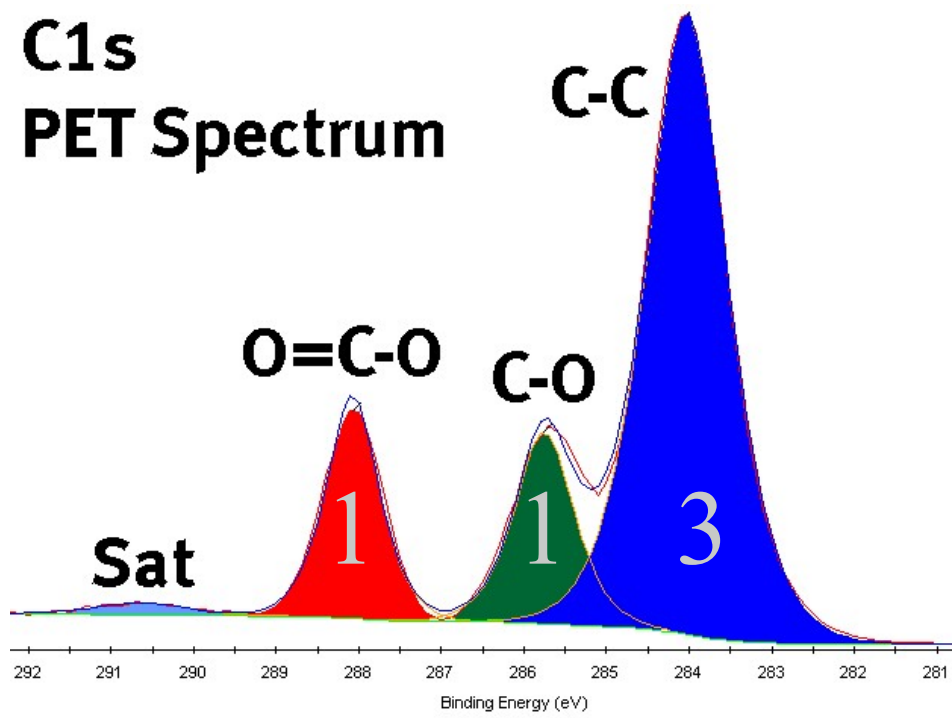
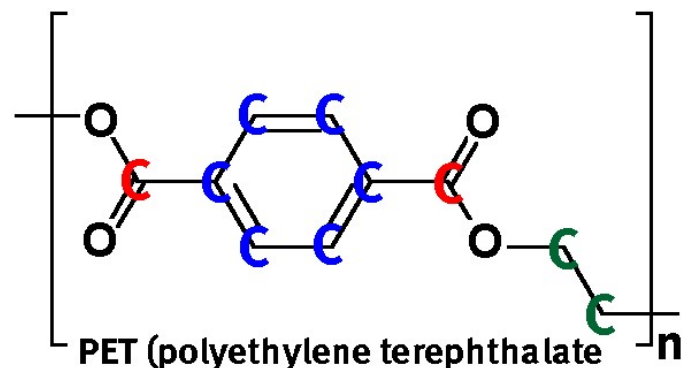
- The number of each type of carbon species for PET is:
  - **C-C**                    6            (= 3)
  - **C-O**                        2            (= 1)
  - **O=C-O**                    2            (= 1)

This is mirrored by the intensities shown in the spectrum

Thus intensity of a peak (Area) gives

## Quantification

i.e. how much of a species is there in the sample



# Quantification

The intensity of a peak is related in some way to the number of atoms that generate that peak

e.g.  $I_A \propto N_A$

Where  $I_A$  is the intensity of a peak and  $N_A$  is the number of atoms of element A

Each transition (e.g. C1s, Al2p, Si2s) has its own 'probability' of occurring - referred to a 'sensitivity factor' and are obtained from libraries.

These are generally referred to the Scofield or Wagner libraries

e.g.  $I_A = NF \cdot N_A$  ( $N_A = I_A / NF$ )

where NF is some kind of normalisation factor, which includes terms for the efficiency (transmission) of the analyser at different kinetic energies, electron mean free path ( $\lambda$ ) and the 'Sensitivity' factor

# Quantification

Normalised areas are calculated using the peak area as the intensity of the peak ( $I_A$ )

$$N_A = \text{Peak Area}/NF$$

Normalisation factors include several terms:

- **X-ray Cross-Section Term**  
(How many photoelectrons a particular transition will generate)
- **Transmission Function**  
(How well does the spectrometer detect electrons at a particular kinetic energy)
- **Depth of Analysis Term**  
(incorporation of a  $\lambda$  value)
- **Normalisation between sensitivity factors generated on different instruments**  
(i.e. between a CMA or HSA )

This is done for any elements or species in the sample (e.g. A, B, C..)  
Atomic concentration is then given by:

$$\text{At}\%_A = (N_A / (N_A + N_B + N_{C..})) \times 100$$

## X-ray cross section term

Two libraries are used but they have to be used in slightly different ways

**Scofield** - A *theoretical* sensitivity factor data base, based on  $C1s = 1$  (i.e. A calculation which gives a number relating to the number of photoelectrons generated by a number of photons hitting the sample)

For this we need to add in a term to account for the depth of analysis (i.e.  $\lambda$  and is generally  $KE^{0.6}$ )

**Wagner** - An *empirical* sensitivity factor data base, based on  $F1s = 1$  (i.e. Real measurements done on an instrument on a large number of known compounds and working out relative sensitivity factors).  
For this we need to add in a term to correct for the fact this was generated on a different type of analyser (A CMA rather than our HSA).  
This is done by multiplying by the KE of the peak used.  
(The term  $\lambda$  is already included in the analysis)

Both libraries can be used - but different results on the same set of data may be obtained!!

# How Accurate is the Atomic Percent?

Although people use the numbers there are several sources of uncertainty in the result - These can be due to:

- **Determination of the peak intensity?**  
How do you measure a peak area, where do you start from and to, what do you include, what shape background etc
- **Accuracy of Sensitivity Peak Libraries?**  
Different libraries give different results - which is right?
- **Accuracy of the Transmission Function?**  
How well defined is the function for a particular instrument
- **Other Factors include determination of  $\lambda$**

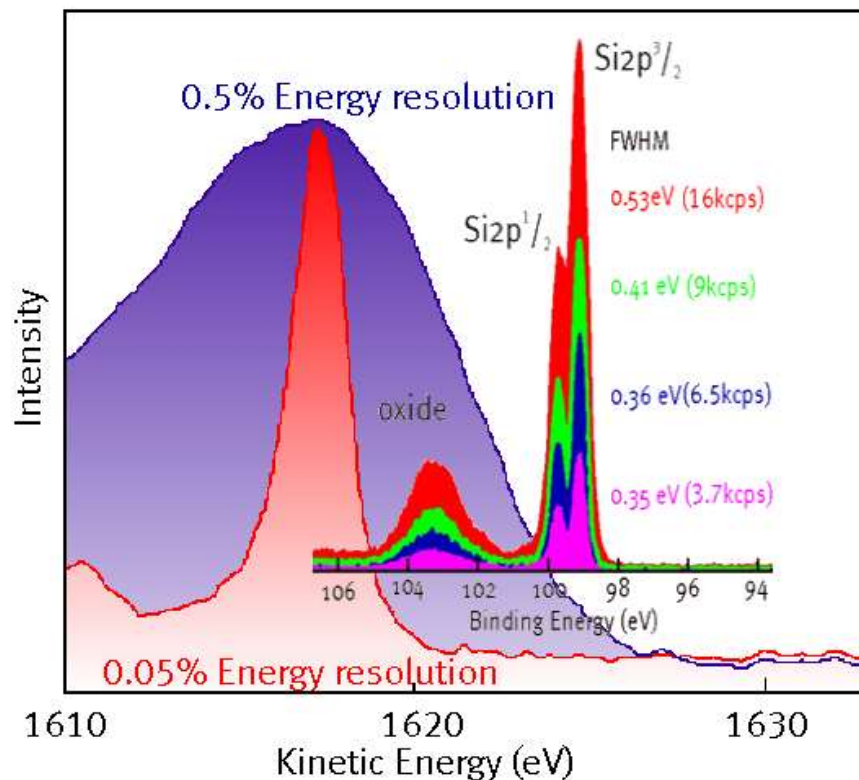
XPS is good for quantification on a relative scale - comparing similar samples, consistent measurement and data treatment and looking for trends

But absolute numbers have a great deal of uncertainty due to above



# What information can we get from AES spectra?

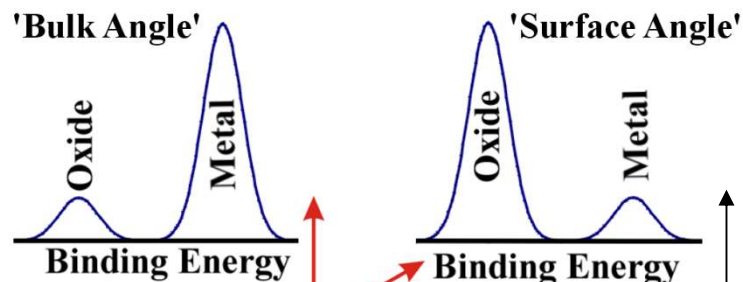
- As with XPS the spectrum contains information that is useful. However compared to XPS this information is sometimes more difficult to interpret.



- the natural width of an AES peak is broader than an XPS peak thus:
- it is less easy to note chemical shifts (i.e. chemical state information)
- it is sometimes more difficult to determine an intensity of a peak as the start/end points are less well defined
- The relative peak intensities vary with the primary beam energy i.e. we need a set of sensitivity factors for each electron beam energy (1 kV, 2 kV 5 kV, 10 kV etc)
- The relative peak intensities vary with retard ratios i.e. we need a set of sensitivity factors for each retard ratio used CRR4, CRR10, CRR40 etc

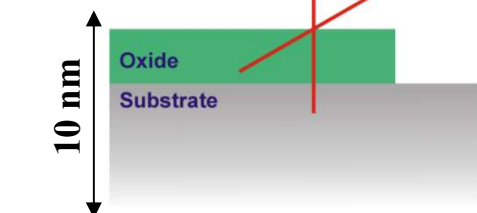
# Thickness Measurement

- In some cases what we want to know may not only be at the surface, but maybe located lower down in the sample.
- There are two methods which we use to determine this information however only the ion etching depth profiling is the method on the K-Alpha

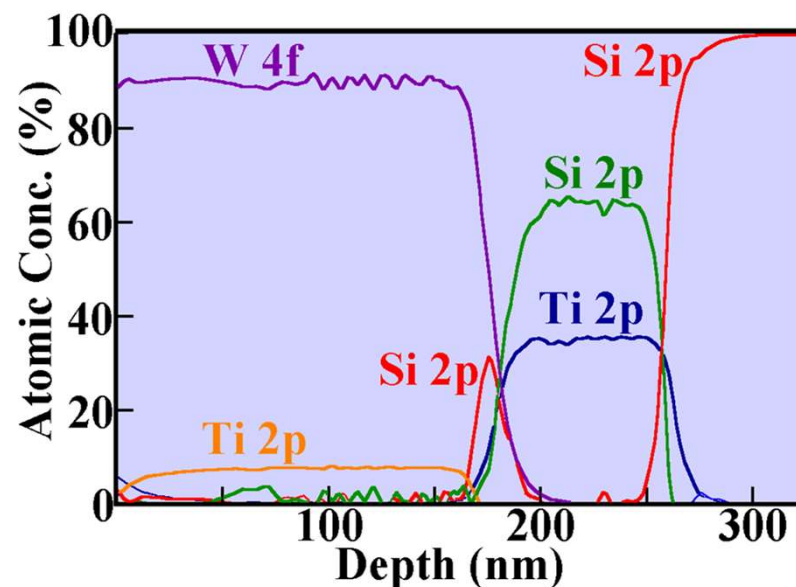
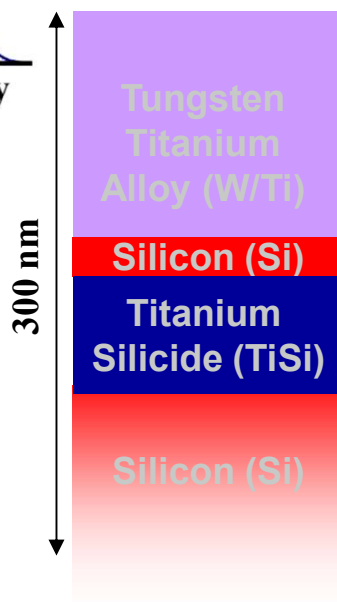


Angular resolved XPS (ARXPS)

For analysis less than the analysis depth of XPS



Ion etch depth profiling for analysis up to about 1 $\mu$ m

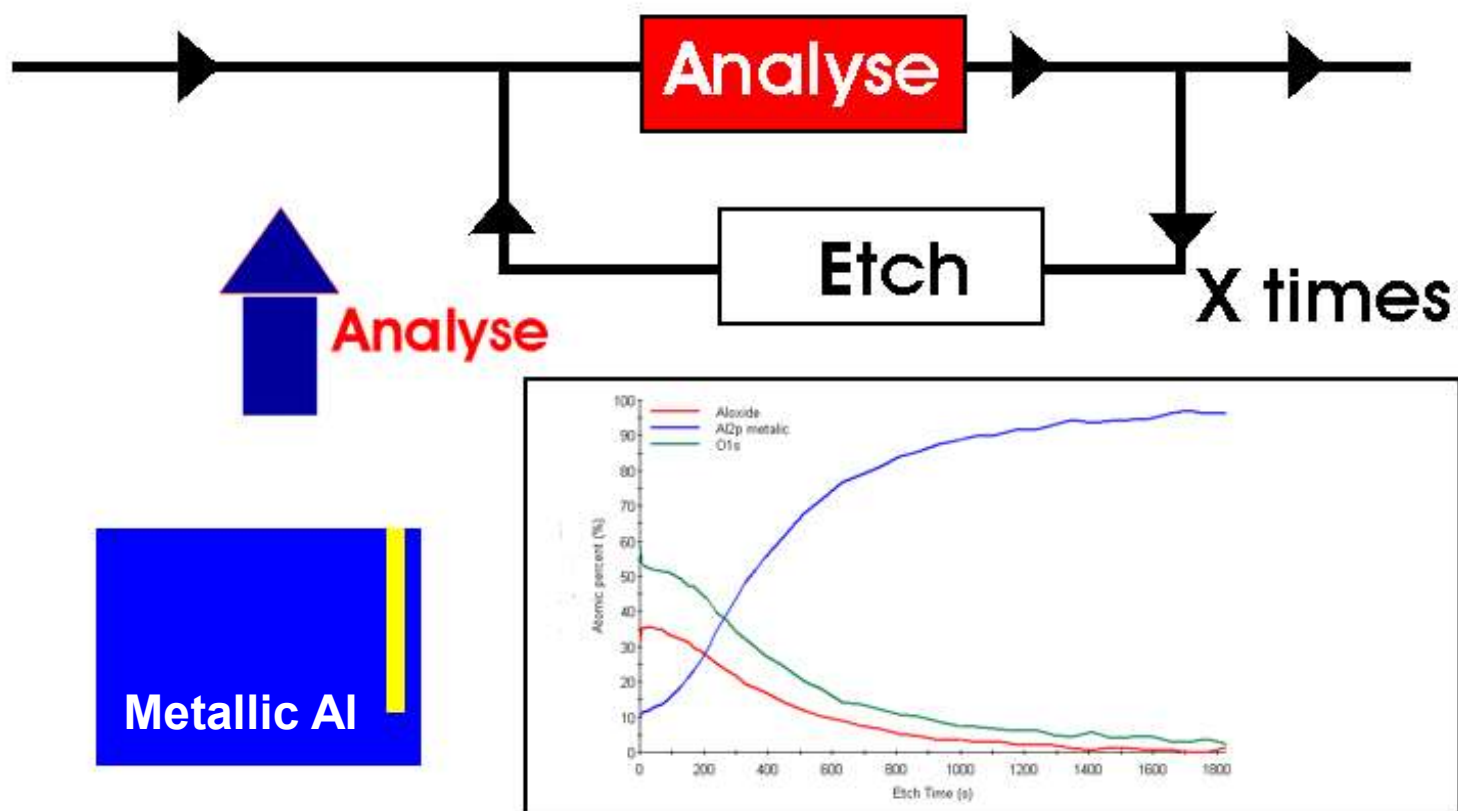


# Thickness Measurement Ion Etch Depth Profiling

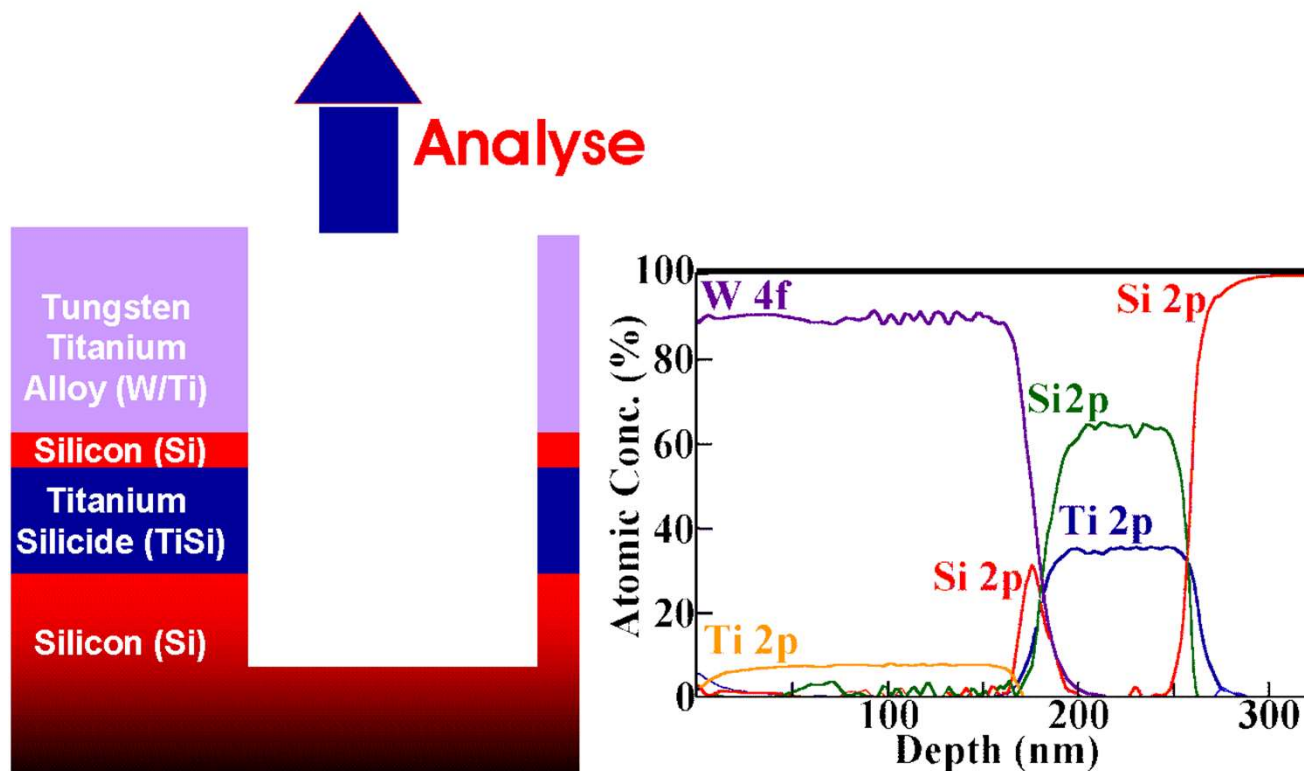
- When an Ion beam (e.g. Ar<sup>+</sup>) hits a sample surface it removes some atoms from the surface.
- The rate of which atoms removed depends on:
  - The type of gas used - heavier ions (e.g. Ar<sup>+</sup>) remove more rapidly than lighter ones (e.g. He<sup>+</sup>)
  - The energy of the ions (how 'fast' they are going) - 5 kV ions (fast) remove more rapidly than 1 kV ions (slow)
  - The number (or current) of ions - 1  $\mu\text{A}$  ion current will remove at a rate of 10x more atoms than a 0.1  $\mu\text{A}$  ion current
  - The rate also depends on what the sample is made from e.g. Silicon etches more rapidly than Tantalum

# Ion etch depth profiling

- A depth profiling experiment consists of alternate analysis followed by a period of etching then more analysis. The change in the concentration or chemical state with depth can be noted

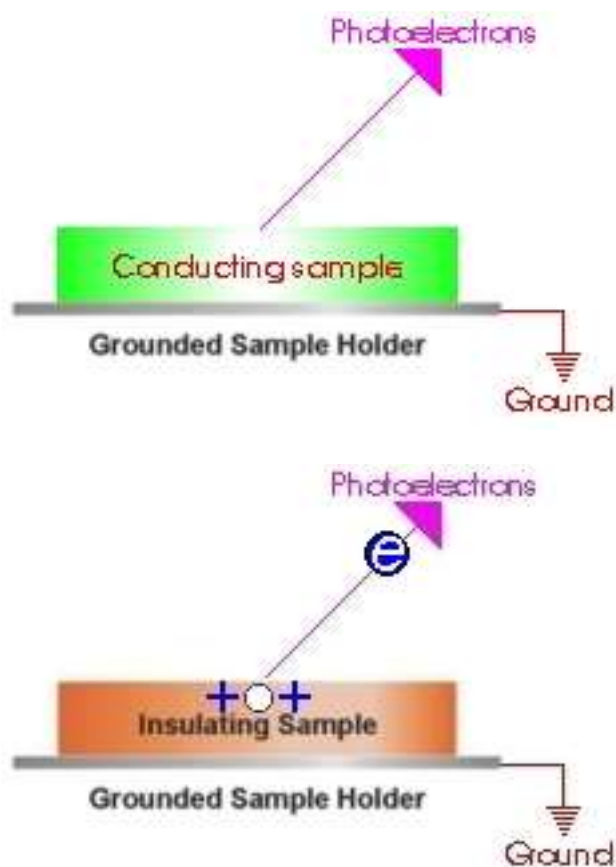


# Ion etch depth profiling



# Charge Compensation

## ■ The Concept



### Conducting Samples:

As photoelectrons leave the sample is neutralised by electrons from earth (ground)

### Insulating Samples:

As more photoelectrons leave the sample the surface becomes more positively charged. This reduces the kinetic energy of the photoelectrons

$$KE = h\nu - BE - \psi - \delta$$

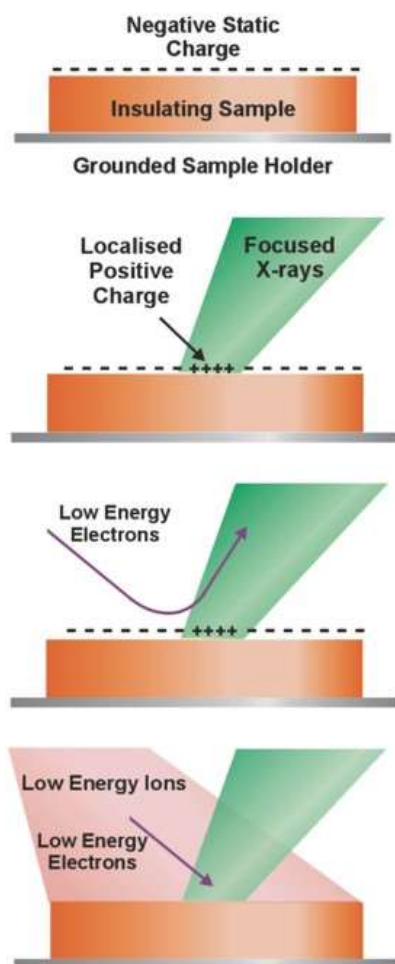
Where  $\delta$  is retardation of the photoelectrons

As  $\delta$  becomes larger less photoelectrons can be detected and peaks move to apparently higher binding energies, become distorted or lost completely.

**THIS IS NOT A GOOD THING!**

# Charge compensation

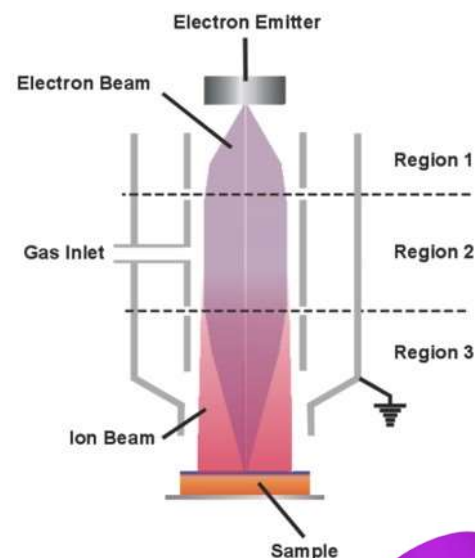
## ■ The Concept



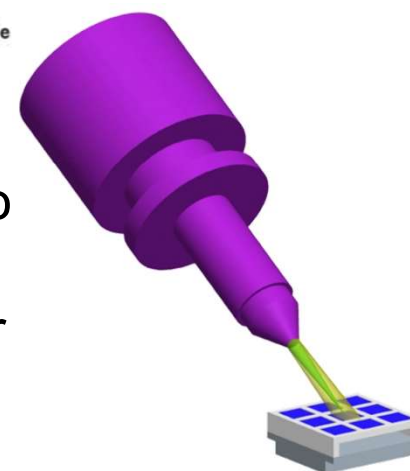
Low energy electrons neutralise the localised positive charge ('holes') left by the photoelectrons generated by the X-ray spot.

The low energy ions ensure that the surface does not become negatively charged and the low energy electrons arrive at the required area on the sample

## ■ The Implementation



Requires no adjustment  
Either on or off





# Conclusion

- Surface analysis techniques give us valuable information about the samples surface which maybe different to 'bulk analysis':
- They tells us:
  - Where it is
  - What it is
  - How much of it there is
- and
- How thick it is
  
- Insulating materials can be analysed by use of charge compensation