

LABORATORY OF SURFACE ANALYSIS

I. Objectives of the laboratory

1. To introduce XPS and AES surface analysis technique principals
- 2 To provide XPS and AES analysis of the samples, including qualitative, quantitative analysis and depth profile

II References

1. Practical surface analysis by auger and X-Ray photoelectron spectroscopy D. Briggs and M.P. Seah
2. Introduction to surfactant analysis, D.C. Cullum, 1994

III. Principles of XPS and AES

X-ray **photoelectron** spectroscopy (XPS) and Auger **electron** spectroscopy (AES) can answer important questions:

- 1. Which elements are present at the surface?**
- 2. What chemical states of these elements are present?**
- 3. How much of each chemical state of each element is present?**
- 4. What is the spatial distribution of the materials in three dimensions?**
- 5. If material is present as a thin film at the surface,**
 - (a) how thick is the film?**
 - (b) how uniform is the thickness?**
 - (c) how uniform is the chemical composition of the film?**

For XPS and AES analysis vacuum chamber operating in the ultra-high vacuum (UHV) regime is used.

In XPS and AES the emission and energy analysis of low-energy electrons (in the range 20—2000 eV) are concerned with. These electrons are liberated from the examined specimen as a result of the photoemission process (**XPS**) or by the radiationless deexcitation of an ionized atom by the Auger emission process in AES .

The source of the primary radiation for the two methods is different:

- X-ray photoelectron spectroscopy makes use of soft X-rays, generally $AlK\alpha$ or $MgK\alpha$,
- AES rely on the use of an electron gun

The same energy analyser may be used for both XPS and AES.

XPS and AES measure the energy of electrons emitted from a material. It is necessary, therefore, to have some formalism to describe which electrons are involved with each of the observed transitions.

X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

Notation in XPS

XPS uses the chemists' notation: the observed photoelectrons are described by means of their quantum numbers.

Transitions are usually labelled according to the scheme nl_j . The first part of this notation is the principal quantum number, n . This takes values of 1, 2, 3 etc. The second part of the nomenclature, l , is the quantum number which describes the orbital angular momentum of the electron. This takes values 0, 1, 2, 3 etc. This quantum number is usually given a letter (Table 1)

Table 1 Notation given to the quantum numbers which describe orbital angular momentum

Value of l	Usual notation
0	s
1	p
2	d
3	f

The peaks in XPS spectra, derived from orbital whose angular momentum quantum number is greater than 0 (p, d, f), are usually split into two. This is a result of the interaction of the electron angular momentum due to its spin with its orbital angular momentum. The value of s can be either $+1/2$ or $-1/2$. The two angular momenta are added vectorially to produce the quantity j in the expression nl_j , i.e.,

$$j = |l + s|.$$

An electron from p orbital can have j value of $1/2$ ($l - s$) or $3/2$ ($l + s$);

An electrons from d orbital can have j values of either $3/2$ or $5/2$.

Figure 1 shows an XPS spectrum from Sn with the peaks labeled according to the notation and illustrating the splitting observed in the peaks due to electrons in 3p and 3d orbitals while splitting in the 4d and 4p peaks is too small to be observed.

In X-ray notation, the principal quantum numbers are given letters K, L, M, etc. while subscript numbers refer to the j values described above. The relationship between the notations is given in Table 2.

Table 2. The relationship between quantum numbers, spectroscopists' notation and X-ray notation

Quantum numbers				Spectroscopists' notation	X-ray notation
n	l	s	j		
1	0	+1/2, -1/2	1/2	$1s_{1/2}$	K
2	0	+1/2, -1/2	1/2	$2s_{1/2}$	L_1
2	1	+1/2	1/2	$2p_{1/2}$	L_2
2	1	-1/2	3/2	$2p_{3/2}$	L_3
3	0	+1/2, -1/2	1/2	$3s_{1/2}$	M_1
3	1	+1/2	1/2	$3p_{1/2}$	M_2
3	1	-1/2	3/2	$3p_{3/2}$	M_3
3	2	+1/2	3/2	$3d_{3/2}$	M_4
3	2	-1/2	5/2	$3d_{5/2}$	M_5
					etc.

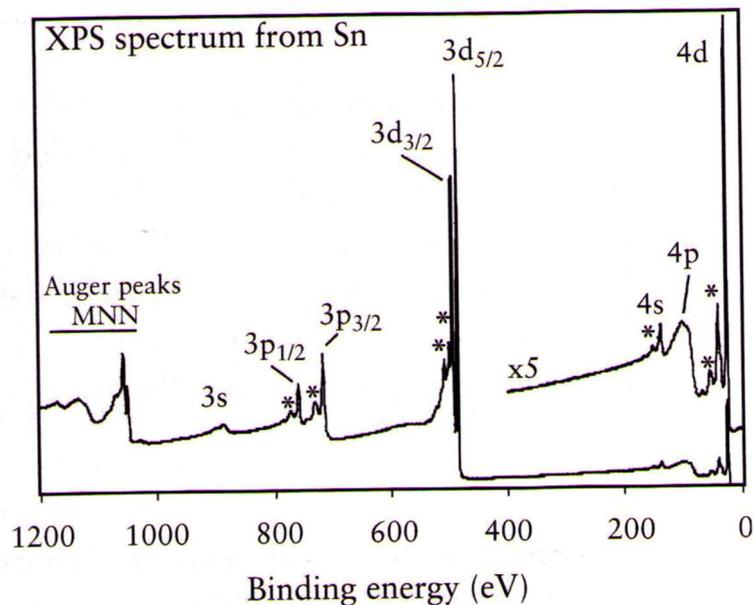


Figure 1. Survey spectrum from Sn showing the XPS transitions accessible using $AlK\alpha$ radiation, the features marked with an asterisk are electron energy loss features due to plasmon excitation

In XPS a special form of photoemission is concerned, i.e., the ejection of an electron from a core level by an X-ray photon of energy $h\nu$. The energy of the emitted photoelectrons is then analysed by the electron spectrometer and the data presented as a graph of intensity (counts or counts/s) versus electron energy \rightarrow *X-ray induced photoelectron spectrum*.

The kinetic energy (E_K) of the electron is the experimental quantity measured by the spectrometer, but this is dependent on the photon energy of the X-rays employed and is therefore not an intrinsic material property.

The binding energy of the electron (E_B) is the parameter which identifies the electron specifically, both in terms of its parent element and atomic energy level. The relationship between the parameters involved in the XPS experiment is:

$$E_B = h\nu - E_K - W$$

where $h\nu$ is the photon energy, E_K is the kinetic energy of the electron, and W is the spectrometer work function.

As all three quantities on the right-hand side of the equation are known or measurable, it is a simple matter to calculate the binding energy of the electron.

The process of photoemission is shown schematically in Figure 2, where an electron from the K shell is ejected from the atom. The photoelectron spectrum will reproduce the electronic structure of an element quite accurately since all electrons with a binding energy less than the photon energy will feature in the spectrum (Figure 3). Those electrons which are excited and escape without energy loss contribute to the characteristic peaks in the spectrum; those which undergo inelastic scattering and suffer energy loss contribute to the background of the spectrum. Once a photoelectron has been emitted, the ionized atom must relax in some way. This can be achieved by the emission of an X-ray photon (X-ray fluorescence). The other possibility is the ejection of an Auger electron. **Thus Auger electrons are produced as a consequence of the XPS process.**

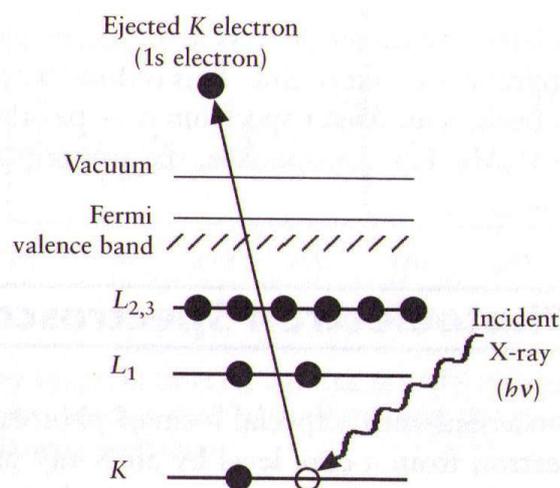


Figure 2 Schematic diagram of the XPS process, showing photoionization of an atom by the ejection of a is electron

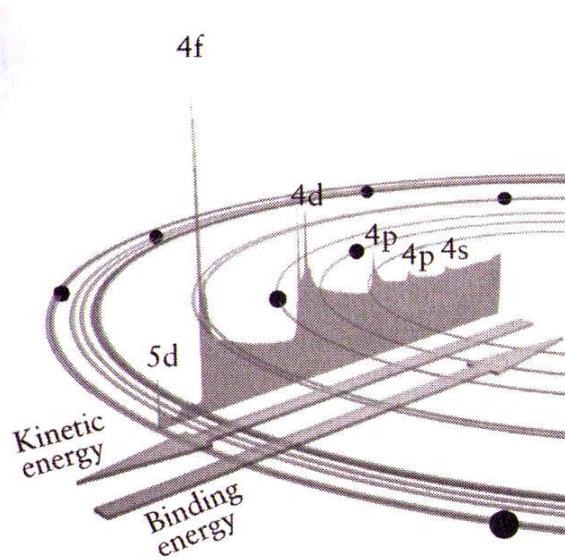


Figure 3. Photoelectron spectrum of lead showing the manner in which electrons escaping from the solid can contribute to discrete peaks or suffer energy loss and contribute to the background; the spectrum is superimposed on a schematic of the electronic structure of lead to illustrate how each orbital gives rise to photoelectron lines

AUGER ELECTRON SPECTROSCOPY

Notation in Auger spectroscopy

Auger electrons are identified by the X-ray notation. The Auger process involves three electrons and so the notation has to take account of this. This is done simply by listing the three electrons; a peak in an Auger spectrum may be labeled, for example, KL_1L_3 or $L_2M_5M_5$. For convenience, the subscripts are some times omitted.

Once an atom has been ionized it must return to its ground state. The emission of an X-ray photon may occur. The other possibility is that the core hole (for instance a K shell vacancy as shown in Figure 2) may be filled by an electron from a higher level, the $L_{2,3}$ level (Figure.4). In order to conform with the principle of the conservation of energy, another electron must be ejected from the atom, e.g., another $L_{2,3}$ electron in the schematic of Figure 4. **This electron is termed the $KL_{2,3}L_{2,3}$ Auger electron.**

It is common to omit the subscripts when referring to the group of Auger emissions involving the same principal quantum numbers, for example the term Si KLL is used to refer to the whole group of KLL emissions from silicon.

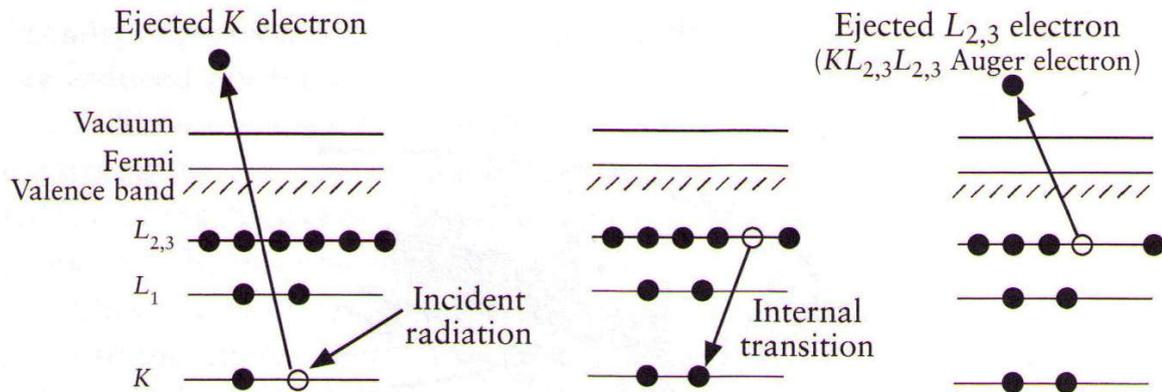


Figure 4. Relaxation of the ionized atom of Figure 2 by the emission of a KL_{2,3}L_{2,3} Auger electron

The kinetic energy of a KL_{2,3}L_{2,3} Auger electron is approximately equal to the difference between the energy of the core hole and the energy levels of the two outer electrons, $E_{KL_2,3L_2,3}$ (the term L_{2,3} is used in this case because, for light elements, L₂ and L₃ cannot be resolved):

$$E_{KL_2,3L_2,3} \approx E_K - E_{L_2,3} - E_{L_2,3}$$

This equation does not take into account the interaction energies between the core holes (L_{2,3} and L_{2,3}) in the final atomic state nor the inter- and extra-relaxation energies which come about as a result of the additional core screening needed. Clearly, the calculation of the energy of Auger electron transitions is much more complex than the simple model outlined above, but there is a satisfactory empirical approach which considers the energies of the atomic levels involved and those of the next element in the periodic table.

It is the kinetic energy of the Auger electron ($E_{KL_2,3L_2,3}$) that is the characteristic material quantity irrespective of the primary beam energy. **For this reason Auger spectra are always plotted on a kinetic energy scale.**

The use of a finely focused electron beam for AES enables to achieve surface analysis at a high spatial resolution, in a manner analogous to EPMA in the scanning electron microscope. By combining an electron spectrometer with an ultra-high vacuum (UHV) SEM it becomes possible to carry out scanning Auger microscopy. In this mode of operation various imaging and chemical mapping procedures become possible.

THE DEPTH OF ANALYSIS IN X-RAY PHOTOELECTRON AND AUGER SPECTROSCOPY

The depth of analysis in both XPS and AES varies with the kinetic energy of the electrons under consideration. It is determined by a quantity known as the attenuation length (λ) of the electrons, which is related to the inelastic mean free path (IMFP). The relationship between λ , electron energy and material properties is given below:

$$\lambda = \frac{538a_A}{E_A^2} + 0.41a_A(a_A E_A)^{0.5}$$

where E_A is the energy of the electron in eV, a is the volume of the atom in nm^3 and λ , is in nm.

The intensity of electrons (I) emitted from all depths greater than d in a direction normal to the surface is given by the Beer—Lambert relationship:

$$I = I_0 \exp(-d/\lambda),$$

where I is the intensity from an infinitely thick, uniform substrate. For electrons emitted at an angle θ to the surface normal, this expression becomes:

$$I = I_0 \exp(-d/\lambda \cos \theta)$$

ELECTRON SPECTROMETER DESIGN

X-ray Sources for XPS

X-rays are generated by bombarding an anode material with high-energy electrons. The electrons are emitted from a thermal source (an electrically heated tungsten filament or a lanthanum hexaboride emitter).

The choice of anode material for XPS determines the energy of the X-ray transition generated. It must be **of high enough photon energy** to excite an intense photoelectron peak from all elements of the periodic table; it must also possess a natural X-ray **line width that will not broaden the resultant spectrum excessively**.

The most popular anode materials are **aluminum and magnesium**. These are providing AlK α or MgK α photons of energy 1486.6eV and 1253.6eV respectively. The twin anode assemblies (with Al and Mg) provides the ability to differentiate between Auger and photoelectron transitions when the two overlap in one radiation. XPS peaks will change to a position 233 eV higher on a **kinetic energy scale** on switching from MgK α to AlK α whereas the energy of Auger transition remains constant. On a **binding energy scale**, of course, the reverse is true (Figure 5). The photon energies and peak widths of MgK α and AlK α are compared with those of other elements in Table 3

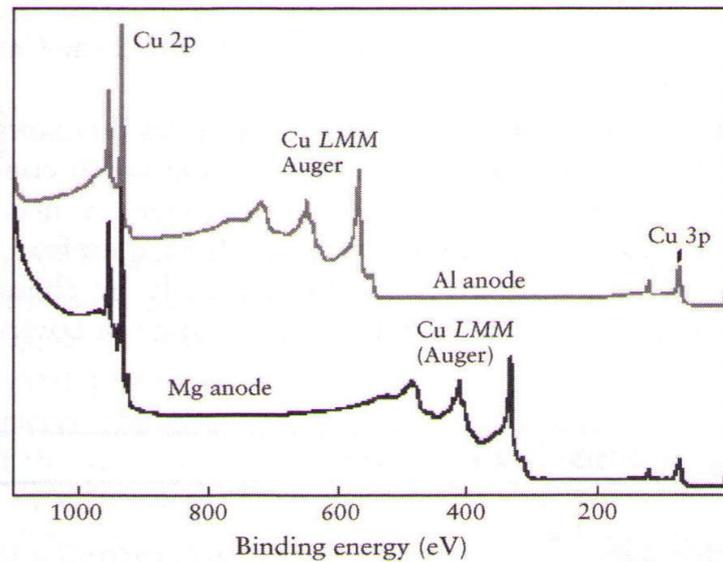


Figure 5. Comparison of XPS spectra recorded from copper using AlK α (upper) and MgK α (lower) radiation; note that on a binding energy scale the XPS peaks remain at constant values but the X-AES transitions move by 233 eV on switching between the two sources.

Table 3 Possible anode materials for XPS

Element	Line	Energy (eV)	Full-width half maximum (eV)
Y	M ζ	132.3	0.47
Zr	M ζ	151.4	0.77
Mg	K $\alpha_{1,2}$	1253.6	0.7
Al	K $\alpha_{1,2}$	1486.6	0.9
Si	K α	1739.6	1.0
Zr	L α	2042.4	1.7
Ag	L α	2984.4	2.6
Ti	K α	4510.9	2.0
Cr	K α	5417.0	2.1

X-ray monochromators

The purpose of an X-ray monochromator is to produce a narrow X-ray line by using diffraction in a crystal lattice (Figure 6). X-rays strike the parallel crystal planes at an angle θ and are reflected at the same angle.

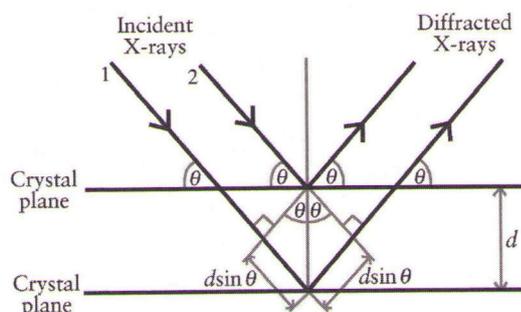


Figure. 6. Diffraction of X-rays at a quartz crystal

Usually, the monochromator on an XPS instrument is used for AlK α radiation. Quartz crystal is a convenient material used for monochromator because it is relatively inert, compatible with UHV conditions, it can be bent and/or ground into the correct shape and its lattice spacing provides a convenient diffraction angle for AlK α radiation.

The reasons for choosing to use an X-ray monochromator on an XPS spectrometer:

1. The primary reason for using monochromated radiation is the reduction in X-ray line width, for example, from 0.9 eV to approximately 0.25 eV for AlK α , and from 2.6 eV to 1.2 eV for AgL α . Narrower X-ray line width results in narrower XPS peaks and consequently better chemical state information.
2. Unwanted portions of the X-ray spectrum, i.e., satellite peaks are also removed.
3. It is possible to focus X-rays into a small spot using the monochromator. This means that small area XPS can be conducted with high sensitivity.

The XPS spectrum of Ag 3d electrons acquired using monochromatic and non-monochromatic X-rays is shown in Figure 7. There is a clear difference in the peak width, the background is higher using the non-monochromatic X-rays and X-ray satellites are clearly visible when the non-monochromatic source is used.

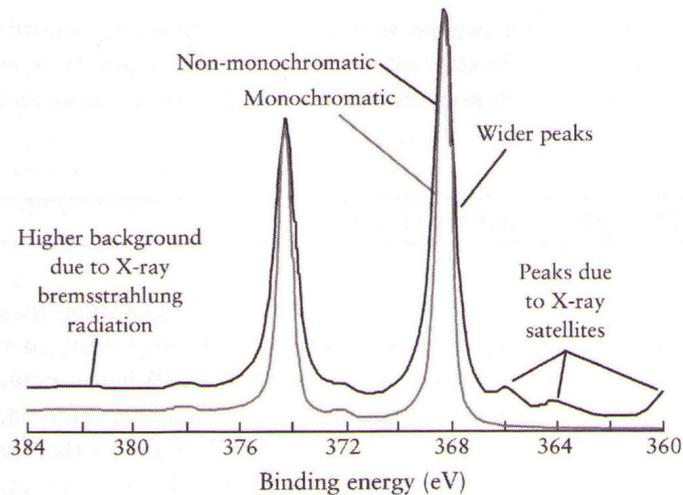


Figure 7 A comparison of the Ag 3d spectra acquired with monochromatic and non-monochromatic X-rays.

THE ELECTRON GUN FOR AES

The electron guns for AES improve from the 500 μ m resolution to the <10nm lateral resolution.

The critical components of the electron gun are the electron source and the lens assemblies for beam focusing, shaping and scanning.

Electron sources may be either thermionic emitters or field emitters, lenses for the electron gun may be electrostatic or, for high-resolution applications, electromagnetic.

The criterion, which distinguishes an electron gun for AES from one conventional in electron microscopy, is the need to operate in a **UHV environment**. The major step forward was the development of a gun with bakeable electromagnetic lenses; such lenses, with a spatial resolution of 50 nm and a thermionic emitter, became routinely available.

To be useful as an electron source for Auger electron spectroscopy a source should have the following properties

1. **Stability.** The current emitted from the source should be highly stable over long period.
2. **Brightness.** High emission currents from a small emitted area are required if the eventual spot size at the specimen is to be small.
3. **Mono-energetic.** The focal length of electromagnetic and electrostatic lenses is dependent upon the energy of the electrons. This means that the optimum focusing conditions can only occur for electrons having a very small range of kinetic energy. A wide energy spread will therefore result in a large spot size at the sample.
4. **Longevity.** Under normal operating conditions the emitter must not need to be replaced for many hundreds of hours

Thermionic emitter

The simplest form of thermionic source is a tungsten wire. When an electric current is passed through it, the temperature rises giving electrons sufficient energy to overcome the work function and be released into free space. The work function is the energy required for an electron to escape from a solid surface; for tungsten this is about 4.5 eV. Simple thermionic emitters are lack brightness and so it is difficult, using this type of source, to attain spot sizes for Auger analysis below about 200 nm.

Lanthanum hexaboride emitter

A widely used material for high-brightness sources is single crystal lanthanum hexaboride (LaB₆). The Source consists of a small, indirectly heated, crystal of LaB₆ cylindrical in shape and conical at one end. This material has a much lower work function than tungsten (2.6 eV), which means that it has a high emission density even at a much lower temperature.

Cold field emitter

A type of emitter which has found use in Auger microscopy is that based on the field emission source. The operating principle of a field emission source is not to give the electrons sufficient energy to jump the work function barrier but to reduce the magnitude of the barrier itself, both in height and in width. The small area of emission from the tip into a small solid angle provides a high brightness compared with thermionic sources.

ANALYSERS FOR ELECTRON SPECTROSCOPY

There are two types of electron energy analyser in general use for XPS and AES

- the cylindrical mirror analyser (CMA)
- the hemispherical analyser (HSA).

The cylindrical mirror analyser

The CMA consists of two concentric cylinders as illustrated in Figure 8, the inner cylinder is held at earth potential while the outer ramped at a negative potential. An electron gun is often mounted coaxially within the analyser. A certain proportion of the Auger electrons emitted will pass through the defining aperture in the inner cylinder and, depending on the potential applied to the outer cylinder; electrons of the desired energy will pass through the detector aperture and be re-focused at the electron detector. Thus, the direct energy spectrum can be built up by merely scanning the potential on the outer cylinder to produce a spectrum of intensity (in counts per second) versus electron kinetic energy. This spectrum will contain not only Auger electrons but all the other emitted

electrons, the Auger peaks being superimposed, as weak features, on an intense background. For this reason the differential spectrum is often recorded rather than the direct energy spectrum. In modern Auger spectrometers, however, the differential spectrum, if required, is calculated within the data system. A comparison of direct (pulse counted) and differential Auger electron spectra, from a copper foil, is presented in Figure 9.

While the CMA can provide good sensitivity for AES, it suffers from a number of disadvantages which make it unsuitable for XPS.

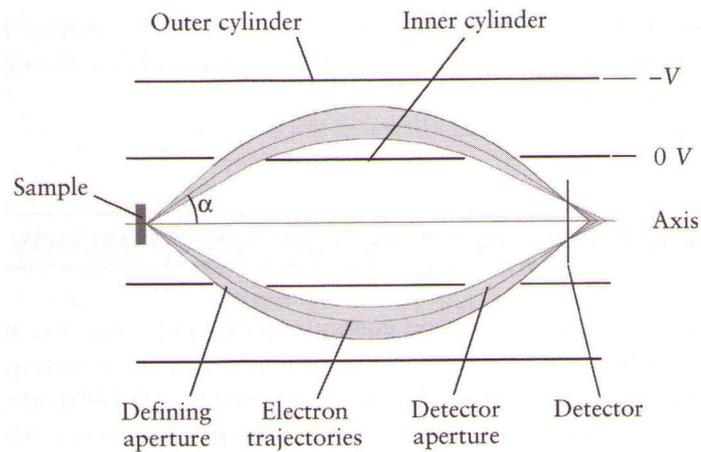


Figure 8 Schematic diagram of the cylindrical mirror analyser (CMA)

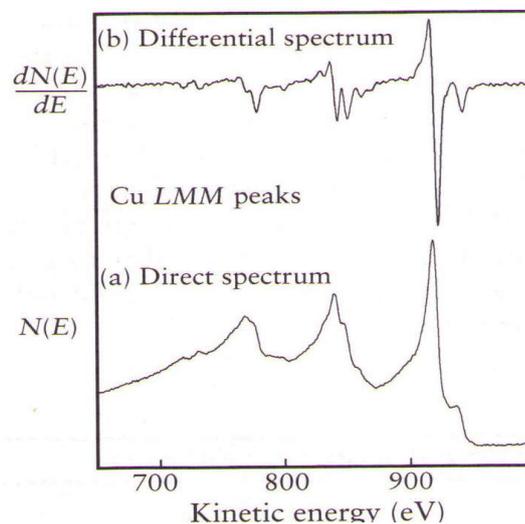


Figure 9 Comparison of (a) direct, and (b) differential Auger spectra for copper

The hemispherical sector analyser

A hemispherical sector analyser (HAS) consists of a pair of concentric hemispherical electrodes between which there is a gap for the electrons to pass. Between the sample and the analyser there is

usually a lens, or a series of lenses. The kinetic energy of the electrons as they are ejected from the sample is usually too great for the analyzer to produce sufficiently high resolution so they must be retarded. This retardation is achieved either within the lens or, using parallel grids, between the lens and the analyser. The schematic diagram of Figure 10 shows a typical HSA configuration for XPS. A potential difference is applied across the two hemispheres with the outer hemisphere being more negative than the inner one. Electrons injected tangentially at the input to the analyser will only reach the detector if their energy is given by

$$E = ke \Delta V$$

where the kinetic energy of the electrons is given by E , e is the charge on the electron, ΔV is the potential difference between the hemispheres, k is known as the spectrometer constant and depends upon the design of the analyser.

Electrons whose energy is higher than that given by the above expression will follow a path whose radius is larger than the mean radius of analyser and those with a lower kinetic energy will follow a path with smaller radius.

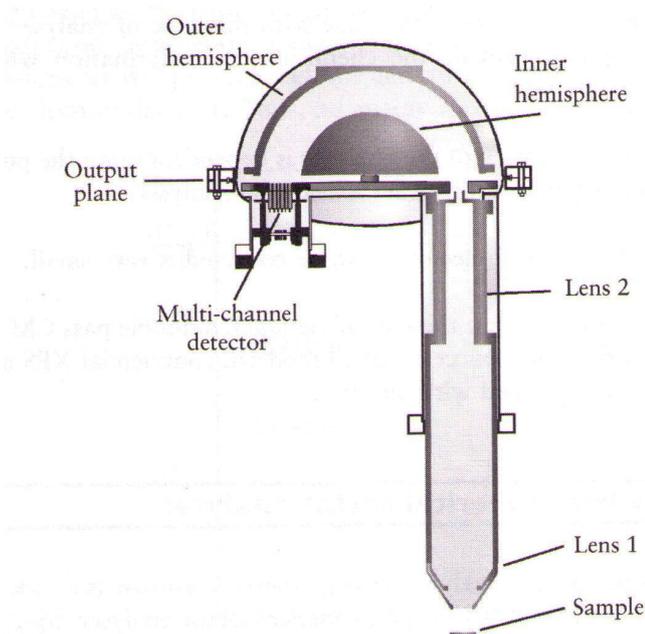


Figure 10. Schematic diagram of a modern HSA and transfer lens

DETECTORS

In most electron spectrometers it is necessary to count the individual electrons arriving at the detector. To achieve this, electron channeltrons multipliers is used. It consists of a spiral-shaped glass tube with a conical collector at one end and a metal anode at the other. The internal walls of the detector are coated with a material which, when struck by an electron having more than some threshold

kinetic energy, will emit many secondary electrons. Channeltrons can be capable of detecting up to about 3×10^6 counts/s.

POSSIBILITIES OF XPS ANALYSIS

CHEMICAL STATE INFORMATION BY X-RAY PHOTOELECTRONSPECTROSCOPY

Almost all elements in the periodic table exhibit a chemical shift, which can vary from a fraction of an eV up to several eVs. The shifts observed in XPS have their origin in either **initial-state** or **final-state** effects.

Initial-state effects, it is the charge on the atom prior to photoemission that plays the major role in the determination of the magnitude of the chemical shift. For example, the C—O bond in an organic polymer is shifted relative to the unfunctionalized (C-C) carbon, by 1.6 eV. The more bonds with electronegative atoms that are in place the greater the positive XPS chemical shift. For F-C species; the C is chemical shifts being larger than those of C-O compounds as fluorine is a more electronegative element. The C—F group is shifted by 2.9 eV whilst CF₂ and CF₃ functionalities are shifted by 5.9eV and 7.7eV respectively. An example of the e peak fitting of a complex C spectrum from an organic molecule is shown in Figure 11. By the consideration of the structure of the molecule it is possible to build up a synthesized spectrum, the relative intensities of the individual components reflecting the stoichiometry of the sample.

Final-state effects that occur following photoelectron emission, such as core hole screening, relaxation of electron orbitals and the polarization of surrounding ions are often dominant in influencing the magnitude of the chemical shift.

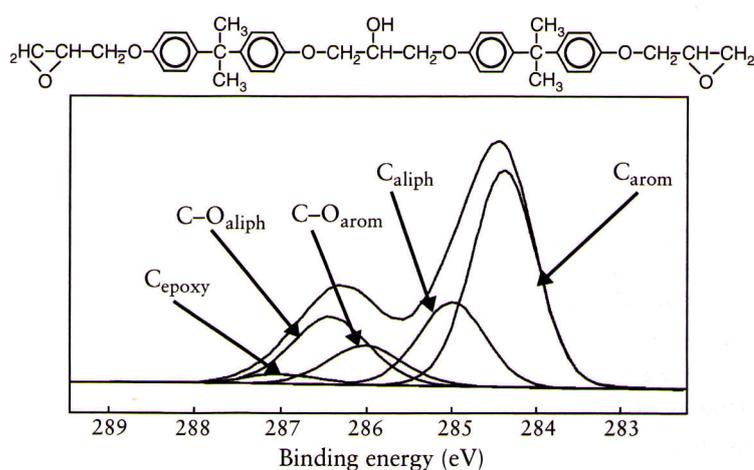


Figure 11 C is spectrum of the basic building block of epoxy product, the structure of which is shown above the spectrum; this spectrum was recorded using monochromatic Al radiation

ANGLE RESOLVED XPS

The information depth in XPS analysis is of the order of a few nanometers if the electrons are detected at a direction normal to the sample surface. If electrons are detected at some angle to the normal, the information depth is reduced by an amount equal to the cosine of the angle between the surface normal and the analysis direction. This is the basis for angle resolved XPS (ARXPS). This method can be applied to films which are too thin to be analysed by conventional depth profiling techniques or those that are irretrievably damaged by such methods (polymers). Another reason to use ARXPS is that it is a non-destructive technique which can provide chemical state information, unlike methods based upon sputtering (Figure12).

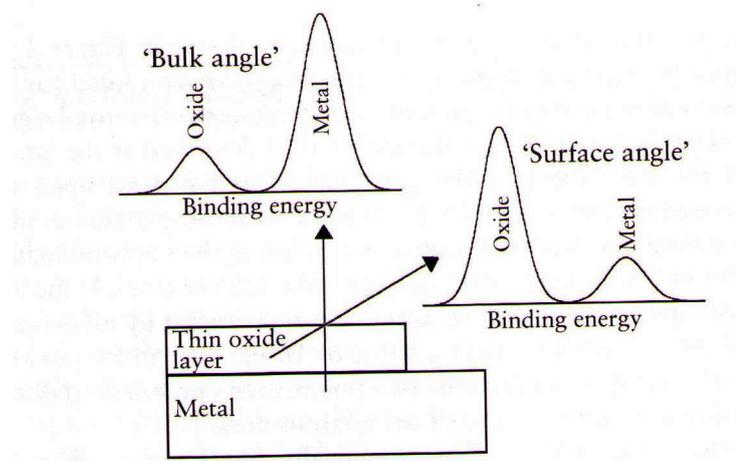


Figure12. Illustration of XPS spectra taken from a thin oxide film on a metal a near normal collection angle (bulk angle) and near grazing collection angle (surface angle)

QUANTIFICATION IN XPS

The intensity (I) of a photoelectron peak from a homogeneous solid is given, in a very simplified form, by:

$$I = J\rho\sigma K\lambda$$

where J is the photon flux, ρ is the concentration of the atom or ion in the solid, σ is the cross-section for photoelectron production (which depends on the element and energy being considered), K is a term which covers all of the instrumental factors and λ is the electron attenuation length. The intensity referred to will usually be taken as the integrated area under the peak following the **subtraction of a linear or S-shaped background**. The above equation can be used for direct

quantification (the so-called first principles approach) but, more usually, experimentally determined sensitivity factors (SF) is employed. Once a set of peak areas has been calculated for the elements detected, intensity (I) in the above equation has been determined. If the X-ray flux remains constant during the experiment the atomic percentage of the elements concerned can be determined by dividing the peak area by SF of the corresponding element line and expressing it as a fraction of the summation of all normalized intensities:

$$[A] \text{ atomic \%} = \{(I_A/SF_A)/\Sigma(I/SF)\} \times 100\%$$

The calculation of surface composition by this method assumes that the specimen is homogeneous within the volume sampled by XPS.

POSSIBILITIES OF AES ANALYSIS

QUANTIFICATION IN AES

The quantitative interpretation of Auger spectra is not so straightforward. The first problem encountered is the form of the spectrum. In the differential mode the intensity measurement is the peak-to-peak height. For low-resolution spectrometers, this is approximately proportional to peak area; for high-resolution studies, fine structure, which becomes apparent in the spectrum, reduces apparent peak-to-peak height. It is for this reason that the integrated peak area of a direct energy spectrum is often preferred for quantitative AES. The relative peak areas in a spectrum will depend on the primary beam energy used for the analysis and also the composition of the specimen. It is the latter, matrix, effect that has prevented the production of a series of AES sensitivity factors of the type widely used for XPS. Instead, it is necessary to fabricate binary or ternary alloys and compounds of the type under investigation to provide calibration by means of a similar Auger spectrum; however, the sensitivity factors (SF) produced have a narrow range of applicability. It is possible to determine the concentration of an element of interest (N_A) as follows:

$$[A] \text{ atomic \%} = \{(I_A/SF_A)/\Sigma(I/SF)\} \times 100\%$$

DEPTH PROFILING BY EROSION WITH NOBLE GAS IONS

To obtain data from depths greater than 10nm it is necessary to remove material by ion bombardment within the spectrometer. The primary process is that of sputtering surface atoms to expose underlying atomic layers. At the same time, some of the primary ions are implanted into the substrate and will appear in subsequent spectra. Atomic mixing results from the interaction of the primary ion beam with the specimen and leads to a degradation of depth resolution. Enhanced diffusion and segregation

may also occur and will have the same effect. During sputtering process there may be preferential sputtering of particular type of ion or atom. Ion-induced reactions may occur; for instance copper (II) is reduced to copper (I) after exposure to a low- energy low-dose ion beam. As more and more material is removed so the base of the etch crater increases in roughness and eventually interface definition may become very poor indeed.

A high-quality vacuum is essential if a good depth profile is to be measured. If there are high partial pressures of reactive impurities present the surface which is analysed may not reflect the material composition. Oxygen, water and carbonaceous materials are common contaminants. For this reason the gas feed to the ion gun must be free from impurities.

The experimental procedure used to obtain a depth profile begins with an analysis of the undisturbed surface using either XPS or AES. The sample then undergoes a period of Sputtering (ion etching) using ions whose energy is in the range of a few hundred to a few thousand eV. Following this, the ion beam is then switched off (blanked) and the sample is analysed again. This process is continued until the required depth is reached.

The current density profile of an ion beam is generally not uniform. Such a beam cross-section would produce a crater in the sample which does not have a fiat bottom. Poor depth resolution would result from extracting data from such a crater. To overcome this difficulty, the ion beam is usually scanned or rastered over an area which is large with respect to the diameter of the beam. Rastering produces a crater which has a flat area at the centre from which compositional data can be obtained. Figure 12 is XPS depth profile through a layer of tantalum oxide on tantalum metal. There are many points to bear in mind when selecting the experimental conditions for a depth profile. Most of these are concerned with either the speed of acquisition or the depth resolution.

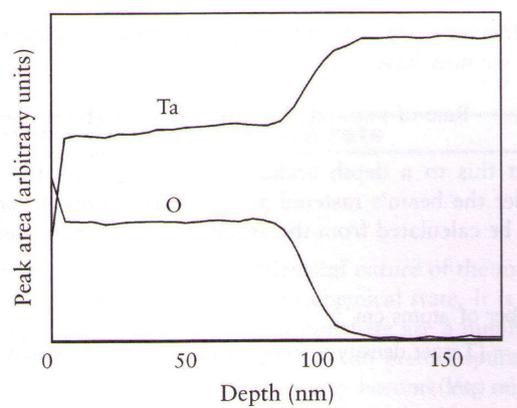


Figure 127 XPS depth profile through a tantalum oxide layer grown on tantalum metal.

Sputter yield and etch rate

The sputter yield is the physical property which determines the rate at which material is removed from the sample during bombardment by energetic ions.

Factors affecting the etch rate

The sputter rate depends upon the chemical nature of the material, not only the elements present but also their chemical state. It is usually preferable to measure the sputter yield experimentally under the conditions normally employed.

-Ion current The etch rate is directly proportional to the ion current. It is possible to increase the etch rate by using the maximum beam current available.

-Ion energy The sputter yield increases with ion energy. Higher energies also mean smaller spot sizes at a given beam current and so will lead to better crater quality. The higher etch rate will be accompanied by poorer depth resolution because the ions can penetrate deeper into the material causing atomic mixing.

-Nature of the ion beam In XPS and Auger profiling, it is customary to use the ions of the noble gases for sputtering, **in practice Ar is the gas which is selected.**

ION GUN DESIGN

Ion guns based on the electron impact source are very popular for depth profiling applications in XPS and AES. In this type of source, electrons from a heated filament are accelerated into a cylindrical grid where they collide with gas atoms, giving rise to the formation of ions. The ions are then extracted from the ionization region. The kinetic energy of the ions is controlled by the magnitude of the potential applied to the grid (up to 5kv). This ion source produces a small energy spread with only a small fraction of neutrals (i.e., unionized atoms) present in the beam. Spot sizes commercially available vary from 2mm down to 50 μ m. The beam can usually be scanned (rastered) over the surface to produce high-quality craters. A schematic diagram of a typical ion gun of this type is shown in Figure 13

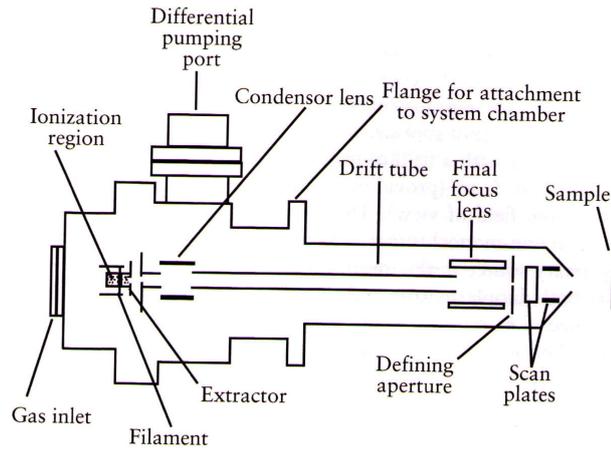


Figure 13 Schematic diagram of a typical ion gun with electron impact source

COMPARISON OF XPS AND AES

The major strength of XPS as an analytical technique is its chemical specificity. It means the ability to define not only the elements present in the analysis but also the chemical state. XPS is usually regarded as an area averaging technique. Small area XPS is available on most modern instruments and, when operating in this mode, a spectroscopic spatial resolution of about $10 \sim \mu\text{m}$ is possible. Many modern instruments offer imaging XPS and such imaging may have a spatial resolution of $<3 \sim \mu\text{m}$. Set beside a spatial resolution of 10 to 15 nm which can be achieved on the latest commercial Auger microprobes, it becomes clear that the XPS is not the way to proceed for surface analysis at very high spatial resolution, but the advantages of the levels of information available from an XPS analysis (the ease with which a quantitative analysis can be achieved, its applicability to insulators, and the ready availability of chemical state information) will often offset this.