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Spectroscopy

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Spectroscopic Techniques for the Characterization of Nanostructures

- **Surface sensitive spectroscopies**
  - X-Ray photoelectron spectroscopy (XPS)
  - Auger Electron Spectroscopy (AES)
  - Vibrational Spectroscopies

- **Spectroscopies with good spatial resolution** (e.g. in an electron microscope)
  - Energy-dispersive X-ray spectroscopy (EDX or EDS)
  - Auger Electron Spectroscopy (AES)
  - Electron energy loss spectrometry (EELS)

Electron Spectroscopies

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Suggested readings

MATERIALS CHARACTERIZATION 25:37–71 (1990) 37

Quantitative Surface Microanalysis by Auger and X-ray Photoelectron Spectroscopy

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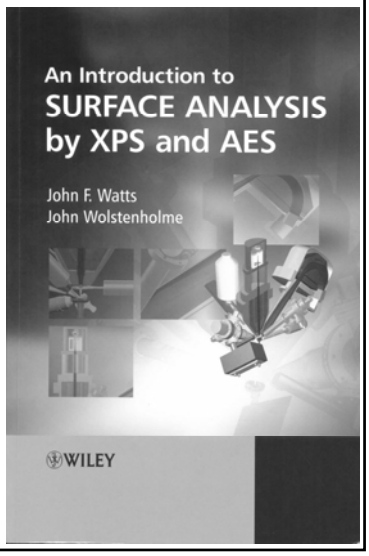
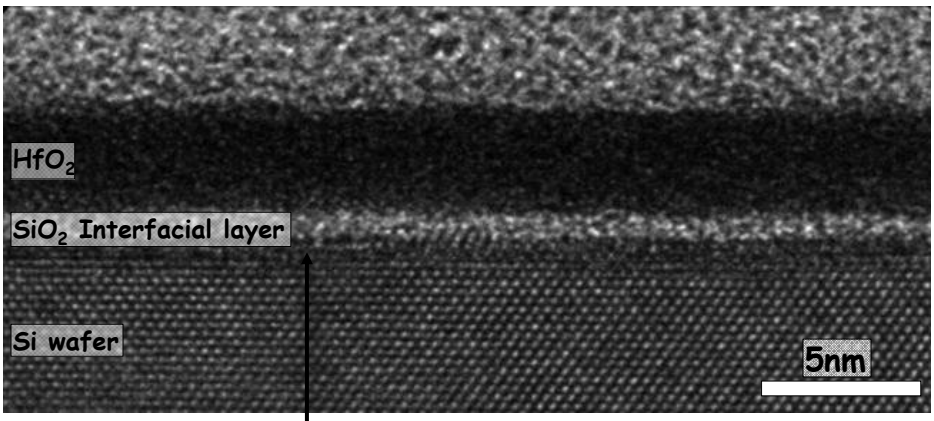
All materials and structures interact with their environment through surfaces, and consequently the importance of surface as opposed to bulk analysis is increasingly recognized in the design and development of advanced materials. Electron spectroscopic methods such as Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) have the capability for microanalysis of the top few atom layers of solid samples. Traditionally, AES uses electron beam excitation, with correspondingly high spatial resolution, but was thought to give only limited chemical state information, whereas XPS was used for surface chemical analysis at an early stage of its development but with poor spatial resolution. Recent developments in both theory and instrumentation tend to blur this distinction, with chemical information available from AES together with a trend in XPS toward microarea analysis and, lately, imaging. In this article, the two techniques are compared and contrasted, with an emphasis on their microanalytical capability and potential for full quantification. Examples are taken from various areas of metallurgy and materials science.



XPS spectrum of a thin layer (~4 nm) of HfO_2 onto Si/SiO_2



Substrate Thickness: ~ 0.5 mm

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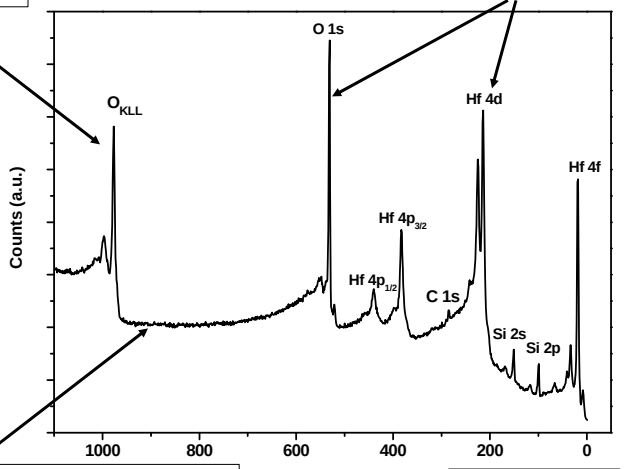
Auger process

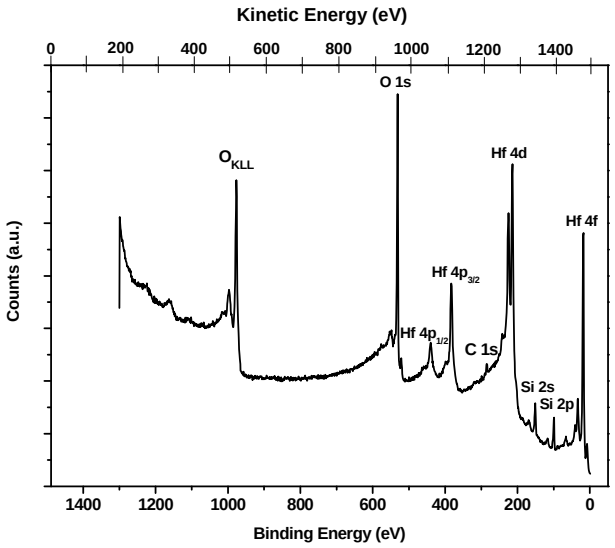
Peaks due to photoemitted electrons



Background: Secondary electrons inelastically scattered before they escape from the surface

Kinetic energy

Source Al Kα 1486.6 eV



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Surface Sensitive Spectroscopies

1. Sensitivity Problems

The problems of sensitivity and detection limits are common to all forms of spectroscopy.
Some techniques are simply better than others in this respect.

Is it possible to detect the desired signal above the noise level?

In surface studies the sensitivity is a major problem.
A sample with a surface of 1 cm^2 will have around 10^{15} atoms in the surface layer.
It should be compared to bulk samples (1 cm^3 correspond to around 10^{22} atoms)

Therefore, there are spectroscopic techniques that cannot be applied to the study of surfaces. (e.g. NMR)

2. Surface "Sensitivity" or "Specificity"

Even though a technique is sensitive enough for detecting a signal from surface species, the major problem is to distinguish between the signal arising from the surface and the bulk of the sample.

This can be solved by ensuring that the signal due to the bulk is small compared to the signal due to the surface species.

→ The technique is: Surface Sensitive

Techniques that have such a property are for example the ones that make use of low energy electrons

- Auger Electron Spectroscopy (AES)
- X-ray Photoelectron Spectroscopy (XPS)

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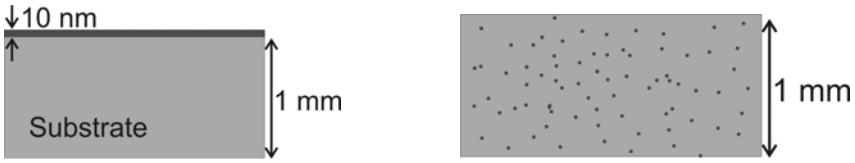
The large majority of the techniques used in chemistry are "bulk" techniques. i.e. they measure all the atoms within a typical sample

The typical problem in surface analysis consist in analyzing the property of a sample made of a few nm thick layer of a material deposited on a substrate (of a thickness generally around 1 mm)



If the material constituting the surface layer of 10 nm was homogeneously distributed in the bulk (substrate) it would correspond to a concentration of 10 ppm.

A surface sensitive technique is more sensitive to those atoms which are located at or near to the surface.

Therefore, the intensity of the signal arising from the surface is more pronounced than the one arising from the bulk

→ $I_{surface} / I_{bulk} >> 10^{-5}$

The signal measured from a truly surface specific technique should be due to atoms in the "surface region".

XPS as other electron spectroscopy techniques is not a truly surface specific due to the fact that even though the signal mainly arise from first few atomic layers a part of the signal comes from deeper regions.

→ Why XPS is surface sensitive?

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Why XPS and AES are surface sensitive?

The X-rays employed in XPS and AES (aluminum Kα 1486.7 eV) penetrate relatively deeply into the sample (~μm).

Therefore, it is not the excitation method that makes the XPS technique surface sensitive!

In the XPS spectrum the observed peaks are due to photoelectrons that are generated in the immediate surface layer.

Because the distance an electron can travel in a solid without suffering inelastic scattering is only few nm.

This property of the electrons makes XPS surface sensitive

The inelastic mean free path (IMFP) is a measure of the average distance travelled by an electron through a solid before it is inelastically scattered

The IMFP depends on:
- The initial kinetic energy of the electron
- The nature of the solid

In the energy range 30-100 eV the IMFP is lower than 1 nm for metals!

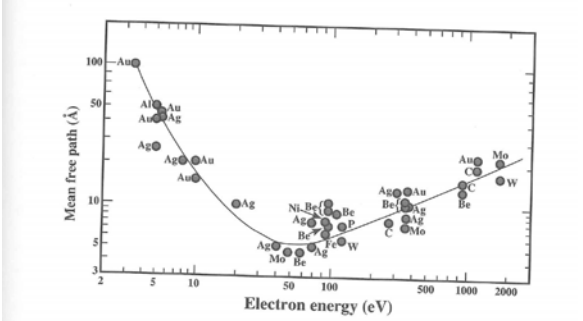

Figure 8.3 Attenuation length for electrons detected normal to the surface for a variety of different solids as a function of their energy. Note the broad minimum in the range 10–500 eV that corresponds to just a few atomic layers. (Courtesy of L.C. Feldman and J.W. Mayer, Fundamentals of Surface and Thin Film Analysis, *Elsevier Science Publishing Co.*).

For insulators IMFP can reach few nanometers in this energy range

Typical values of λ for scattering at TEM voltages are of the order of tens of nm.

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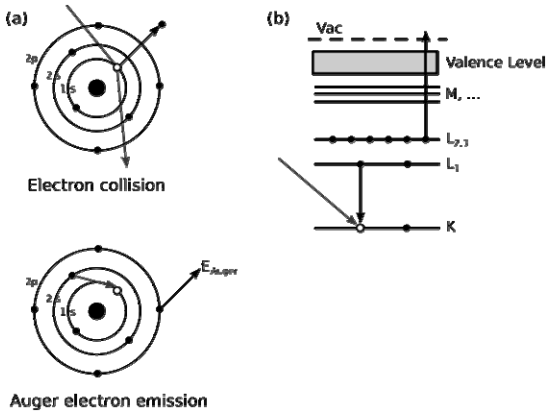
Auger Effect

The Auger effect is a phenomenon in physics in which the transition of an electron in an atom filling in an inner-shell vacancy causes the emission of another electron.

When an electron is removed from a core level of an atom, leaving a vacancy, an electron from a higher energy level may fall into the vacancy, resulting in a release of energy. Although this energy can be released in the form of an emitted photon (X-ray fluorescence), the energy can also be transferred to another electron, which is ejected from the atom. This second ejected electron is called an Auger electron.

Upon ejection the kinetic energy of the Auger electron corresponds to the difference between the energy of the initial electronic transition and the ionization energy for the electron shell from which the Auger electron was ejected. These energy levels depend on the type of atom and the chemical environment in which the atom was located. Auger electron spectroscopy involves the emission of Auger electrons by bombarding a sample with either X-rays or energetic electrons and measures the intensity of Auger electrons as a function of the Auger electron energy. The resulting spectra can be used to determine the identity of the emitting atoms and some information about their environment.



Two views of the Auger process. (a) illustrates sequentially the steps involved in Auger deexcitation. An incident electron creates a core hole in the 1s level. An electron from the 2s level fills in the 1s hole and the transition energy is imparted to a 2p electron which is emitted. The final atomic state thus has two holes, one in the 2s orbital and the other in the 2p orbital. (b) illustrates the same process using spectroscopic notation, $KL_1L_{2,3}$.

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The Kinetic Energy (KE) of this process can be roughly estimated:

$$KE = E_{K\,L_1\,L_{2,3}} = (E_K - E_{L1}) - E_{L2,3}$$

The KE of the Auger electron is independent of the filling mechanism of the first core hole.

It could be the electron from the E_{L1} or $E_{L2,3}$

It is impossible to say which electron fills the initial core hole and which is ejected as an Auger electron: they are indistinguishable.

If one considers these 3 levels only there are 3 possible Auger transitions

$K\,L_1\,L_1$	$K\,L_1\,L_{2,3}$	$K\,L_{2,3}\,L_{2,3}$

Notation: the initial hole location is given first, followed by the locations of the final two holes in order of decreasing binding energy.

Ex: What is the Auger electron having the larger kinetic energy?

$K L_1 L_1$	$K L_1 L_{2,3}$	$K L_{2,3} L_{2,3}$

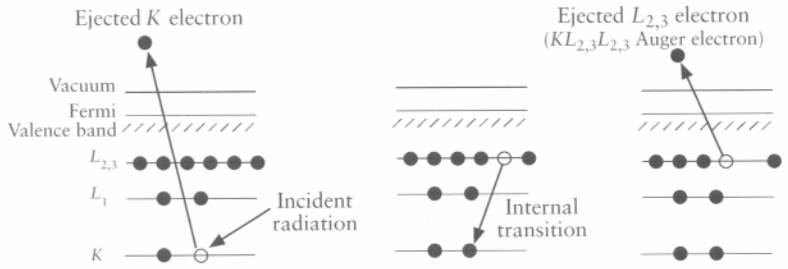

Figure 1.4 Relaxation of the ionized atom of Figure 1.2 by the emission of a $KL_{2,3}L_{2,3}$ Auger electron

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The equation of the kinetic energy does not take into account the interaction energies between the core holes in the final atomic state nor the inter- and extra-relaxation energies which come about as a result of the additional core screening needed

→ The calculation of the energy of Auger electron transitions is much more complicated that the simple relation given above

There is a simple and satisfactory empirical approach which consist in considering the energies of the atomic levels involved and those of the next element in the periodic table

$$E_{KL_1L_{2,3}}(Z) = E_K(Z) - \frac{1}{2}\left[E_{L_1}(Z) + E_{L_1}(Z+1)\right] - \frac{1}{2}\left[E_{L_{2,3}}(Z) + E_{L_{2,3}}(Z+1)\right]$$

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a quantitative surface spectroscopic technique that measures the elemental composition, chemical state and electronic state of the elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy (KE) and number of electrons that escape from the top 1 to 10 nm of the material being analyzed.

XPS is also known as **ESCA**, an abbreviation for **Electron Spectroscopy for Chemical Analysis**.

XPS detects all elements with an atomic number (Z) of 3 (lithium) and above. It cannot detect hydrogen ($Z = 1$) or helium ($Z = 2$).

XPS requires ultra high vacuum (UHV) conditions.

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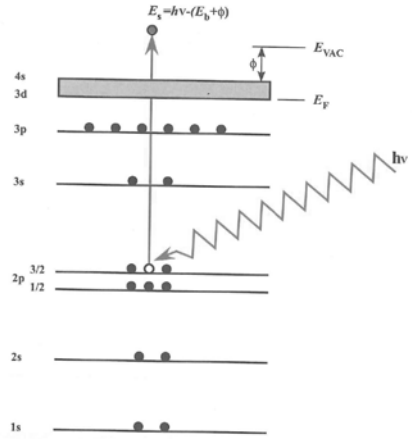
Photoelectric Effect

The energy carried by an incoming X-ray photon is absorbed by the target atom raising it to an excited state from which it relaxes by emission of a photoelectron with kinetic energy equal to the difference between the incident X-ray energy, the binding energy of the level concerned and the work function.



Φ: workfunction of the material

E_s: kinetic energy

E_b: binding energy

hν: incident photon energy

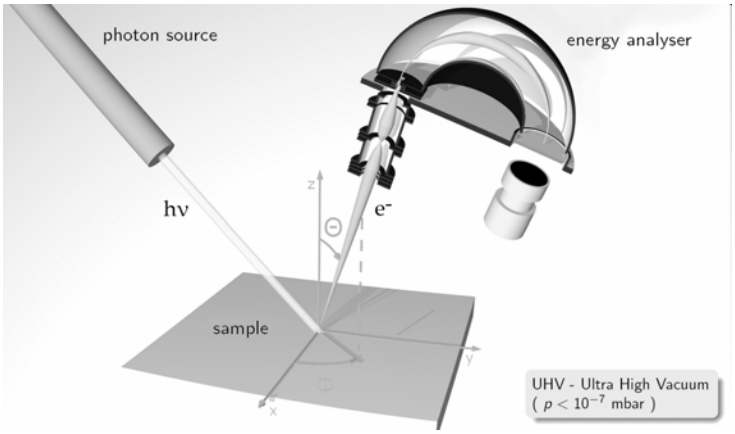
A 2p photoelectron is emitted from copper as the result of the excitation by absorption of an X-ray photon

Experimental Setup (XPS - AES)

Electron spectrometers are based on systems designed to operate in the ultra-high vacuum range (UHV) (10^{-8} – 10^{-10} mbar)

- Low energy electrons are easily scattered by the residual gas molecules.

- At higher pressures gas molecules rapidly adsorb onto the solid surface



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The sample should be stable under UHV conditions

The sample should also be conductive enough (especially for AES where an electron source is generally used -> same requirement as for SEM except that the sample, in order to avoiding charging problems cannot be coated by a conductive material as in SEM)

XPS – the x-ray sources most commonly used in XPS are the Al Kα and Mg Kα providing photon energies of 1486.6 and 1253.6 eV, respectively

Additional X-ray sources can be used such as the tunable radiation obtained in synchrotrons

It is interesting to modify the photon energy for mainly 3 reasons:

- Distinguish between photoelectrons and Auger electrons

- Energy levels that are not accessible by conventional X-ray sources become accessible by employing higher energy

- Tuning the incident energy permits to increase or decrease the kinetic energy of the photoelectron. -> Possibility to modify the surface sensitivity

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

The cylindrical mirror analyzer (CMA) and the hemispherical sector analyzer

The cylindrical mirror analyzer is historically the first analyzer developed for AES spectroscopy.

It is characterized by high sensitivity but poor resolution and, therefore does not permit chemical analysis

The CMA consists of two concentric cylinders. The inner one is held at earth potential while the outer is ramped at a negative potential

A certain portion 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 can then be detected.

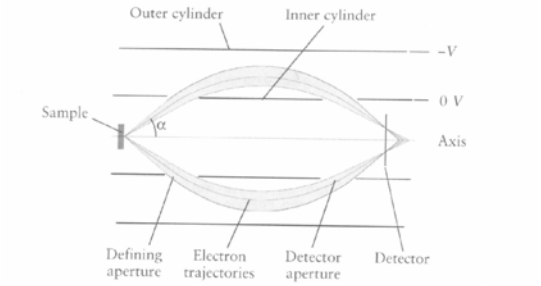

Figure 2.7 Schematic diagram of the cylindrical mirror analyser (CMA)

As the detected electrons are not only Auger electrons an intense background is observed

The Auger peaks are weak features superimposed on an intense background

Therefore, the differential energy spectrum is often plotted rather than the direct spectrum

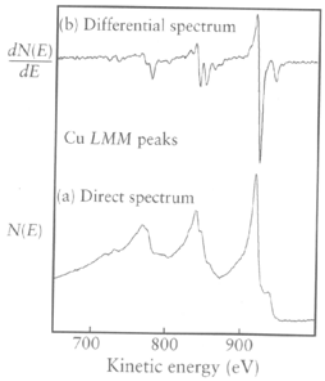

Figure 2.8 Comparison of (a) direct, and (b) differential Auger spectra for copper

The need for high energy resolution led to the development of the hemispherical sector analyzer (HSA)

It consists of a pair of concentric hemispherical electrodes between which there is a gap for the electron to pass

The potential applied between the two electrodes permits to select the electrons that will reach the detector

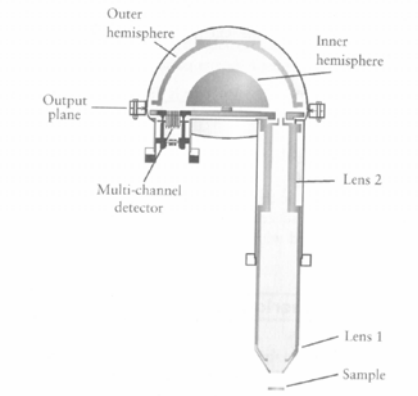

Figure 2.9 Schematic diagram of a modern HSA and transfer lens

Electrons will only be detected if their energy is given by:

$$E = e\Delta V\left(\frac{R_1 R_2}{R_2^2 - R_1^2}\right)$$

E is the kinetic energy of the photoelectrons, e is the charge of the electron, ΔV is the potential difference and R_1 and R_2 are the radii of the inner and outer hemispheres, respectively

Electrons those energy is higher than that given in the expression above will follow a path whose radius is larger than the mean radius of the analyzer

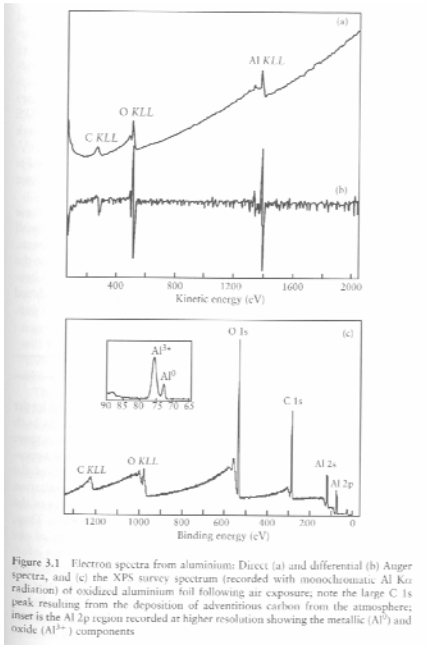

Figure 3.1 Electron spectra from aluminium: Direct (a) and differential (b) Auger spectra, and (c) the XPS survey spectrum (recorded with monochromatic Al Kα radiation) of oxidized aluminium foil following air exposure; note the large C 1s peak resulting from the deposition of adventitious carbon from the atmosphere; inset is the Al 2p region recorded at higher resolution showing the metallic (Al^0) and oxide (Al^{3+}) components

The use of different photon energies permits to differentiate between Auger and photoelectron transitions!

XPS peaks will change to a position 233 eV higher on a kinetic energy scale on switching from Mg Kα to Al Kα

On the other hand, the energy of the Auger transitions remains constant

On a binding energy scale, of course, the reverse is true

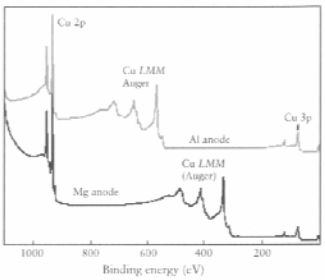

Figure 2.2 Comparison of XPS spectra recorded from copper using AlKα (upper) and MgKα (lower) radiation; note that on a binding energy scale the XPS peaks remain at constant values but the X-AES transitions move by 233 eV on switching between the two sources

Table 2.1 Possible anode materials for XPS

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

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Qualitative and quantitative analysis

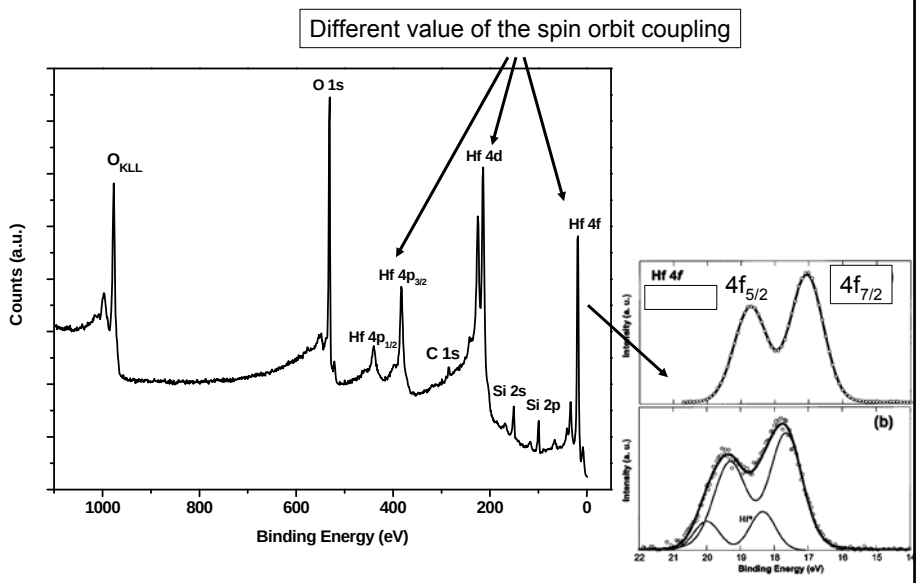
The relative intensity of the components of doublets formed by the spin orbit coupling is dependent upon their relative populations (degeneracies) which are given by the expression (2j+1)

Ex: for an electron from a *p* orbital, the relative intensities of the 1/2 and 3/2 peaks are 1:2

The spacing between the components of the doublets depends upon the strength of the spin-orbit coupling

For a given value of both *n* and /the separation increases with the atomic number of the atom

For a given atom, it decreases with both increasing *n* and /



Chemical shift

In XPS the chemical shift refers to small changes in electron energy that are the results of the chemical environment of the emitting atom

The XPS chemical shift is probably the most important feature of the technique

Almost all elements in the periodic table exhibit a chemical shift, which can vary from a fraction of an electron volt up to several eVs.

Data processing by fitting the high resolution XPS spectra is often required for extracting information on the different chemical environments of an atom

The origin of the chemical shift is attributed to the charge of the atom prior to photoemission. It plays the major role in the determination of the magnitude of the chemical shift

As a general rule, more the emitting atom forms bonds with electronegative species, greater is the positive XPS chemical shift

Ex: Chemical shift for carbon species (e.g. in polymers)

C-O	1.6 eV
C=O	2.9 eV
O-C-O	2.9 eV

C-F	2.9 eV
$C-F_2$	5.9 eV
$C-F_3$	7.7 eV

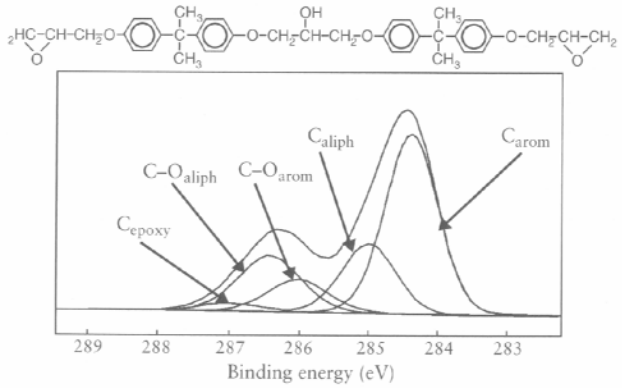


Figure 3.2 C 1s spectrum of the basic building block of epoxy product, the diglycidyl ether of bisphenol A, the structure of which is shown above the spectrum; this spectrum was recorded using monochromatic Al radiation

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Chemical Information (XPS)

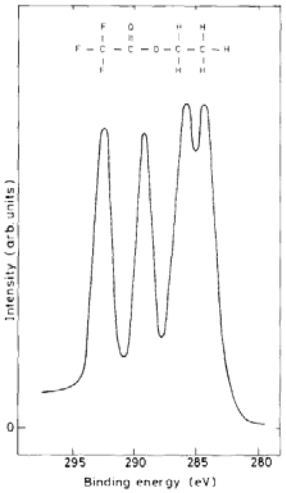

FIG. 4. Showing the change in energy of the carbon 1-s photoelectron peak as the bonding state of the atom changes. The spectrum, taken from Siegbahn et al. [2], is from the molecule shown in the figure with the energy scale adjusted so that peaks are aligned with the corresponding emitting atom. Reprinted by permission of the author.

MATERIALS CHARACTERIZATION 25:37–71 (1990)

Figure 5 shows data taken from the XPS handbook [4] for the 2p emission line of titanium in both the pure and the oxide state. The titanium $2p_{1/2}$ and $2p_{3/2}$ peaks are well resolved. with a separation of around 6 eV. A clear shift of approximately 4 eV to higher binding energy is observed on oxidation. together with a small reduction in the doublet separation.

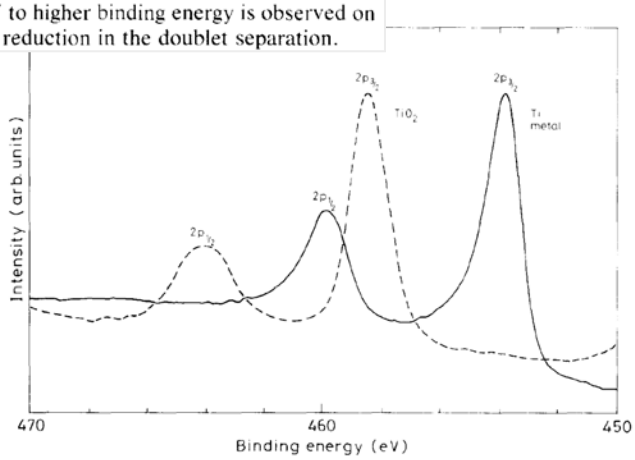

FIG. 5. Showing the shift to higher binding energy of the Ti photoelectron peak on oxidation to TiO_2. The dashed line represents the spectrum for the metal in the oxidized state (from Wagner et al. [4]). Reprinted by permission of Perkin Elmer (Physical Electronics Division).

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Deconvolution (peak fitting) of the XPS signals

In XPS it is possible to deconvolute the complex signal that is the result of the different chemical environment of the emitting atom

Sadly, while central to XPS, peak fitting of line-shapes to spectra is far from simple

The problem is that a good fit is always achieved by a sufficient number of Gaussian-Lorentzian curves when optimized without constraints

Understanding the chemistry is important as it suggests the number of chemical states and therefore number of peaks, introducing parameter constraints to restrict the peak widths and relative intensities of the peaks force the peak model to obey the chemistry

Without these inputs any model designed purely on the spectral envelope would be a cause for concern

When peak-fitting XPS spectra a further issue is the nature of the background signal on top of which the peaks must sit

Core level electrons ejected by x-rays appear in spectra with a variety of shapes. These shapes arise due to a combination of the physics involved in the ionization process and also distortions due to the measurement mechanism.

An idealization of these influences is the specification of an observed peak as a convolution of a Gaussian and Lorentzian function; where in principle the Gaussian described the measurement process (instrumental response, x-ray line-shape, Doppler and thermal broadening) while the Lorentzian models the lifetime broadening (Natural broadening) due to the uncertainty principle relating lifetime and energy of the ejected electrons.

Ref: Manual of a fitting program that explain in detail the challenges in peak fitting in XPS and the various parameters that have to be taken into account: http://www.casaxps.com/help_manual/manual_updates/peak_fitting_in_xps.pdf

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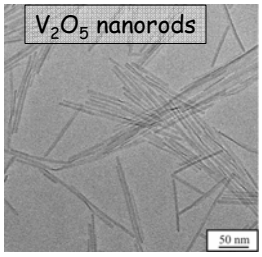
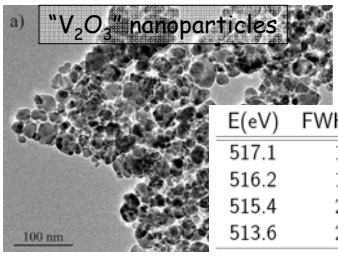
Vanadium oxide nanoparticles

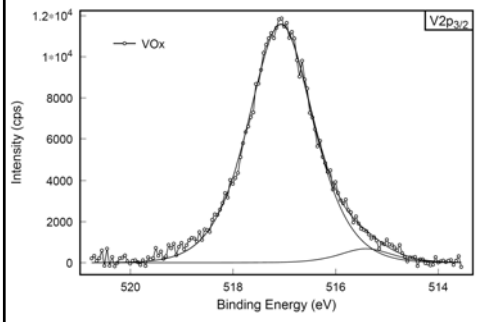
V_2O_5 nanorods

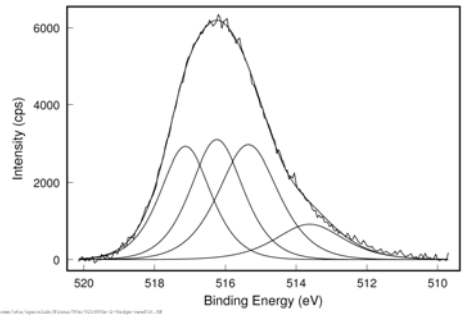


"V_2O_3" nanoparticles



E(eV)	FWHM(eV)	%
517.1	1.87	27.0
516.2	1.94	29.7
515.4	2.20	32.1
513.6	2.50	11.2





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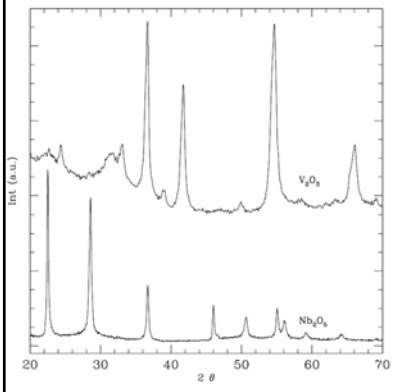
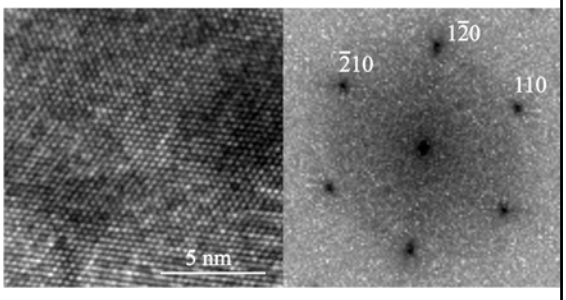
Vanadium oxide nanoparticles

"V_2O_3" nanoparticles





Chemical Information (AES)

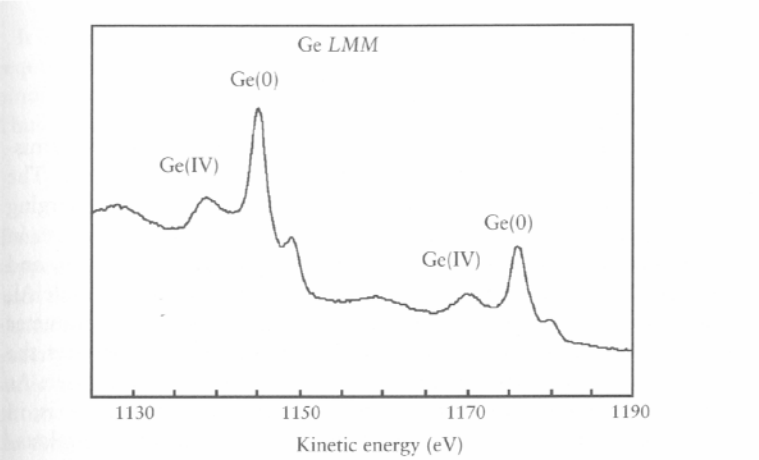


Figure 3.3 Auger chemical state information for a germanium single crystal with a thin layer of oxide

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Quantification in XPS

In order to quantify spectra in XPS one must convert peak areas to atomic concentrations

Main factors affecting the quantification of XPS spectra:

1 – Photoelectron cross section – probability of the emission of an electron due to the incoming X-ray photons

2 - The kinetic energy of the photoelectrons (the mean free path is a function of the kinetic energy)

3 – Spectrometer related factors such as transmission function of the spectrometer and the efficiency of the detector

The intensity (I) of a photoelectron peak from an homogeneous solid is given by:

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

J is the photon flux, ρ is the concentration of the atom, σ is the cross section for photoelectron production, K is a term which covers the instrumental factors and λ is the mean free path.

This equation cannot be easily used directly

Usually sensitivity factors (F) are determined experimentally

The sensitivity factors already include the terms σ, K and λ

Once a set of peak areas has been calculated for the element detected, I in the equation above has been determined

The atomic percentage of the elements concerned is determined by dividing the peak area by the sensitivity factor:

$$[A]\ atomic\ \% = \left(\frac{I_A/F_A}{\sum(I/F)}\right) \times 100\%$$

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

For a more rigorous analysis, angular dependent XPS may be employed to elucidate the hierarchy of the overlayers present

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Inelastic mean free path

$$P(x+dx) = P(x) + \frac{dP(x)}{dx}dx = P(x)\left(1 - \frac{dx}{\lambda}\right)$$

$$\frac{dP(x)}{dx} = -\frac{1}{\lambda}P(x) \quad \xrightarrow{\text{Integration}} \quad P(x) = e^{-\frac{x}{\lambda}}$$

This relation permits to estimate the depth from where the electron emitted can be detected for a take off angle θ=0° (i.e. normal to the surface)

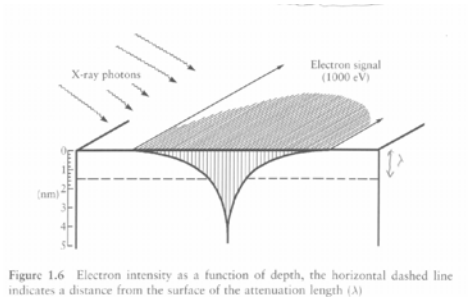

Figure 1.6 Electron intensity as a function of depth, the horizontal dashed line indicates a distance from the surface of the attenuation length (λ)

We already calculated these probabilities:

P(1λ) = exp (-x/λ) = exp (-1) = 0.368

P(2λ) = exp (-x/λ) = exp (-2) = 0.135

P(3λ) = exp (-x/λ) = exp (-3) = 0.050

In order to increase the surface sensitivity we can record spectra at high take-off angle relative to the sample normal.

In this case we can modify the probability calculated before as:

$$P(x) = e^{-\frac{x}{\lambda cos\theta}}$$

3λ is often referred to as the XPS analysis depth. It should be replaced by $3\lambda\, cos\theta$ when the take off angle is not zero.

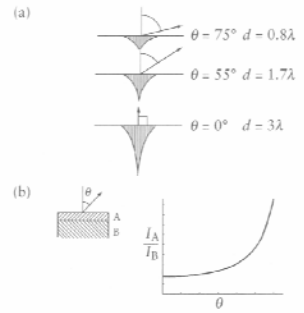

Figure 4.1 Angular electron emission: (a) sampling depth as a function of electron take-off angle (θ) – the width of the shaded areas represent the proportion of the detected electrons emitted as a function of depth; (b) overlayer (A)/substrate (B) and intensity (I) versus θ

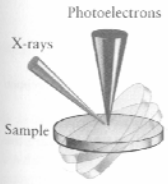

Figure 4.2 Conventional ARXPS, using sample tilting

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Angular resolved XPS: Tuning the surface sensitivity

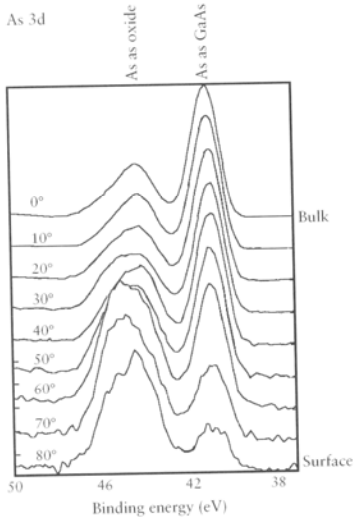
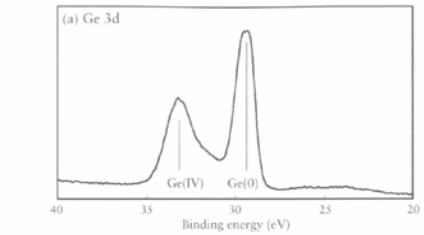
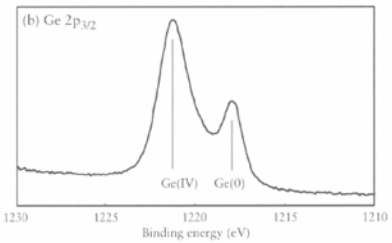


Figure 4.3 ARXPS data acquired by tilting the specimen; in this case the specimen is gallium arsenide

Different kinetic energy: tuning the surface sensitivity





	Kinetic energy	Attenuation length
Ge 3d	1453 eV	2.8 nm
Ge $2p_{3/2}$	264 eV	0.8 nm

Figure 4.10 Ge 3d and Ge $2p_{3/2}$ spectra showing variation of sampling depth with electron kinetic energy

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Spatial Resolution

XPS is characterized by a poor spatial resolution.

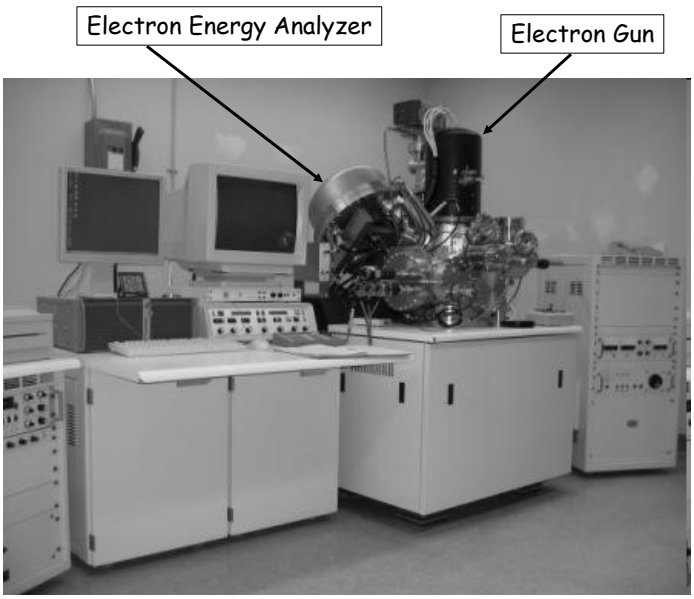
This is due to the fact that incident X-rays are difficult to be focused and scanned.

By using electrons as excitation source it is possible to achieve a high spatial resolution (e.g. under an electron microscope)

Therefore, Auger electrons can be used for the chemical analysis of surfaces with resolution at the nanoscale

Scanning Auger Microscopy (SAM) enables images of the elements in the near surface layer of conducting samples to be acquired. SAM is a combination of the techniques of SEM and AES. An electron beam is scanned over the surface and the electrons excited from the surface are energy analyzed to detect Auger peaks. The intensity of the Auger peaks as a function of the position of the electron beam provides an image of the element to which the Auger peak corresponds. As for AES, the near surface layer typically means the first 2 or 3 atomic layers of the surface.

SEM equipped with an electron energy analyzer



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23450 J. Phys. Chem. B 2006, 110, 23450−23459

High-Resolution Soft X-ray Photoelectron Spectroscopic Studies and Scanning Auger Microscopy Studies of the Air Oxidation of Alkylated Silicon(111) Surfaces

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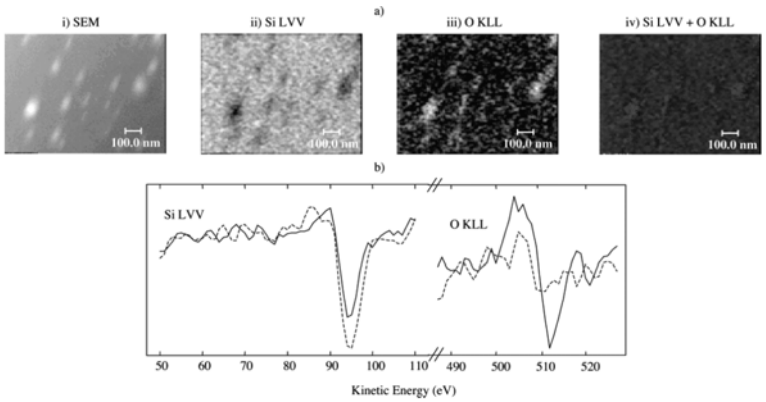
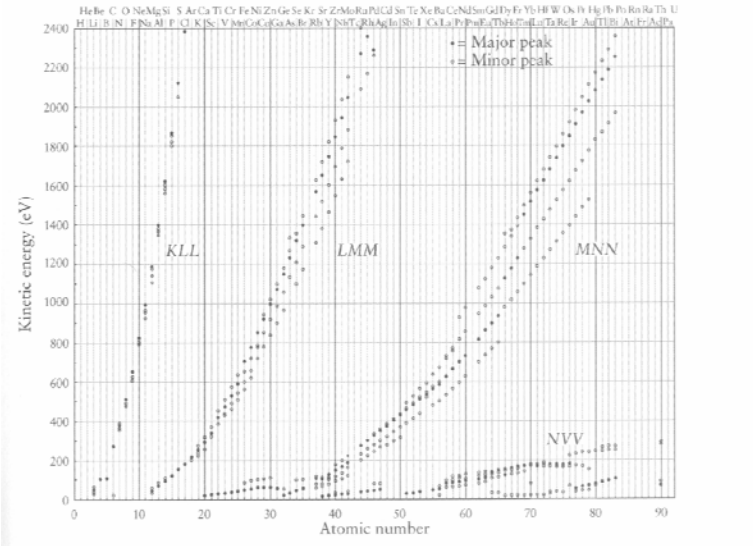


Figure 8. Auger electron spectroscopy of a C_2H_5-terminated Si(111) surface exposed to air for 8 days. (a) SAM images of a ~1 μm^2 area of the surface: (i) SEM image of the surface; (ii) SAM image collected by scanning in the Si LVV energy region (92 eV) (lighter gray indicates a greater Si signal); (iii) SAM image collected by scanning in the O KLL energy region (510 eV) (lighter gray indicates a greater O signal); (iv) composite SAM image of the overlayed maps of the Si LVV (red) and O KLL (blue) energy regions. SAM images were collected in 128 × 128 point scans with an electron beam held at 20 kV and 10 nA with a spatial resolution of 15 nm. The individual pixels were then combined to form an image map. (b) AES spectra of a point on an isolated white discolored region in the SEM image (solid line) and of a point on the dark background in the SEM image (dashed line).

Appendix 1: Auger Electron Energies



Appendix 2: Table of Binding Energies Accessible with AlKα Radiation

	1s* K	2s1/2 L1	2p1/2 LII	2p3/2* LIII	3s1/2 MI	3p1/2 MII	3p3/2 MIII	3d3/2 MIV	3d5/2* MV	4s1/2 NI	4p1/2 NII	4p3/2 NIII	4d3/2 NIV	4d5/2 NV	4f5/2 NVI	4f7/2* NVII	5s1/2 OI	5p1/2 OII	5p3/2 OIII	5d3/2 OIV	5d5/2 OV
1 H	14																				
2 He	25																				
3 Li	55																				
4 Be	111																				
5 B	188			5																	
6 C	284			7																	
7 N	399			9																	
8 O	532	24		7																	
9 F	686	31		9																	
10 Ne	867	45		18																	
11 Na	1072	63		31	1																
12 Mg	1305	89		52	2																
13 Al		118	74	73	1																
14 Si		149	100	99	8	3															
15 P		189	136	135	16	10															
16 S		229	165	164	16	8															
17 Cl		270	202	200	18	7															
18 A		320	247	245	25	12															
19 K		377	297	294	34	18															
20 Ca		438	350	347	44	26			5												
21 Sc		500	407	402	54	32			7												
22 Ti		564	461	455	59	34			5												
23 V		628	520	513	66	38			2												
24 Cr		695	584	575	74	43			2												
25 Mn		769	652	641	84	49			4												
26 Fe		846	723	710	95	56			6												
27 Co		926	794	779	101	60			3												
28 Ni		1008	872	855	112	68			4												
29 Cu		1096	951	931	120	74			2												
30 Zn		1194	1044	1021	137	87			9												
31 Ga		1298	1143	1116	158	107	103		18			1									
32 Ge		1413	1249	1217	181	129	122		29			3									
33 As			1359	1323	204	147	141		41			3									
34 Se					232	168	162		57			6									
35 Br					257	189	182	70	69	27		5									
36 Kr					289	223	214	89		24		11									
37 Rb					322	248	239	112	111	30	15	14									
38 Sr					358	280	269	135	133	38		20									
39 Y					395	313	301	160	158	46		26		3							
40 Zr					431	345	331	183	180	52		29		3							
41 Nb					469	379	363	208	205	58		34		4							
42 Mo					505	410	393	230	227	62		35		2							
43 Tc					544	445	425	257	253	68		39		2							

	6s1/2 P1	6p1/2 PII	6p3/2 PIII	6d3/2 PIV	6d5/2 PV
82 Pb	3		1		
83 Bi	8		3		
84 Po	12		5		
85 At	18		8		
86 Rn	26		11		
87 Fr	34		15		
88 Ra	44		19		
90 Th	60	49	43	2	2

		$3s_{1/2}$ M_I	$3p_{1/2}$ M_{II}	$3p_{3/2}$ M_{III}	$3d_{3/2}$ M_{IV}	$3d_{5/2}$* M_V	$4s_{1/2}$ N_I	$4p_{1/2}$ N_{II}	$4p_{3/2}$ N_{III}	$4d_{3/2}$ N_{IV}	$4d_{5/2}$ N_V	$4f_{5/2}$ N_{VI}	$4f_{7/2}$* N_{VII}	$5s_{1/2}$ O_I	$5p_{1/2}$ O_{II}	$5p_{3/2}$ O_{III}	$5d_{3/2}$ O_{IV}	$5d$ O_V
44	Ru	585	483	461	284	279	75	43		2								
45	Rh	627	521	496	312	307	81	48		3								
46	Pd	670	559	531	340	335	86	51		1								
47	Ag	717	602	571	373	367	95	62	56	3								
48	Cd	770	651	617	411	404	108	67		9					2			
49	In	826	702	664	451	443	122	77		16					1			
50	Sn	884	757	715	494	485	137	89		24				1	1			
51	Sb	944	812	766	537	528	152	99		32				7	2			
52	Te	1006	870	819	582	572	168	110		40				12	2			
53	I	1072	931	875	631	620	186	123		50				14	3			
54	Xe	1145	999	937	685	672	208	147		63				18	7			
55	Cs	1217	1065	998	740	726	231	172	162	79	77			23	13	12		
56	Ba	1293	1137	1063	796	781	253	192	180	93	90			40	17	15		
57	La	1362	1205	1124	849	832	271	206	192		99			33		15		
58	Ce	1435	1273	1186	902	884	290	224	208		111		1	38		20		
59	Pr		1338	1243	951	931	305	237	218		114		2	38		23		
60	Nd		1403	1298	1000	978	316	244	225		118		2	38		22		
61	Pm			1357	1052	1027	331	255	237		121		4	38		22		
62	Sm			1421	1107	1081	347	267	249		130		7	39		22		
63	Eu				1161	1131	360	284	257		134		0	32		22		
64	Gd				1218	1186	376	289	271		141		0	36		21		
65	Tb				1276	1242	398	311	286		148		3	40		26		
66	Dy				1332	1295	416	332	293		154		4	63		26		
67	Ho				1391	1351	436	343	306		161		4	51		20		
68	Er				1453	1409	449	366	320	177	168		4	60		29		
69	Tm						472	386	337		180		5	53		32		
70	Yb						487	396	343	197	184		6	53		23		
71	Lu						506	410	359	205	195		7	57		28		5
72	Hf						538	437	380	224	214	19	18	65	38	31		7
73	Ta						566	465	405	242	230	27	25	71	45	37		6
74	W						595	492	426	259	246	37	34	77	47	37		6
75	Re						625	518	445	274	260	47	45	83	46	35		4
76	Os						655	547	469	290	273	52	50	84	58	46		0
77	Ir						690	577	495	312	295	63	60	96	63	51		4
78	Pt						724	608	519	331	314	74	70	102	66	51		2
79	Au						759	644	546	352	334	87	83	108	72	54		3
80	Hg						800	677	571	379	360	103	99	170	81	58		7
81	Tl						846	722	609	407	386	122	118	137	100	76	16	13
82	Pb						894	764	645	435	413	143	138	148	105	86	22	20
83	Bi						939	806	679	464	440	163	158	160	117	93	27	25
84	Po						995	851	705	500	473	184		177	132	104	31	
85	At						1042	886	740	533	507	210		195	148	115	40	
86	Rn						1097	929	768	567	541	238		214	164	127	48	
87	Fr						1153	980	810	603	577	268		234	182	140	58	
88	Ra						1208	1058	879	636	603	299		254	200	153	68	
89	Ac						1269	1080	900	675	639	319		272	215	167	80	
90	Th						1330	1168	968	714	677	344	335	290	229	182	95	88

The most intense lines are marked with an asterisk. Thus for elements He to Mg the *1s* orbital is usually studied, for Al to As the $2p_{3/2}$, and so on

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Comparison of AES and XPS with other techniques

Table 6.1 Features of various analytical methods discussed in the text

	Incident radiation	Emitted radiation	Property monitored	Elements detectable	Depth of analysis	Spatial resolution	Information level E = elemental C = chemical	Quantification*	Applicability to inorganics*	Applicability to organics*
AES	e	e^-	Energy	Li on	3–10 nm	<12 nm	E (C)	✓	0	X
EDX	e	X-ray	Energy	Be on	1 μm	1 μm	E	✓	0†	X†
EELS	e^-	e^-	Energy	Li on	Depends on foil thickness	10 nm	E	0	✓	X
ISS	ions	ions	Energy	Li on	Outer atom layer	100 μm	E	0	✓	0
LAMMS	laser	ions	Mass	All	0.5 μm	1 μm	E, C	X	✓	✓
RBS	ions	ions	Energy	Li on	1 μm	1 mm	E	X	✓	✓‡
SIMS (static)	ions	ions	Mass	All	1.5 nm	1 μm	C (E)	X	✓	✓
SIMS (dynamic)	ions	ions	Mass	All	See text	50 μm	E	0	✓	X
SIMS (imaging)	ions	ions	Mass	All	See text	50 nm	C (E)	X	0	0
XPS	X-rays	e^-	Energy	He on	3–10 nm	STD 1 mm^2 small area: 10 μm imaging XPS: <3 μm	E, C	✓	✓	✓

*✓ = very good, 0 = reasonable, X = poor
†Without conductive coating
‡Cryo-stage required