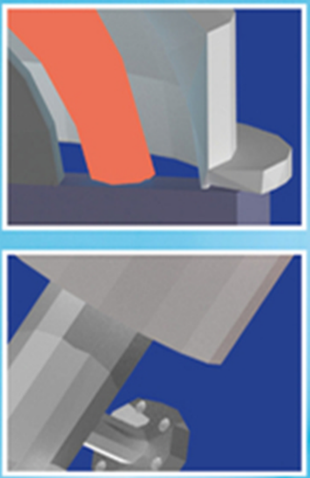
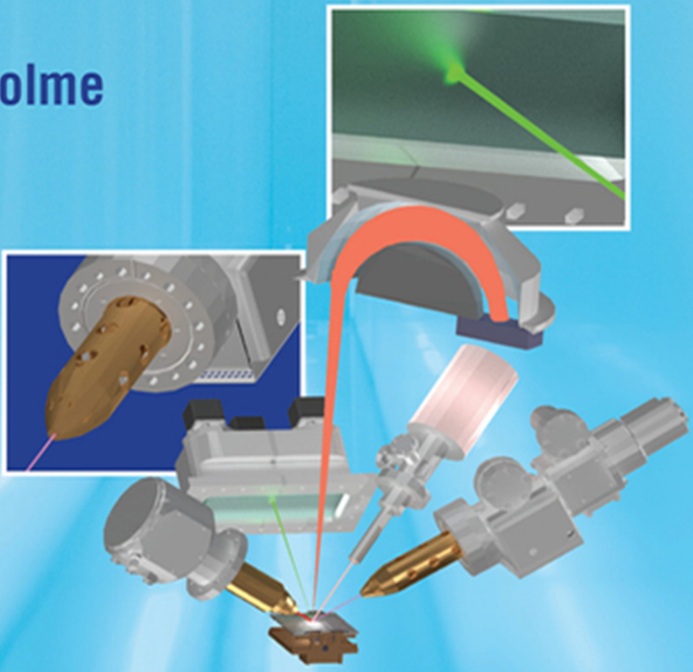
2nd Edition

An Introduction to Surface Analysis by XPS and AES

John F. Watts
John Wolstenholme





WILEY

An Introduction to Surface Analysis by XPS and AES

An Introduction to Surface Analysis by XPS and AES

John F. Watts
University of Surrey, UK

John Wolstenholme
Crowborough, UK

Second Edition

WILEY

This edition first published 2020
© 2020 John Wiley & Sons Ltd

“First edition – John Wiley & Sons Ltd, 2003”.

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, except as permitted by law. Advice on how to obtain permission to reuse material from this title is available at http://www.wiley.com/go/permissions.

The right of John F. Watts and John Wolstenholme to be identified as the authors of this work has been asserted in accordance with law.

Registered Offices
John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, USA
John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, UK

Editorial Office
The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, UK

For details of our global editorial offices, customer services, and more information about Wiley products visit us at www.wiley.com.

Wiley also publishes its books in a variety of electronic formats and by print-on-demand. Some content that appears in standard print versions of this book may not be available in other formats.

Limit of Liability/Disclaimer of Warranty
In view of ongoing research, equipment modifications, changes in governmental regulations, and the constant flow of information relating to the use of experimental reagents, equipment, and devices, the reader is urged to review and evaluate the information provided in the package insert or instructions for each chemical, piece of equipment, reagent, or device for, among other things, any changes in the instructions or indication of usage and for added warnings and precautions. While the publisher and authors have used their best efforts in preparing this work, they make no representations or warranties with respect to the accuracy or completeness of the contents of this work and specifically disclaim all warranties, including without limitation any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives, written sales materials or promotional statements for this work. The fact that an organization, website, or product is referred to in this work as a citation and/or potential source of further information does not mean that the publisher and authors endorse the information or services the organization, website, or product may provide or recommendations it may make. This work is sold with the understanding that the publisher is not engaged in rendering professional services. The advice and strategies contained herein may not be suitable for your situation. You should consult with a specialist where appropriate. Further, readers should be aware that websites listed in this work may have changed or disappeared between when this work was written and when it is read. Neither the publisher nor authors shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

Library of Congress Cataloging-in-Publication Data

Names: Watts, John F., author. | Wolstenholme, John, author.
Title: An introduction to surface analysis by XPS and AES / John F. Watts, The Surface Analysis Laboratory, Department of Mechanical Engineering Sciences, University of Surrey, John Wolstenholme.
Description: Second edition. | Hoboken : Wiley, 2020. | Includes bibliographical references and index.
Identifiers: LCCN 2019023206 (print) | LCCN 2019023207 (ebook) | ISBN 9781119417583 (cloth) | ISBN 9781119417620 (adobe pdf) | ISBN 9781119417644 (epub)
Subjects: LCSH: Surfaces (Technology)–Analysis. | Electron spectroscopy. | Photoelectron spectroscopy. | Auger effect.
Classification: LCC TP156.S95 W373 2020 (print) | LCC TP156.S95 (ebook) | DDC 620/.44–dc23
LC record available at https://lccn.loc.gov/2019023206
LC ebook record available at https://lccn.loc.gov/2019023207

Cover Design: Wiley
Cover Image: Courtesy of Robin Simpson, Thermo Fisher Scientific, Background © Ralf Hiemisch/Getty Images

Set in 10/12pt Warnock by SPi Global, Pondicherry, India

10 9 8 7 6 5 4 3 2 1

Contents

Preface to First Edition *xi*
Preface to Second Edition *xiii*
Acknowledgements *xvii*

1 Electron Spectroscopy: Some Basic Concepts *1*
1.1 Analysis of Surfaces *1*
1.2 Notation *3*
1.2.1 Spectroscopists' Notation *3*
1.2.2 X-ray Notation *4*
1.3 X-ray Photoelectron Spectroscopy *4*
1.4 Auger Electron Spectroscopy (AES) *8*
1.5 Scanning Auger Microscopy *12*
1.6 The Depth of Analysis in Electron Spectroscopy *13*
1.7 Comparison of XPS and AES/SAM *16*
1.8 The Availability of Surface Analytical Equipment *17*

2 Electron Spectrometer Design *19*
2.1 Introduction *19*
2.2 The Vacuum System *19*
2.3 X-ray Sources for XPS *22*
2.3.1 Choice of X-ray Anode *23*
2.3.2 X-ray Monochromators *27*
2.3.3 Synchrotron Sources *30*
2.4 The Electron Gun for AES *31*
2.4.1 Electron Sources *31*
2.4.1.1 Thermionic Emitter *32*
2.4.1.2 Lanthanum Hexaboride Emitter *32*
2.4.1.3 Cold Field Emitter *32*
2.4.1.4 Hot Field Emitter *33*
2.4.1.5 Comparison of Electron Emitters for AES *34*
2.4.2 The Electron Column *35*

2.4.3 Spot Size *35*
2.5 Analysers for Electron Spectroscopy *37*
2.5.1 The Cylindrical Mirror Analyser *38*
2.5.2 The Hemispherical Sector Analyser *41*
2.5.2.1 CAE Mode of Operation *42*
2.5.2.2 CRR Mode of Operation *44*
2.5.2.3 Comparison of CAE and CRR Modes *46*
2.5.2.4 The Transfer Lens *47*
2.5.3 Calibration of the Electron Spectrometer Energy Scale *48*
2.6 Near Ambient Pressure XPS *49*
2.7 Detectors *52*
2.7.1 Channel Electron Multipliers *52*
2.7.2 Microchannel Plates *54*
2.7.3 Two-Dimensional Detectors *54*
2.7.3.1 The Resistive-Anode Detector *55*
2.7.3.2 The Delay-Line Detector *55*
2.8 Small Area XPS *56*
2.8.1 Lens-Defined Small Area XPS *56*
2.8.2 Source-defined Small Area Analysis *57*
2.9 XPS Imaging and Mapping *57*
2.9.1 Serial Acquisition *58*
2.9.2 Parallel Acquisition *59*
2.9.2.1 Parallel Imaging Using a Hemispherical Spectrometer *59*
2.9.2.2 Parallel Imaging Using a Spherical Mirror Analyser *60*
2.9.2.3 Spatial Resolution and Chemical Imaging *61*
2.10 Angle Resolved XPS *64*
2.11 Automation *66*

3 The Electron Spectrum: Qualitative and Quantitative Interpretation *69*
3.1 Introduction *69*
3.2 Qualitative Analysis *69*
3.2.1 Unwanted Features in Electron Spectra *72*
3.2.2 Data Acquisition *72*
3.2.2.1 Core Level Spectra *72*
3.2.2.2 Valence Band Spectra *73*
3.3 Chemical State Information *74*
3.3.1 X-ray Photoelectron Spectroscopy *74*
3.3.2 Peak Fitting of XPS Spectra *78*
3.3.3 Auger Electron Spectroscopy *81*
3.3.4 X-AES *82*
3.3.5 Chemical State Plots *84*
3.3.6 Shakeup Satellites *86*
3.3.7 Multiplet Splitting *87*

3.3.8 Plasmons *87*
3.4 Quantitative Analysis *88*
3.4.1 Quantification in XPS *89*
3.4.1.1 Calculating Atomic Concentration *89*
3.4.1.2 Measuring Peak Intensity *92*
3.4.2 Quantification in AES *94*

4 Compositional Depth Profiling *97*
4.1 Introduction *97*
4.2 Non-destructive Depth Methods *98*
4.2.1 Measurements at a Single Emission Angle *98*
4.2.2 Angle Resolved XPS Measurements *99*
4.2.3 Measurement of Overlayer Thickness Using ARXPS *101*
4.2.4 Elastic Scattering *103*
4.2.5 Multilayer Thickness Calculations Using ARXPS *104*
4.2.6 Compositional Depth Profiles from ARXPS Measurements *107*
4.2.7 Variation of Analysis Depth with Electron Kinetic Energy *110*
4.2.8 Background Analysis *112*
4.3 Depth Profiling by Sputtering with Energetic Ions *115*
4.3.1 The Sputtering Process *115*
4.3.2 Experimental Method *116*
4.3.3 The Nature of the Ion Beam *118*
4.3.3.1 Noble Gas Ions *118*
4.3.3.2 Cluster Ions *119*
4.3.3.3 Metal Ions *121*
4.3.4 Sputter Yield and Etch Rate *122*
4.3.5 Factors Affecting the Etch Rate *123*
4.3.5.1 Material *123*
4.3.5.2 Ion Current *123*
4.3.5.3 Ion Energy *123*
4.3.5.4 Nature of the Ion Beam *124*
4.3.5.5 Angle of Incidence *124*
4.3.6 Factors Affecting the Depth Resolution *124*
4.3.6.1 Ion Beam Characteristics *124*
4.3.6.2 Crater Quality *125*
4.3.6.3 Beam Impurities *125*
4.3.6.4 Information Depth *126*
4.3.6.5 Original Surface Roughness *127*
4.3.6.6 Induced Roughness *127*
4.3.6.7 Preferential Sputtering *127*
4.3.6.8 Redeposition of Sputtered Material *128*
4.3.7 Calibration *128*
4.3.8 Ion Gun Design *128*
4.3.8.1 Electron Impact Ion Guns *128*

4.3.8.2 Argon-Cluster Ion Guns *129*
4.3.8.3 Liquid Metal Ion Guns *131*
4.4 Sectioning *131*
4.4.1 FIB Sectioning *131*
4.4.2 Angle Lapping *132*
4.4.3 Ball Cratering *133*

5 Multi-technique Analysis *135*
5.1 Introduction *135*
5.2 Ultraviolet Photoelectron Spectroscopy (UPS) *135*
5.3 Low Energy Ion Scattering Spectroscopy (LEISS) *137*
5.4 Reflection Electron Energy Loss Spectroscopy (REELS) *139*
5.4.1 Elastic Scattering *140*
5.4.2 Inelastic Scattering *141*
5.5 Work Function Measurements *142*
5.6 Energy Dispersive X-ray Analysis (EDX) *143*

6 The Sample *145*
6.1 Sample Handling *145*
6.2 Sample Preparation *147*
6.3 Sample Mounting *149*
6.4 Sample Stability *149*
6.5 Contamination and Damage During Analysis *151*
6.6 Controlling Sample Charging *152*
6.6.1 Sample Charging in XPS *152*
6.6.2 Sample Charging in AES *154*

7 Applications of Electron Spectroscopy in Materials Science *157*
7.1 Introduction *157*
7.2 Metallurgy *157*
7.2.1 Grain Boundary Segregation *158*
7.2.2 Electronic Structure of Metallic Alloys *160*
7.2.3 Surface Engineering *163*
7.3 Corrosion Science *168*
7.4 Ceramics *176*
7.5 Microelectronics and Semiconductor Materials *181*
7.5.1 Mapping Semiconductor Devices Using AES *182*
7.5.2 XPS Failure Analysis of Microelectronic Devices *186*
7.5.3 Depth Profiling of Semiconductor Materials *188*
7.5.3.1 Transistor Gate Dielectrics *188*
7.5.3.2 Inorganic Chemical State Profiling *189*
7.5.3.3 Organic Semiconductor Profiling *190*
7.6 Polymeric Materials *193*
7.7 Adhesion Science *202*

7.8 Nanotechnology *210*
7.9 Biology *215*
7.10 Energy *219*

8 Comparison of XPS and AES with Other Analytical Techniques *223*

Glossary *229*
Bibliography *239*
Appendix 1 *247*
Auger Electron Energies *247*
Appendix 2 *249*
Table of Binding Energies Accessible with Al Kα Radiation *250*
Appendix 3 *255*
Documentary Standards in Surface Analysis *255*
  The Scope of TC201 *255*
  The Purpose of TC201 *255*
  International Standards Relevant to Electron Spectroscopies *256*
Index *259*

Preface to First Edition

When one of us (JFW) wrote an earlier introductory text in electron spectroscopy the aim was to fill a gap in the market of the time (1990) and produce an accessible text for undergraduates, first-year postgraduates, and occasional industrial users of XPS and AES. In the intervening years the techniques have advanced in both the area of use and, particularly, in instrument design. In XPS, X-ray monochromators are now becoming the norm and imaging has become commonplace. In AES, field emission sources are to be seen on high-performance systems. Against that backdrop it was clear that a new, broader introductory book was required that explored the basic principles and applications of the techniques, along with the emerging innovation in instrument design.

We hope that this book has achieved that aim and will be of use to newcomers to the field, both as a supplement to undergraduate and master's level lectures, and as a stand-alone volume for private study. The reader should obtain a good working knowledge of the two techniques (although not, of course, of the operation of the spectrometers themselves) in order to be able to hold a meaningful dialogue with the provider of an XPS or AES service at, for example, a corporate research laboratory or service organisation.

Further information on all the topics can be found in the Bibliography and the titles of papers and so on have been included along with the more usual citations to guide such reading. The internet provides a valuable resource for those seeking guidance on XPS and AES and rather than attempt to be inclusive in our listing of such sites we merely refer readers to the UKSAF site and its myriad of links. Finally, we have both been somewhat perturbed by the degree of confusion and sometimes contradictory definitions regarding some of the terms used in electron spectroscopy. In an attempt to clarify the situation, we have included a glossary of the more common terms. This has been taken from ISO 18115 and we thank ISO for permission to reproduce this from their original document.

John F. Watts
Guildford, Surrey, UK
John Wolstenholme
East Grinstead, West Sussex, UK

Preface to Second Edition

It is now some 16 years since the publication of the first edition of this book. We have both been gratified by the positive manner in which it has been received by the community, testament to the need for an introductory text written by experienced practitioners. It gives us much satisfaction to see it in research and contract labs across the globe and frequently referenced in undergraduate and postgraduate reports. It thus appears to have fulfilled the perceived need outlined in the Preface to the first edition.

This perhaps begs the question 'why wait sixteen years to produce the second edition?' The answer to this is probably familiar to many practicing scientists and engineers in that the plan had informally been in place for several years, as had a formal contract; it was merely a question of allocating time in busy schedules.

The aim of the text remains the same, as enunciated in the first edition, and we have retained the same overall format. Basic principles remain, but instrumentation is constantly changing and improving as manufacturers seek better and better performance and functionality from their products. We have tried to reflect such developments in the text and make sure that it is as up to date as possible. In particular, we deal with a number of recent innovations in a manner accessible to newcomers to surface analysis. These include:

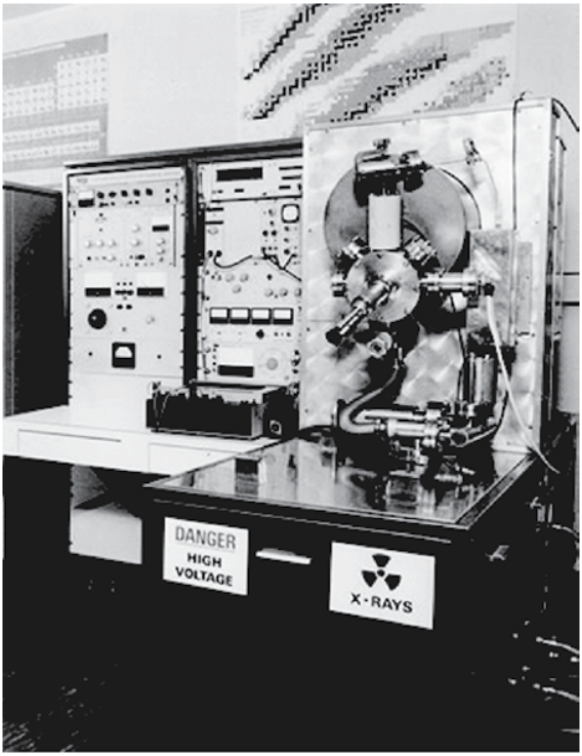
- Gas cluster ion sources.
- Newly developed high-energy X-ray sources (CrKα and GaKα) that are now available on commercial XPS systems.
- Near ambient pressure XPS, (a technique which is in its infancy but where the UK is arguably developing a lead).
- Fully automated, entry-level, high-performance systems.

Certain areas, such as sample preparation, sample mounting, quantification, peak fitting, energy loss background analysis, multi-technique analysis and multi-technique profiling are treated in more detail than before.

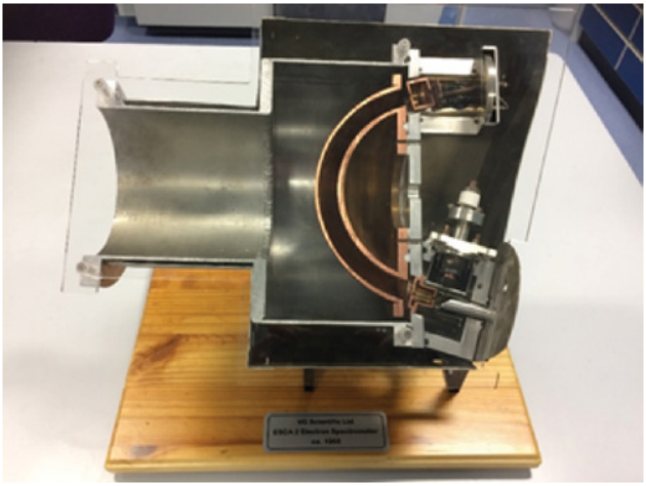
The year of publication (2019) is the Golden Jubilee of the launch of XPS and AES as commercially available analysis methods. It is a rather salutary thought that both of us have been involved with applied surface analysis for more than three quarters of this time, which gives us cause to reflect on the many innovations that have taken place during this time. As a celebration of 50 years of XPS we include images of one of the first commercial XPS systems and a sectioned analyser from such a system, overleaf.

As they say at all Golden Jubilee celebrations 'Here's to the next fifty years!'

John F. Watts
Guildford, Surrey, UK
John Wolstenholme
Crowborough, East Sussex, UK



The first commercial XPS system from VG Scientific (now Thermo Fisher Scientific), a 1969 ESCA 2 electron spectrometer, installed at the University of Surrey



Sectioned concentric hemispherical analyser from the above spectrometer.

Acknowledgements

There are many who have contributed ideas and data to this book; current and former colleagues and students in particular. Specifically, those in The Surface Analysis Laboratory at the University of Surrey (Drs Marie-Laure Abel, Simon Bacon, Jorge Bañuls Ciscar, Rossana Grilli, Chris Mallinson, Sabrina Tardio) and Drs Richard White, Tim Nunney and the staff at Thermo Fisher Scientific, have provided much new data to replace or complement that provided for the first edition. Dr Andreas Thissen at SPECS Surface Nano Analysis GmbH provided information and examples related to near ambient pressure XPS. In this, the golden jubilee year of XPS and AES, most of the innovators associated with XPS in the early days are no longer active. One notable exception being Professor Jim Castle who continues to edit a journal, publish papers, sit on ISO/TC201 and present work at conferences, in addition to being a source of inspiration to all associated with The Surface Analysis Laboratory at the University of Surrey.

Certain figures and data have been reproduced from other sources and we thank the copyright holder's for their permission to do so. In particular, the Wiley journal ***Surface and Interface Analysis*** has provided many valuable illustrations of the application of the techniques of XPS and AES. The cover design makes use of original graphics by Dr Robin Simpson (Thermo Fisher Scientific) and features the Nexsa™ automated XPS system.

The following figures are based on the data and other material provided by these organizations:

Organization	Figures
JEOL Ltd, 3-1-2 Musashino, Akishima, Tokyo 196-8558, Japan.	2.1, 2.9, 7.24
Physical Electronics USA Inc. 18725 Lake Drive East, Chanhassen, Minnesota, USA	7.17 (Sample courtesy of Fujifilm Corp), 7.25, 7.26

(*Continued*)

Organization	Figures
Scienta Omicron AB, P.O. Box 15120, 750 15 Uppsala, Sweden	2.3
SPECS Surface Nano Analysis GmbH, Voltastrasse 5, Berlin, Germany	2.19, 2.20, 7.59, 7.60
Thermo Fisher Scientific Inc., Unit 19, The Birches Industrial Estate, East Grinstead RH19 1XZ UK	1.1, 1.4, 1.6, 1.7, 1.8, 2.2, 2.6, 2.8, 2.11, 2.15, 2.17, 2.25, 3.2, 3.4, 3.6, 3.8, 3.12, 3.13, 4.2, 4.4, 4.5, 4.6, 4.7, 4.8, 4.9, 4.10, 4.11, 4.12, 4.14, 4.15, 4.22, 4.23, 4.24, 4.26, 4.27, 4.28, 5.1, 5.4, 5.6, 5.7, 5.8, 5.9, 5.10, 6.1, 6.2, 7.1, 7.19, 7.27, 7.28, 7.29, 7.30, 7.31, 7.32, 7.33, 7.34, 7.35, 7.37, 7.38, 7.39, 7.50, 7.62, 7.63

1

Electron Spectroscopy: Some Basic Concepts

1.1 Analysis of Surfaces

All solid materials interact with their surroundings through their surfaces. The physical and chemical composition of these surfaces determine the nature of the interactions. Their surface chemistry will influence such factors as corrosion rates, catalytic activity, adhesive properties, wettability, contact potential, failure mechanisms, etc. Surfaces, therefore, influence many crucially important properties of the solid.

Despite the undoubted importance of surfaces, only a very small proportion of the atoms of most solids are found at the surface. Consider, for example, a 1 cm cube of a typical transition metal (e.g. nickel). The cube contains about 9×10^{22} atoms of which about 6×10^{15} are at the surface. The proportion of surface atoms is therefore approximately 1 in 10^8 or 10 ppb. If we want to detect impurities at the nickel surface at a concentration of 0.1% then we need to detect materials at a concentration level of 0.01 ppb within the cube. The exact proportion of atoms at the surface will depend upon the shape and surface roughness of the material as well as its composition. The above figures simply illustrate that a successful technique for analysing surfaces must have at least two characteristics:

a) It must be extremely sensitive.
b) It must be efficient at filtering out signal from the vast majority of the atoms present in the sample.

This book is largely concerned with X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). As will be shown, each of these techniques has the required characteristics but, in addition, they can answer other important questions:

a) Which elements are present in the near-surface region of a solid?
b) Which chemical states of these elements are present?

An Introduction to Surface Analysis by XPS and AES, Second Edition.
John F. Watts and John Wolstenholme.

c) How much of each chemical state of each element is present?
d) What is the spatial distribution of the materials in the near surface region in three-dimensions and how does that vary with time?
e) If material is present as a thin film at the surface:
    i) How thick is the film?
    ii) How uniform is the thickness?
    iii) How uniform is the chemical composition of the film?

In electron spectroscopy, we are concerned with the emission and energy analysis of low energy electrons, usually in the range 20–2000 eV[1] (the use of X-ray anodes that generate X-rays having a photon energy much higher than 2000 eV is becoming more popular). These electrons are liberated from the sample being examined as a result of the photoemission process (in XPS) or the radiationless de-excitation of an ionised atom by the Auger emission process in AES and scanning Auger microscopy (SAM). The distinction between AES and SAM is worthy of consideration. AES is a broad term that implies excitation of Auger electrons using a beam of electrons but makes no claim to be a technique that features high spatial resolution. SAM, on the other hand, always makes use of a finely focussed electron beam, typically in the range 10–100 nm, and provides results in the form of spatially resolved images derived from Auger electron data.

In the simplest terms, an electron spectrometer consists of the sample under investigation, a source of primary radiation, and an electron energy analyser all contained within a vacuum chamber, preferably operating in the ultra-high vacuum (UHV) regime. In practice, there will often be a secondary UHV chamber fitted with various sample preparation facilities and perhaps ancillary analytical facilities. A data system will be used for data acquisition and subsequent processing. The source of the primary radiation for the two methods is different; XPS making use of soft X-rays, most commonly monochromated Al Kα X-rays, although a twin anode arrangement is still often used (the most popular being Al Kα combined with Mg Kα), whereas AES and SAM rely on the use of an electron gun. The specification for electron guns used in Auger analysis varies tremendously, particularly as far as the spatial resolution is concerned, which, for finely focused guns, may be between 5 μm and < 10 nm. In principle, the same energy analyser may be used for both XPS and AES; consequently, the two techniques are often to be found in the same analytical instrument.

Before considering the uses and applications of the two methods, it is helpful to review the physical principles of the two processes along with their strengths and weaknesses.

---

[1] Units: In electron spectroscopy, energies are usually expressed in the non-SI unit 'electron volt (eV)' which is a unit of energy equal to the work done on an electron in accelerating it through a potential difference of 1 V. $1\ \text{eV} \approx 1.6 \times 10^{-19}$ J.

1.2 Notation

XPS and AES measure the energy of electrons emitted from a material. It is necessary therefore to have some formal way to describe which electrons are involved with each of the observed transitions. The notation used in XPS is different from that used in AES. XPS uses the so-called spectroscopists' or chemists' notation while Auger electrons are identified by the X-ray notation.

1.2.1 Spectroscopists' Notation

In this notation, the photoelectrons observed 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 integer 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 integer values 0, 1, 2, 3, etc. However, this quantum number is usually given a letter rather than a number as shown in Table 1.1.

The peaks in XPS spectra derived from orbitals whose angular momentum quantum number is greater than 0 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. Each electron has a quantum number associated with its spin angular momentum[2], s. The value of s can be either +½ or −½. The two angular momenta are added vectorially to produce the quantity j in the expression nl_j, i.e. $j = |l + s|$. Thus, an electron from a p orbital can have a j value of ½ (l-s) or $^3/_2$ (l + s); similarly, electrons from a d orbital can have j values of either $^3/_2$ or $^5/_2$. The relative intensity of the components of the doublets formed by the spin orbit coupling is dependent upon their relative populations (degeneracies) which are given by the expression (2j + 1) so, for an electron from a d

Table 1.1 Notation given to the quantum numbers which describe orbital angular momentum.

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

---

[2] The electron spin quantum number, s, should not be confused with the description of the orbitals whose angular momentum is equal to zero were the S is normally given in upper case.

Table 1.2 The relationship between quantum numbers, spectroscopists' notation and X-ray notation.

Quantum numbers				
n	l	s	Spectroscopy notation	X-ray notation
1	0	±½	$1s_{1/2}$[a]	K
2	0	±½	$2s_{1/2}$[a]	L_1
2	1	+½	$2p_{1/2}$	L_2
2	1	±½	$2p_{3/2}$	L_3
3	0	±½	$3s_{1/2}$[a]	M_1
3	1	±½	$3p_{1/2}$	M_2
3	1	±½	$3p_{3/2}$	M_3
3	2	±½	$3d_{3/2}$	M_4
3	2	±½	$3d_{5/2}$	M_5
				etc.

[a] usually identified as 1s, 2s, 3s, in XPS, the subscript is omitted.

orbital, the relative intensities of the 3/2 and 5/2 peaks are 2 : 3. 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 l, the separation increases with the atomic number of the atom. For a given atom, it decreases both with increasing n and with increasing l.

1.2.2 X-ray Notation

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 1.2.

As will be seen later, the Auger process involves three electrons and so the notation must take account of this. This is done simply by listing the three electrons, for example a peak in an Auger spectrum may be labelled KL_1L_3 or $L_2M_5M_5$. For convenience, the subscripts are sometimes omitted.

1.3 X-ray Photoelectron Spectroscopy

In XPS we are concerned with a special form of photoemission, i.e. the ejection of an electron from a core level caused by an X-ray photon of energy $h\nu$. The energy of the emitted photoelectron is then analysed by the electron spectrometer and the data presented as a graph of intensity (usually expressed as counts or counts per second) versus electron energy; the 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 energy of the X-ray source 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 as follows:

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

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

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. In practice, this task will be performed by the control electronics or data system associated with the spectrometer and the operator merely selects a binding or kinetic energy scale whichever is considered the more appropriate. It should be emphasised that the positions of XPS peaks on the binding energy scale are independent of the X-ray photon energy but the positions of X-ray induced Auger peaks will depend upon the photon energy. On the other hand, if the spectrum is displayed on a kinetic energy scale then the position of the Auger peaks will remain constant while the position of the XPS peaks will change with photon energy.

Figure 1.1a is a schematic representation of the arrangement of the electrons in a carbon atom as a 1s electron is being ejected following an interaction with an X-ray photon. The carbon 1s (C 1s) region of the XPS spectrum of diamond is shown in Figure 1.1b.

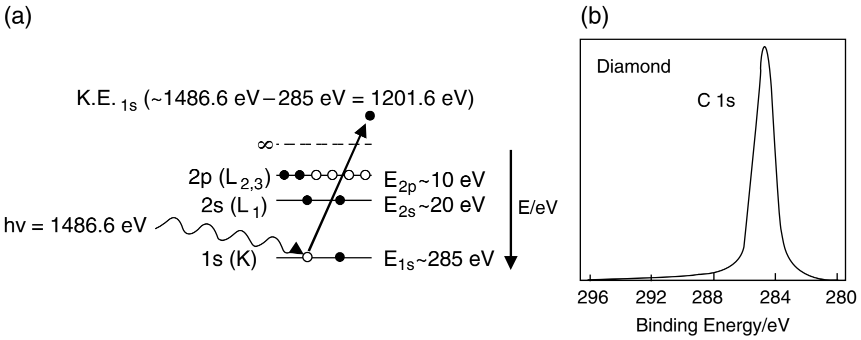


Figure 1.1 (a) Schematic of the XPS process, showing photoionisation of an atom by the ejection of a 1s electron from an atom of carbon; (b) The C 1s region of the XPS spectrum of diamond. [Note: the arrangement of the electrons in diamond differs from that shown in (a) because, in diamond, the 2s and 2p orbitals form a set of four equivalent sp^3 hybrid orbitals resulting in a single peak in the XPS spectrum.]

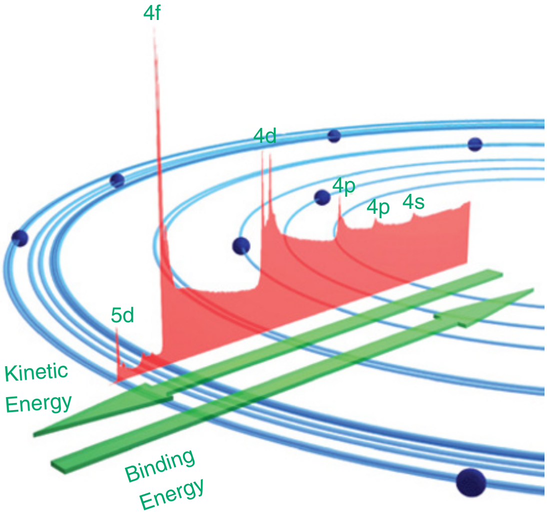


Figure 1.2 Photo electron spectrum of lead showing the manner in which electrons escaping from the solid can contribute to discrete peaks or suffer energy loss and contribute to the background. The spectrum is superimposed on a schematic of the electronic structure of lead to illustrate how each orbital gives rise to photoelectron lines.

The photoelectron spectrum will reproduce the electronic structure of an element quite accurately as all electrons with a binding energy less than the photon energy will feature in the spectrum. This is illustrated in Figure 1.2 where the XPS spectrum of lead is superimposed on a representation of the electron orbitals (represented as circular orbits in Figure 1.2).

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 ionised atom must relax in some way. This can be achieved by the emission of an X-ray photon, known as X-ray fluorescence (XRF). The other possibility is the ejection of an Auger electron. Auger peaks may be seen in the XPS spectrum of tin shown in Figure 1.3. As will be seen later, the position of the Auger peaks in the XPS spectrum can provide valuable chemical information.

Figure 1.3 shows the XPS spectrum of Sn with the peaks labelled according to the above 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.

XPS provides sensitive elemental analysis of a surface, but its great advantage is that it can provide a chemical state analysis as well. This is because the binding energy of the core electrons in an atom is affected by the chemical environment of the atom. Figure 1.4 illustrates this with a C 1s spectrum of poly(ethylene terephthalate) (PET). The spectrum consists of three major peaks; one due to the carbon atoms in the aromatic ring (carbon with no oxygen attached), one due to

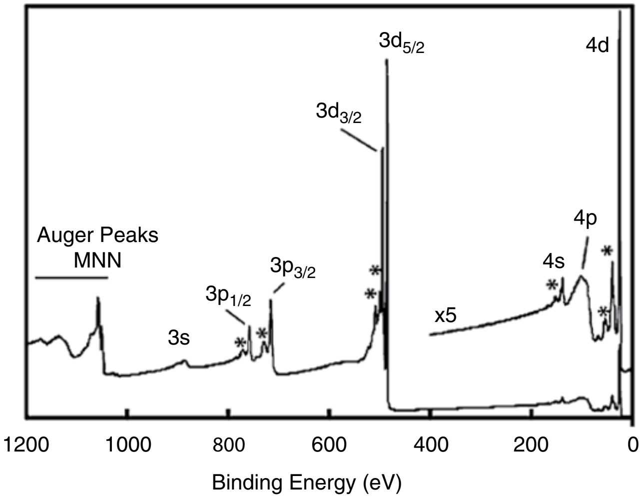


Figure 1.3 Survey spectrum from Sn showing the XPS transitions accessible using Al Kα radiation. The features marked with an asterisk are electron energy-loss features due to plasmon excitation (see Section 3.3.8).

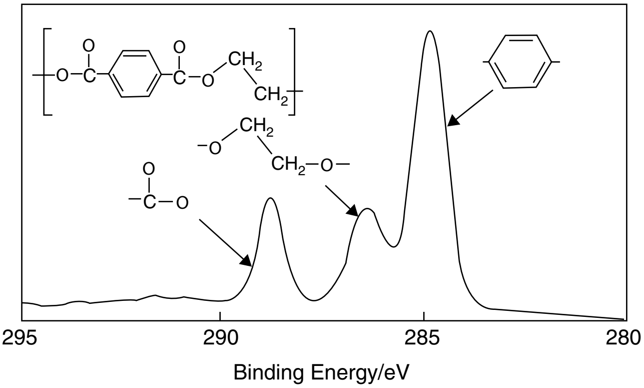


Figure 1.4 The C 1s region of the XPS spectrum of poly (ethylene terephthalate) (PET).

the carbon atoms in the ethylene group (carbon with one oxygen atom attached), and one due to the carbon atoms in the ester group (carbon with two oxygen atoms attached). It should be noted that the oxygen atoms in the two different chemical environments also show a chemical shift in their 1s spectrum.

Table 1.3 shows examples of C 1s binding energies for a range of compound types, many more may be found in, for example, the National Institute of Standards and Technology (NIST) data base (https://srdata.nist.gov/xps/Default.aspx).

Table 1.3 C 1s binding energies for a range of compound types.

Chemical state	Example	C 1s Binding energy/eV
sp^2 carbon	Graphite, graphene, aromatic polymer, e.g. polystyrene	284.4
C-C	Polyethylene	284.8
sp^3 carbon	Diamond	284.8
C-O	Poly(ethylene terephthalate) (PET)	286
C-Cl	Poly(vinyl chloride) (PVC)	287
C=O	Poly(ethyl ketone) (PEK)	288
O=C-O	Poly(methyl methacrylate) (PMMA)	288.5
CF_2	Polytetrafluoroethylene (PTFE)	292
CO_3^{2-}	Metal carbonate	288–290
C^{n-}	Metal carbide	283–284
CF_3	CF_4 plasma treated polymers	294

1.4 Auger Electron Spectroscopy (AES)

The processes of Auger electron emission and X-ray emission are illustrated in Figure 1.5. A high-energy incident electron causes the emission of an electron from an atom, (a K electron in this example). The incident electron loses energy and is scattered within the sample. The scattered incident electron and the emitted K electron contribute to the background signal in an Auger spectrum. The emission of the K electron from the atom leaves a ‘hole’ in the electronic structure which means that the ionised atom is in an excited state and will relax to a lower energy state in one of two ways.

1) An electron from a higher level, an L electron in this example, fills the hole causing an X-ray photon to be emitted. This is the basis of electron probe microanalysis (EPMA), carried out in many electron microscopes by either energy dispersive X-ray spectroscopy (EDX) or wavelength dispersive X-ray spectroscopy (WDX) spectrometers.
2) The core hole may be filled by an electron from a higher level, the $L_{2,3}$ level in Figure 1.5. In accordance with the principle of the conservation of energy, another electron is ejected from the atom, e.g. an L_1 electron in the schematic of Figure 1.5. This electron is termed the $KL_1L_{2,3}$ Auger electron.

With increasing atomic number, the relative yield of Auger electrons decreases, see Figure 1.6, while the yield of X-ray photons increases. Implicit in this observation is the fact that AES, in common with XPS, has good sensitivity for light elements.

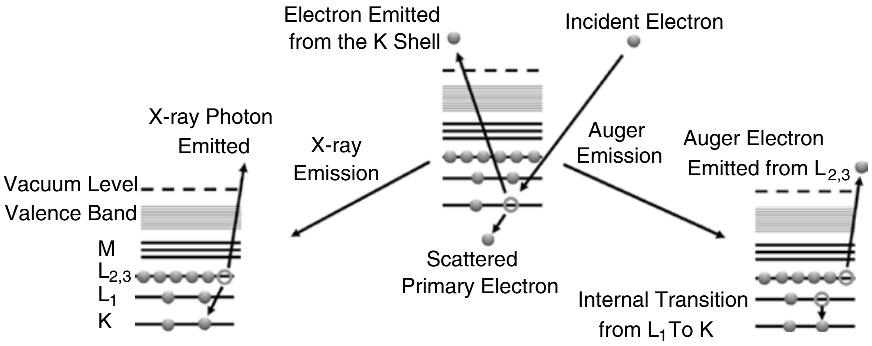


Figure 1.5 The competing processes of X-ray photon emission and Auger electron emission as a result of the ejection of a core level electron caused by a high-energy, incident electron.

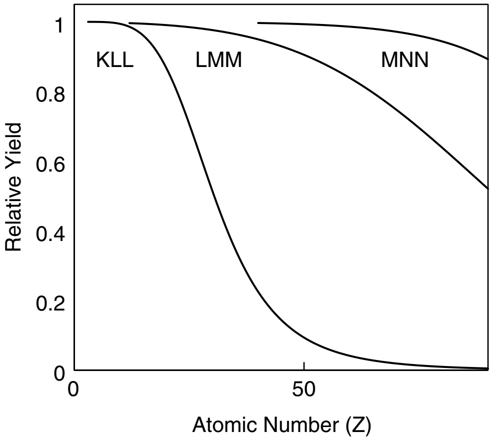


Figure 1.6 The relative yield of Auger electrons as a function of atomic number.

Abbreviated forms of the Auger notation are often used, for example:

- *KLL* is used, omitting the subscripts, to refer to the whole group of *KLL* emissions from silicon.
- *NVV* is a general term used to refer to Auger emissions in which an electron is removed from the N orbital, replaced by an electron from the valence shell, causing a second valence electron to be emitted.
- *CVV* is a general term to indicate the involvement of one electron from a core level and two from the valence band. The broadness of the valence band is convoluted within the final Auger distribution leading to very broad peaks.
- *VVV* is a general term to indicate Auger emissions involving three valence electrons.