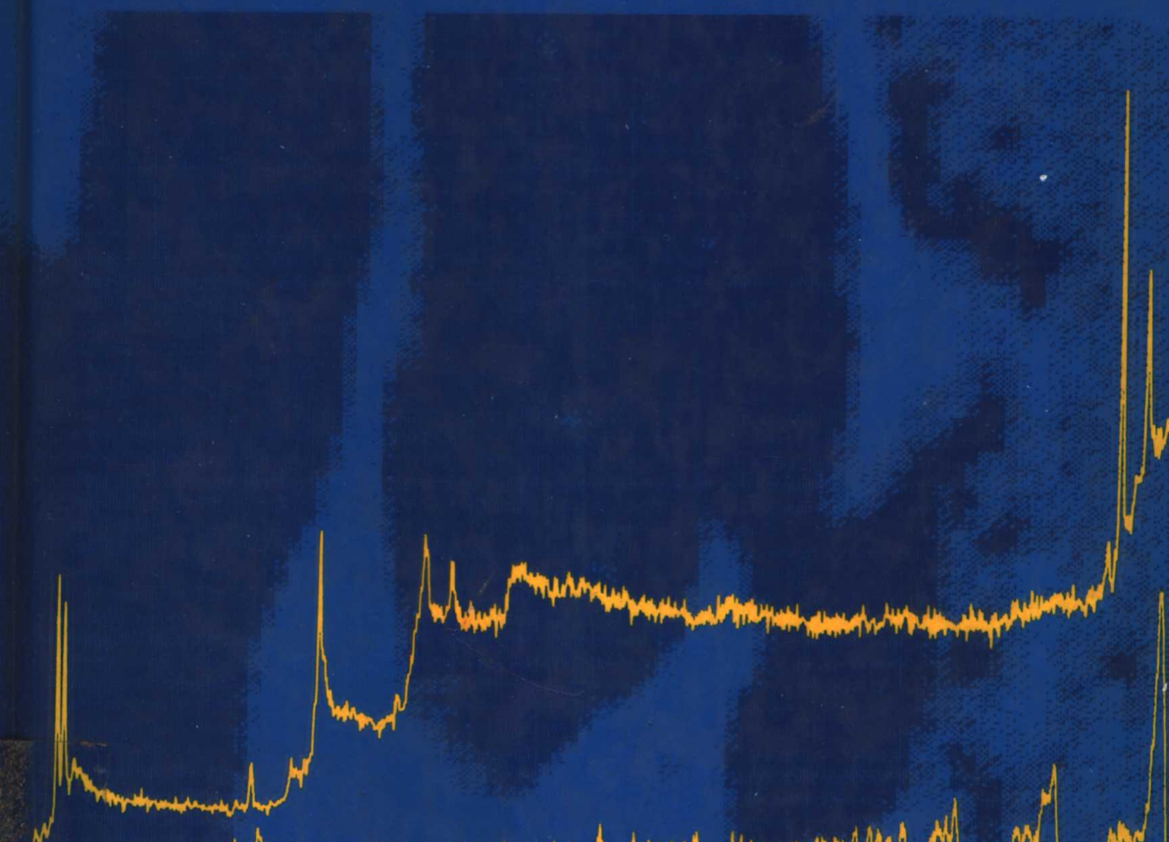
PRACTICAL SURFACE ANALYSIS

by Auger and X-ray Photoelectron Spectroscopy



Edited by

D. Briggs and M. P. Seah

Practical Surface Analysis

by Auger and X-ray Photoelectron Spectroscopy

Edited by

D. BRIGGS
ICI PLC, Petrochemicals and Plastics Division,
Wilton, Middlesbrough, Cleveland, UK

and

M. P. SEAH
Division of Materials Applications,
National Physical Laboratory,
Teddington, Middlesex, UK

JOHN WILEY & SONS
Chichester · New York · Brisbane · Toronto · Singapore

Library of Congress Cataloging in Publication Data:

Main entry under title:

Practical surface analysis.

Includes bibliographical references and index.
1. Surfaces (Technology)—Analysis. 2. Electron spectroscopy. I. Briggs, D. II. Seah, M. P.
TP156.S95P73 1983 620.1′1292 83-6618

ISBN 0 471 26279 X

British Library Cataloguing in Publication Data:

Practical surface analysis.
1. Auger effect 2. Photoelectron spectroscopy
3. Solids–Spectra
I. Briggs, D. II. Seah, M. P.
530.4′1 QC454.E4

ISBN 0 471 26279 X

Typeset by Preface Ltd, Salisbury, Wilts.
Printed by Page Bros. (Norwich) Ltd.

Preface

The amazing growth and diversification of surface analytical techniques began in the 1960s with the development of electron spectroscopy—first Auger electron spectroscopy (AES), closely followed by X-ray photoelectron spectroscopy (XPS or ESCA). Today these two complementary techniques still dominate the surface analysis scene with the total number of operational instruments well over one thousand. Since the 'heart' of either technique is an electron energy analyser, AES and XPS are frequently found in combination, with essentially no loss of performance in current fourth generation instruments. AES in the form of high resolution scanning Auger microscopy adds the surface compositional dimension to scanning electron microscopy. The addition of an ion source for sputter removal of surface layers allows either XPS or AES to perform composition depth profiling.

In recent years these techniques have rapidly matured with the generation of a large body of literature, the growth of 'user' groups in Europe, the United States and Japan, the systematic improvement of standards of operation and procedures for quantification, and so on. AES and XPS are now routinely used in a large number of industries; indeed, in some cases their development has been intimately connected with the growth of new industries (e.g. AES and the microelectronics industry). Many centres offering contract research facilities have appeared. Each year more and more people come into contact with the techniques through the need to solve problems relating to surface or interface composition and many people became practically involved in using the techniques without the advantage of relevant formal academic training. Although literature reviews of aspects of AES and XPS are legion, no text exists which reflects the new maturity of these techniques in a way which is useful *practically*, especially for newcomers to applied surface analysis.

The aim of this book is to correct this omission and to present, in one volume, all of the important concepts and tabulated data. A brief introduction gives the historical background to AES and XPS and sets them in the perspective of surface analytical techniques as a whole. The essentials of technique are covered in chapters on instrumentation, spectral interpretation, depth profiling and quantification. The remaining chapters are intended to give an insight into the major fields of application, both in terms of the special attributes of AES and XPS and the contribution they have made. These fields are microelectronics, metallurgy, catalysis, polymer technology and corrosion science. Throughout, the underlying electron spectroscopy link between AES and XPS is stressed. Aspects of technique which have fundamental importance in day-to-day operation such as instrument calibration, XPS binding energy referencing and XPS data processing (especially complex curve resolution) are discussed in the Appendices. Finally, there are full tabulations of major peak positions in AES and XPS, relative sensitivity factors for XPS and binding energy/Auger parameter data for elements and compounds.

Wilton
Teddington
February 1983

D. BRIGGS
M. P. SEAH

Contents

Practical Surface Analysis
by Auger and X-ray Photoelectron Spectroscopy
Edited by D. Briggs and M. P. Seah

Chapter 1

A Perspective on the Analysis of Surfaces and Interfaces

M. P. Seah
Division of Materials Applications, National Physical Laboratory,
Teddington, Middlesex, UK

D. Briggs
ICI PLC, Petrochemicals and Plastics Division,
Wilton, Middlesbrough, Cleveland, UK

1.1 Introduction

Surface analysis and surface science are evolutionary disciplines. They are where they are at present as a result of a small number of steps by a very large number of researchers. Progress along the whole front has not been even and advance has been rapid in certain areas but non-existent in others. Some of the pressures for advance come from mission-orientated studies for industry and some from the curiosity-motivated studies of academe. These pressures have led to an amazing plethora of techniques for surface analysis, each with its bureaucratic acronym, and to a very wide range of studies and data. Not all of these techniques and studies are relevant to researchers who wish to understand and solve surface-related problems in applied science. Over the years, Auger electron spectroscopy (AES) and X-ray photo-electron spectroscopy (XPS) have been found to show the greatest applicability. In this chapter, therefore, we chronicle the evolution of these techniques and show how they fit into the jigsaw of modern surface spectroscopies.

We have already mentioned surface analysis without defining what we mean. In its simplest sense we require the elemental composition of the outermost atom layer of a solid. Having found that, there will be immediate requests for detailed knowledge of the chemical binding state, precise sites of atoms in relation to crystal structure, surface homogeneity and the state of adsorbates. For many people surface science still concerns the complete

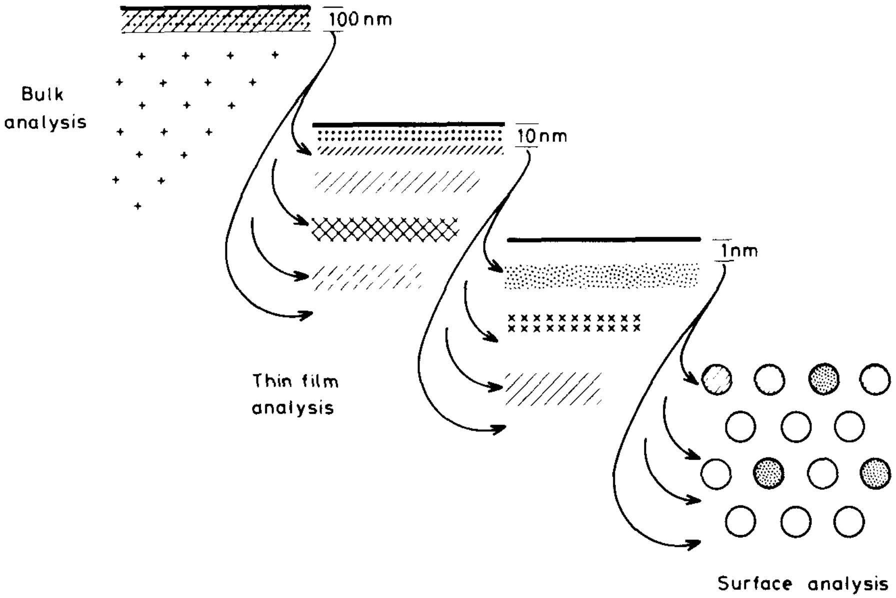
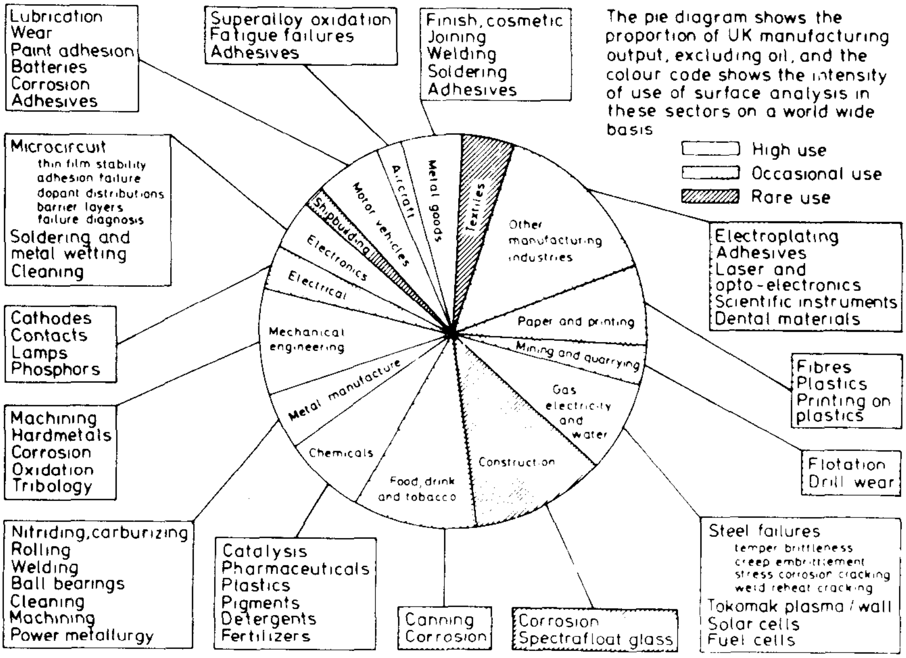


Figure 1.1 The regimes of surface analysis, thin film analysis and bulk analysis



The pie diagram shows the proportion of UK manufacturing output, excluding oil, and the colour code shows the intensity of use of surface analysis in these sectors on a world wide basis

Figure 1.2 The intensity of application of surface analysis, illustrated by the manufacturing sectors of the United Kingdom. After Seah[1] characterization of clean, low index, metal surfaces in vacuum; for others, the occasional adsorbed molecule of carbon monoxide may be added. However, in applied studies, the surfaces will be far more complex and the characterization will not generally be complete—simply adequate for the purpose. In applied studies all of the above will be required but, in addition, there will be requests for similar information for the atom layers below the surface as a function of depth, to depths of 1 μm or so, as shown in Figure 1.1. Each of the many surface analysis techniques approaches one or more of these aspects better than the others so that, in principle, each has a particular advantage. However, the value of a technique to the user depends not only on the theoretical advantage but also on the available experience in that technique, the back-up data and examples of similar approaches by previous workers. This books seeks to provide such information for the two principal surface analysis techniques, AES and XPS.

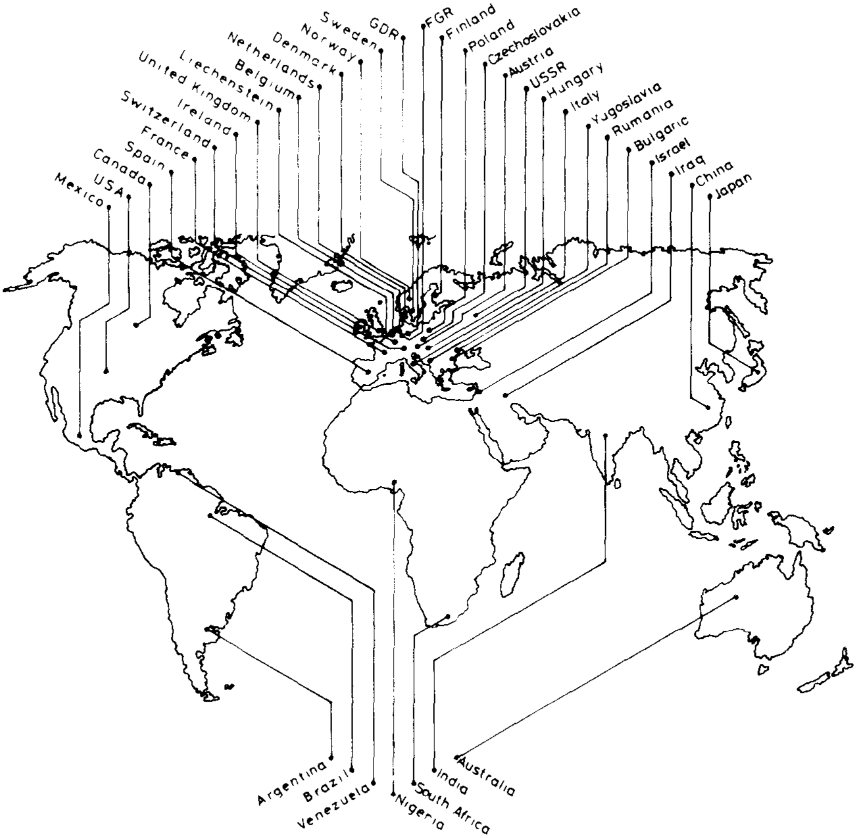


Figure 1.3 Countries operating surface analysis instruments

In the later chapters, examples are given of the use of AES and XPS in the major areas of microelectronics, metallury, catalysis, polymers and corrosion science. Figure 1.2 shows these and other areas in which surface analysis has made considerable contributions, ranging from the wear of cutting edges in strip metal production and the design of lubricant additives to optoelectronics and the architecture of integrated circuits. The ubiquity of surface analysis applications is matched by the range of countries now operating surface analysis instruments, as shown in Figure 1.3. This overall development has occurred in the years since 1970. Some developments took place before 1970 but most are concentrated into the last few years.

1.2 The Background to Electron Beam Techniques

1.2.1 Auger electron spectroscopy

The start of much of the work can be placed in the early 1920s when C. Davisson and H. E. Farnsworth were studying the secondary emission properties of metal surfaces in high vacuum under bombardment by electrons with energies of up to a few hundred electronvolts. Davisson's interests at that time partly concerned the properties of the secondary electron emission of anodes in gas-filled and vacuum triode valves. During his experiments with L. H. Germer, an accident occurred to the glass vacuum system when the nickel target was being outgassed at a high temperature. This led to oxidation of the target which was then cleaned by prolonged heating in hydrogen, causing the originally fine grained target to recrystallize to a few large grains. Low energy electron diffraction (LEED) was observed from these crystals by Davisson and Germer in 1927[2] and was correctly interpreted in terms of de Broglie's publication on wave mechanics. Davisson, Germer, Farnsworth[3] and others then worked on LEED through the 1930s using glass vacuum systems and their own designs of Faraday cup detectors to monitor the LEED beams. The experiments were very difficult but these workers still managed to study many low index single crystal metal surfaces, under what were probably ultra-high vacuum (UHV) conditions, as a function of temperature and gas adsorption. The work had a very limited appeal until Germer[4] revived the display LEED concept of Ehrenberg[5] and the concept was marketed commercially in a metal UHV system by Varian in 1964. Within a few years other manufacturers were producing commercial systems and many laboratories were set up to study single crystal metal surfaces, by LEED, in relation to a whole range of notionally applied problems that today, with the benefit of hindsight, may appear a little far-fetched. Many of the laboratories were, unfortunately, not in a position to handle the theoretical requirements of LEED.

In 1967 Harris published two reports from GE, subsequently appearing in the regular literature,[6,7] which followed the notion of Lander[8] that Auger electrons from solids could be used for surface analysis. Briefly, the principle of the technique is that the sample is bombarded by an electron beam of 1–10 keV energy and this ejects core electrons from a level E_x in atoms in a region of the sample up to 1 μm or so deep. The core hole is then filled by an internal process in the atom whereby an electron from a level E_y falls into the core hole with the energy balance taken by a third electron from a level E_z. This last electron, called an Auger electron after Pierre Auger who first observed such events in a cloud chamber,[9] is then ejected from the atom with an energy E_a, given very approximately by

$$E_a = E_z + E_y - E_x \tag{1.1}$$

The electrons thus have energies unique to each atom and, if the energy spectrum from 0 to 2 KeV is measured, the energies of the Auger electron peaks allow all the elements present, except hydrogen and helium, to be identified. The reason that AES is a surface-sensitive technique lies in the intense inelastic scattering that occurs for electrons in this energy range, so that Auger electrons from only the outermost atom layers of a solid survive to be ejected and measured in the spectrum. Considerably earlier measurements on Auger electrons had been made, but not at these energies and not in relation to surface analysis.[10] Harris realized that the direct energy spectrum, with its small peaks on a large background, could be much easier to present and analyse if differentiated. He thus developed the potential modulation of the analyser to present the differential mode spectra used ever since. Harris also demonstrated the great sensitivity of the technique in measuring surface contaminants with a signal-to-noise ratio of over 200.

In 1967 Harris discussed his work with Peria who immediately realized that the standard LEED apparatus could be modified for AES work with the addition of a small amount of standard electronics. Weber and Peria's publication[11] appeared before those of Harris due to unfortunate refereeing problems.[12] Some of the early euphoria for LEED was fading and so standard LEED apparatuses were rapidly converted to AES work. Many early AES instruments were thus ideally suited for UHV work on single crystal surfaces but, because of the inherent differences of the LEED system as an electron spectrometer compared with the 127° deflection spectromer of Harris, the LEED system was generally used at poor energy resolution. The poor resolution led many workers to believe that Auger electron peaks were broad and that they contained little chemical information. Thus AES developed from the beginning as an elemental analysis technique but was well established for carefully prepared single crystal surfaces in UHV. This enabled Palmberg and Rhodin[13] to show, by depositing single atom layers on low index crystal faces, that AES is characteristic of the surface to a depth of only 5–10 Å. The next major step came with the introduction of the cylindrical mirror analyser by Palmberg, Bohm and Tracy[14] which significantly improved the signal-to-noise