This book provides an in-depth treatment of the instrumentation, physical bases and applications of X-ray photoelectron spectroscopy (XPS) and static secondary ion mass spectrometry (SSIMS) with a specific focus on the subject of polymeric materials.

XPS and SSIMS are widely accepted as the two most powerful techniques for polymer surface chemical analysis, particularly in the context of industrial research and problem solving. Following a decade of rapid advances in instrumental capabilities and data interpretation, the field has reached a stage where it is possible to consolidate that information. In this book, the techniques of XPS and SSIMS are described and in each case the author explains what type of information may be obtained. The book also includes details of case studies emphasising the complementary and joint application of XPS and SSIMS in the investigation of polymer surface structure and its relationship to the properties of the material.

This book will be of value to academic and industrial researchers interested in polymer surfaces and surface analysis.

Surface analysis of polymers by XPS and static SIMS

Cambridge Solid State Science Series

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To Jill and Cherry

Contents

Preface

It is interesting to note that when this monograph was first contemplated, I had two relevant titles from the Cambridge Solid Science Series on my bookshelves: *Polymer Surfaces* by Cherry (now out of print) and *Modern Techniques of Surface Science* by Woodruff and Delchar. The former does not discuss surface analysis techniques whilst the latter does not mention application to polymers!

The behaviour of polymer surfaces is important in many technologies and understanding this behaviour requires surface characterisation with a high degree of chemical specificity, in terms of composition and structure, for species covering a wide range of molecular weight. The application of X-ray photoelectron spectroscopy (XPS or ESCA) and, later, static secondary ion mass spectrometry (SSIMS), in the early stages of the development of the techniques, to polymer surface analysis surely count as major successes. The requirements for polymer surface analysis have continued to be important drivers in the evolution of instrumental capabilities, because of the importance of this materials sector.

There is evidence that the polymer surface analysis field is now consolidating, following a period of major developments in instrumentation, spectroscopic performance and spectral interpretation. Spectral databases have been published, application oriented papers outweigh fundamental papers in the literature and instrument performance appears to have reached a plateau. The relative strengths of XPS and SSIMS are widely appreciated and there are many available reviews which cover, in more or less detail, the application of either technique, *separately*. It is clear, however, that most polymer surface studies benefit from the combined use of XPS and SSIMS, particularly now that time-of-flight (ToF)SIMS instruments are becoming more widely available. This seems an

appropriate time, therefore, to attempt to treat the subject of polymer surface analysis using modern surface science techniques.

The book is organised as follows. Chapter 1 introduces polymer surfaces, describes why XPS and SSIMS have assumed their current importance within the set of potentially useful analytical techniques and gives their brief histories. Chapters 2 and 4 describe, respectively, the instrumentation and physical bases of the two techniques, together with important aspects of polymer-specific studies. Chapters 3 and 5, similarly, discuss the information obtained from polymer surfaces and how this is interpreted. Finally, Chapter 6 describes, in some detail, a series of case studies which illustrate the ways in which XPS and SSIMS are used to investigate polymer surface structure and behaviour *in the real world*, with emphasis on studies which combine the two techniques.

In order to keep the book reasonably concise, a basic level of chemistry (including polymer chemistry) and physics is assumed. This means that the material should at least be accessible to undergraduate students in the later stages of chemistry/materials science courses. The primary aim, however, is to treat the subject in a way which is useful to those already working in the polymer surface/analysis field and which will allow those wanting to enter the field at post-graduate level an up-to-date coverage of the subject.

I have been fortunate to have spent most of my research career to date in the subject area of this monograph. Much of the material used derives from this work and I wish to acknowledge the contribution of ICI and my former colleagues, especially Drs Graham Beamson, Ian Fletcher and Martin Hearn, as well of that of Prof. Buddy Ratner and his colleagues at the University of Washington. A significant fraction of the figures and tables are reproduced from the following publications of John Wiley & Sons (Chichester, UK): the journal *Surface and Interface Analysis* and the books *Practical Surface Analysis*, second edition, vols 1 & 2 (Eds. D. Briggs and M.P. Seah) and *High Resolution XPS of Organic Polymers* (G. Beamson and D. Briggs). I gratefully acknowledge their permission to reproduce this material.

I am indebted to Drs Martin Seah and Graham Leggett for each reading one of the draft chapters and making valuable comments and suggestions for improvement. Finally, my special thanks to Prof. Ian Ward to whom the emergence of this book owes so much. As a series editor he pursued the objective of a book on polymer surface analysis for many years. When I accepted his invitation, I little realised how long the project was going to last! His patient enquiries and encouragement kept me going and he also read, and made detailed comments on, the whole of the manuscript during its preparation.

Malvern
August 1997

D. Briggs

Abbreviations

AES	Auger electron spectroscopy
AFM	atomic force microscopy
ARXPS	angle resolved X-ray photoelectron spectroscopy
CAE	constant analyser energy
CCD	charge coupled detector
CHA	concentric hemispherical analyser
CMA	cylindrical mirror analyser
CRR	constant retard ratio
EELS	electron energy loss spectroscopy
ESCA	electron spectroscopy for chemical analysis
ESD	electron stimulated desorption
ESIE	electron stimulated ion emission
FRS	Rutherford forward recoil scattering spectroscopy
fwhm	full width at half maximum
GIXRD	grazing incidence X-ray diffraction
IRS	infrared spectroscopy
ISS	ion scattering spectroscopy
LEED	low energy electron diffraction
NEXAFS	near edge X-ray absorption fine structure spectroscopy
NR	neutron reflectometry
PSD	position sensitive detector
RBS	Rutherford back scattering spectroscopy
SE	spectroscopic ellipsometry
SEM	scanning electron microscope

SIMS	secondary ion mass spectrometry
SSIMS	static secondary ion mass spectrometry
STM	scanning tunnelling microscopy
TEM	transmission electron microscopy
ToF SIMS	time-of-flight secondary ion mass spectrometry
UHV	ultra-high vacuum
XPS	X-ray photoelectron spectroscopy
XRF	X-ray fluorescence
XRR	X-ray reflectometry