

# HANDBOOK OF **SURFACE AND INTERFACE ANALYSIS**

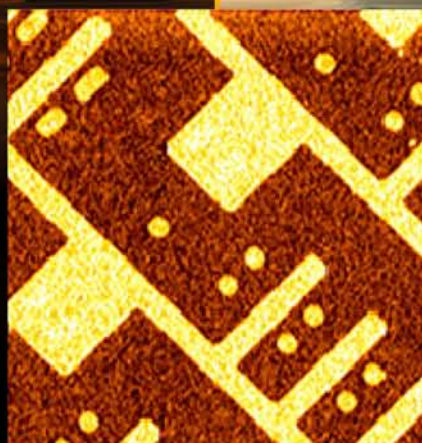
Methods for  
Problem-Solving

SECOND EDITION

Edited by  
John C. Rivière  
Sverre Myhra



CRC Press  
Taylor & Francis Group



HANDBOOK OF  
**SURFACE**  
AND  
**INTERFACE**  
**ANALYSIS**

Methods for  
Problem-Solving

---

SECOND EDITION

---



# HANDBOOK OF **SURFACE** AND **INTERFACE** **ANALYSIS**

Methods for  
Problem-Solving

---

S E C O N D   E D I T I O N

---

Edited by  
John C. Rivi re  
Sverre Myhra



CRC Press

Taylor & Francis Group  
Boca Raton London New York

---

CRC Press is an imprint of the  
Taylor & Francis Group, an **informa** business

CRC Press  
Taylor & Francis Group  
6000 Broken Sound Parkway NW, Suite 300  
Boca Raton, FL 33487-2742

© 2009 by Taylor & Francis Group, LLC  
CRC Press is an imprint of Taylor & Francis Group, an Informa business

No claim to original U.S. Government works  
Printed in the United States of America on acid-free paper  
10 9 8 7 6 5 4 3 2 1

International Standard Book Number-13: 978-0-8493-7558-3 (Hardcover)

This book contains information obtained from authentic and highly regarded sources. Reasonable efforts have been made to publish reliable data and information, but the author and publisher cannot assume responsibility for the validity of all materials or the consequences of their use. The authors and publishers have attempted to trace the copyright holders of all material reproduced in this publication and apologize to copyright holders if permission to publish in this form has not been obtained. If any copyright material has not been acknowledged please write and let us know so we may rectify in any future reprint.

Except as permitted under U.S. Copyright Law, no part of this book may be reprinted, reproduced, transmitted, or utilized in any form by any electronic, mechanical, or other means, now known or hereafter invented, including photocopying, microfilming, and recording, or in any information storage or retrieval system, without written permission from the publishers.

For permission to photocopy or use material electronically from this work, please access [www.copyright.com](http://www.copyright.com) (<http://www.copyright.com/>) or contact the Copyright Clearance Center, Inc. (CCC), 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400. CCC is a not-for-profit organization that provides licenses and registration for a variety of users. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

**Trademark Notice:** Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation without intent to infringe.

---

**Library of Congress Cataloging-in-Publication Data**

---

Handbook of surface and interface analysis methods for problem-solving / editors, John C. Rivière, Sverre Myhra. -- 2nd ed.  
p. cm.

Includes bibliographical references and index.

ISBN 978-0-8493-7558-3 (hardcover : alk. paper)

1. Surfaces (Physics)--Analysis. 2. Interfaces (Physical sciences)--Analysis. 3. Surface chemistry. 4. Surfaces (Technology)--Analysis. I. Rivière, J. C. II. Myhra, S. (Sverre), 1943- III. Title.

QC173.4.S94H35 2009  
620'.44--dc22

2009005505

---

Visit the Taylor & Francis Web site at  
<http://www.taylorandfrancis.com>

and the CRC Press Web site at  
<http://www.crcpress.com>

---

# Contents

Preface.....	vii
Editors.....	xi
Contributors .....	xiii
Authors.....	xv
<b>Chapter 1</b> Introduction .....	1
<i>John C. Rivière and Sverre Myhra</i>	
<b>Chapter 2</b> Problem Solving: Strategy, Tactics, and Resources .....	7
<i>Sverre Myhra and John C. Rivière</i>	
<b>Chapter 3</b> Photoelectron Spectroscopy (XPS and UPS), Auger Electron Spectroscopy (AES), and Ion Scattering Spectroscopy (ISS) .....	19
<i>Vaneica Y. Young and Gar B. Hoflund</i>	
<b>Chapter 4</b> Ion Beam Techniques: Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) .....	65
<i>Birgit Hagenhoff, Reinhard Kersting, and Derk Rading</i>	
<b>Chapter 5</b> Surface and Interface Analysis by Scanning Probe Microscopy .....	97
<i>Sverre Myhra</i>	
<b>Chapter 6</b> Transmission Electron Microscopy: Instrumentation, Imaging Modes, and Analytical Attachments .....	139
<i>John M. Titchmarsh</i>	
<b>Chapter 7</b> Synchrotron-Based Techniques.....	193
<i>Andrea R. Gerson, David J. Cookson, and Kevin C. Prince</i>	
<b>Chapter 8</b> Quantification of Surface and Near-Surface Composition by AES and XPS.....	223
<i>Sven Tougaard</i>	
<b>Chapter 9</b> Structural and Analytical Methods for Surfaces and Interfaces: Transmission Electron Microscopy .....	245
<i>John M. Titchmarsh</i>	
<b>Chapter 10</b> In-Depth Analysis/Profiling .....	281
<i>François Reniers and Craig R. Tewell</i>	

<b>Chapter 11</b>	Characterization of Nanostructured Materials.....	319
	<i>Matthias Werner, Alison Crossley, and Colin Johnston</i>	
<b>Chapter 12</b>	Problem-Solving Methods in Tribology with Surface-Specific Techniques.....	351
	<i>Christophe Donnet and Jean-Michel Martin</i>	
<b>Chapter 13</b>	Problem-Solving Methods in Metallurgy with Surface Analysis .....	389
	<i>R. K. Wild</i>	
<b>Chapter 14</b>	Composites .....	421
	<i>Peter M. A. Sherwood</i>	
<b>Chapter 15</b>	Minerals, Ceramics, and Glasses .....	457
	<i>Roger St. C. Smart and Zhaoming Zhang</i>	
<b>Chapter 16</b>	Catalyst Characterization .....	501
	<i>Wolfgang E. S. Unger and Thomas Gross</i>	
<b>Chapter 17</b>	Surface Analysis of Biomaterials.....	529
	<i>Marek Jasieniak, Daniel Graham, Peter Kingshott, Lara J. Gamble, and Hans J. Griesser</i>	
<b>Chapter 18</b>	Adhesion Science and Technology .....	565
	<i>John F. Watts</i>	
<b>Chapter 19</b>	Electron Spectroscopy in Corrosion Science .....	603
	<i>James E. Castle</i>	
<b>Index</b> .....		635

---

# Preface

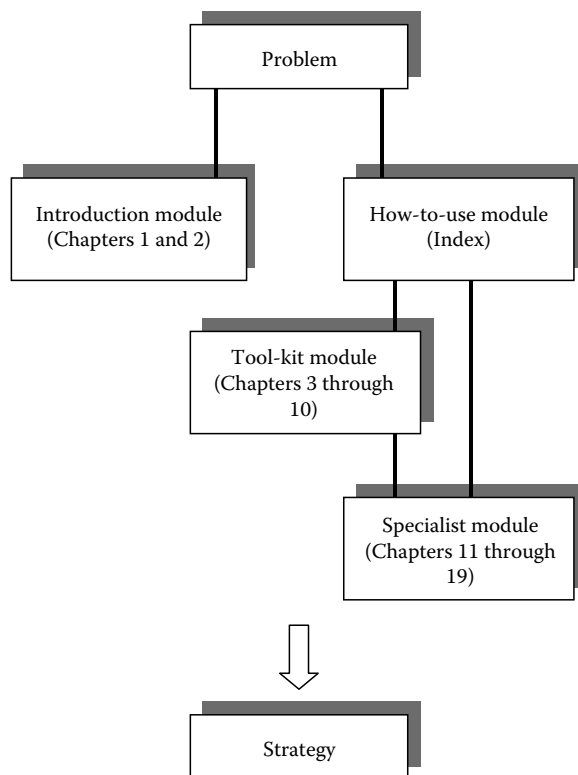
It is with some trepidation that one approaches the task of producing the second edition of a reference monograph. Many questions come to mind. Did the first edition find a sufficiently large audience and did it meet its objective? Can we improve on the first edition, and has the field moved along to the extent that a second edition, 10 years later, can offer a new and fresh perspective on the field, and new and better insights into the state of the art? Last but not least, can we and our coauthors once more gird our loins and find the time and energy in increasingly busy lives to produce effective and readable accounts of our lives' work? As is often the case, one can answer such questions fully only in hindsight, but we believe nevertheless that there are enough positive indicators to make the project worthwhile.

The first edition was based on our belief that the characterization and analysis of surfaces and interfaces should be done in the context of problem solving rather than being based on the capabilities of one or more individual techniques. If anything, that belief is now held by us even more strongly, and, as it has turned out, recent trends in science and technology appear to have vindicated it. Major instrumental assets are now generally funded and maintained as central facilities that can be accessed as and when potential users make informed decisions that one or more facilities can offer tools appropriate to their analytical problem(s). Industry is increasingly making the assessment that it is more cost effective to contract out analytical services than to maintain in-house facilities of sufficient breadth and expertise. Those are the trends that have motivated this book, and it therefore focuses principally on development of the strategic thinking that should be undertaken by those who decide which facilities to access, and where to subcontract analytical work. While good strategy can win a war, actual battles are fought tactically. Thus this book also attempts to cover most of the major tactical issues that are relevant at the location where the data are being produced.

In this second edition, we attempt to broaden the thinking about the techniques and methods that can be brought to bear on surfaces and interfaces. Thus, there are new chapters that deal with electron-optical imaging techniques and associated analytical methods. Likewise, there is also now an introductory chapter on techniques based on synchrotron sources. Ten years (since the first edition) is quite a long time in science and technology. Even in the traditional surface analytical techniques, there have been significant developments. For instance, most new XPS instruments now have an imaging capability as a matter of course, and parallel multichannel counting is standard. Among the more recent arrivals to the family of techniques the scanning probe group has carved out an even greater role by virtue of convenience and versatility; indeed one of the suppliers has, as of mid-2006, just delivered its 7000th instrument. At the forefront of electron microscopy, high resolution analytical instruments are widely available, while aberration correction is now emerging as the next major advance.

Arguably, the most significant trend in materials science during the last few years has been the upsurge of nanotechnology and nanoscience. In spite of the early hype, and the re-branding of some good, and some not-so-good, "traditional" science and technology, there is now real progress and substance on the meso- and nanoscales (we use "meso" to describe the gray and ill-defined range between "micro" and "nano"). The task of interrogating systems on those scales is presenting considerable challenges to the practitioners of characterization and analysis. Traditional techniques and methods are being pressed into service on a size scale for which they were not intended, and new techniques are being invented, while the practitioners are yet again having to climb new learning curves. The second edition attempts to provide new, relevant material in response to that trend.





**FIGURE 1** Schematic overview of the structure of the book.

The structure of the second edition remains the same as for the first (see Figure 1 for a schematic overview). There are two short introductory chapters dealing with problem solving as a strategic issue, and with guidance on how to locate detailed information on techniques, methods, and materials. Then there are a number of chapters providing the essential physical basis and common modes of operation for groups of techniques. The last half of the volume is concerned principally with exploring the tactical issues for surface and interface characterization and analysis of particular types of materials, or for particular applications of materials.

It goes without saying that this book could not have been written without the time and effort that so many contributors have had to find out of their already overcommitted professional lives. Each chapter represents a distillation of the expertise and experience gained by the contributors as a result of their devotion to one or more aspects of surface science and technology. We would like to set on record our appreciation of that time and effort, and to acknowledge the good-humored acceptance of our (sometimes substantial) recasting and rearranging of contributors' material.

Although success and the accumulation of expertise in science can be a purely individual achievement, for most of us it is largely a cooperative social phenomenon. For that reason we are indebted to all those coworkers, too numerous to mention, who have passed through our research groups over the years and participated in the two-way information transfer process that has added inestimably to our own expertise. We hope that they have found it equally rewarding.

We have both had long-standing connections with what used to be called AERE Harwell, but is now known as the Harwell Laboratory, AEA Technology plc, and we wish to acknowledge that

connection. Our special thanks, also, to those individuals at the Harwell Laboratory and elsewhere who have been of particular assistance to us over many years. More recently we have benefited from attachments to the Department of Materials at the University of Oxford, where organizational and collegial support has made it possible to produce the second edition.

Lastly, we would like to express our gratitude to our immediate families. Engagement in a scholarly endeavor may be a source of satisfaction to those directly involved, but tends instead to be an ordeal to those having to live alongside the resultant upheaval.

**John C. Rivière**  
**Sverre Myhra**  
*Oxford*



---

# Editors

**John C. Rivière** worked for AEA Technology, Harwell, England, until his retirement. He is the author or coauthor of numerous scholarly papers and chapters that reflect his research interests in both basic and applied surface science and technology. A pioneer in the early development of electron spectroscopies, he was the recipient of the UK Vacuum Council Medal (1989). He received his MSc (1950) from the University of Western Australia, and his PhD (1955) and DSc (1995) from the University of Bristol.

**Sverre Myhra** is currently a visiting scientist in the Department of Materials at the University of Oxford. Previously, he founded and headed an early scanning probe microscopy group in Australia. He is the author of numerous scholarly papers and chapters in the area of materials science and technology focusing on surface and interface analysis, with an emphasis on recent applications of scanning probe microscopy. He received his PhD (1968) in physics from the University of Utah, Salt Lake City.



---

# Contributors

**James E. Castle**

School of Engineering  
Faculty of Engineering and Physical Science  
University of Surrey  
Guildford, United Kingdom

**David J. Cookson**

Science Operations  
Australian Synchrotron  
Clayton, Victoria, Australia

**Alison Crossley**

BegbrokeNano  
Department of Materials  
University of Oxford  
Oxford, United Kingdom

**Christophe Donnet**

University Institute of France  
Paris, France

and

Laboratoire Hubert Curien  
University Jean Monnet  
Saint-Etienne, France

**Lara J. Gamble**

NESAC-BIO  
Departments of Bioengineering  
and Chemical Engineering  
University of Washington  
Seattle, Washington

**Andrea R. Gerson**

Applied Centre for Structural  
and Synchrotron Studies  
University of South Australia  
Mawson Lakes, South Australia, Australia

**Daniel Graham**

Asemblon, Inc.  
Redmond, Washington

**Hans J. Griesser**

Ian Wark Research Institute  
University of South Australia  
Mawson Lakes, South Australia, Australia

**Thomas Gross**

Bundesanstalt für Materialforschung  
und -prüfung  
Surface and Thin Film Analysis Working  
Group  
Berlin, Germany

**Birgit Hagenhoff**

Materials Characterization GmbH  
Münster, Germany

**Gar B. Hoflund**

Department of Chemical Engineering  
University of Florida  
Gainesville, Florida

**Marek Jasieniak**

Ian Wark Research Institute  
University of South Australia  
Mawson Lakes, South Australia, Australia

**Colin Johnston**

BegbrokeNano  
Department of Materials  
University of Oxford  
Oxford, United Kingdom

**Reinhard Kersting**

Materials Characterization GmbH  
Münster, Germany

**Peter Kingshott**

iNANO  
Faculty of Science  
University of Aarhus  
Aarhus, Denmark

**Jean-Michel Martin**

University Institute of France  
Paris, France

and

Laboratoire de Tribologie et Dynamique des  
Systèmes  
École Centrale de Lyon  
Écully, France

**Sverre Myhra**

Department of Materials  
University of Oxford  
Oxford, United Kingdom

**Kevin C. Prince**

Sincrotrone Trieste  
Trieste, Italy

**Derk Rading**

Mass Spectrometers GmbH  
Münster, Germany

**François Reniers**

Analytical and Interfacial Chemistry  
Department  
Université Libre de Bruxelles  
Brussels, Belgium

**John C. Rivière**

Department of Materials  
University of Oxford  
Oxford, United Kingdom

**Peter M. A. Sherwood**

Department of Physics  
Oklahoma State University  
Stillwater, Oklahoma

**Roger St. C. Smart**

Applied Centre for Structural  
and Synchrotron Studies  
University of South Australia  
Mawson Lakes, South Australia,  
Australia

**Craig R. Tewell**

Sandia National Laboratories  
Livermore, California

**John M. Titchmarsh**

Department of Materials  
University of Oxford  
Oxford, United Kingdom

**Sven Tougaard**

Department of Physics and Chemistry  
University of Southern Denmark  
Odense, Denmark

**Wolfgang E. S. Unger**

Bundesanstalt für Materialforschung  
und Prüfung  
Surface and Thin Film Analysis  
Working Group  
Berlin, Germany

**John F. Watts**

Surrey Materials Institute and Faculty  
of Engineering and Physical Sciences  
University of Surrey  
Guildford, United Kingdom

**Matthias Werner**

Nano & Micro Technology Consulting  
Berlin, Germany

**R. K. Wild**

University of Bristol  
Bristol, United Kingdom

**Vaneica Y. Young**

Department of Chemistry  
University of Florida  
Gainesville, Florida

**Zhaoming Zhang**

Institute of Materials Engineering  
Australian Nuclear Science  
and Technology Organisation  
Lucas Heights, New South Wales, Australia

---

# Authors

**James E. Castle** received his PhD in 1961 for work on the oxidation resistance of the Magnox alloys used in the nuclear power industry. Subsequently, he worked on problems of metal oxidation and corrosion in the power industry before joining the University of Surrey in 1970 where he founded one of the United Kingdom's first surface analysis laboratories, dedicated to understanding the role of surface reactivity in the protection of metals against corrosion, particularly in the industrial context. He is currently the emeritus professor of materials science. He has published more than 200 papers, many dealing with aspects of electron spectroscopy applied to corrosion science and engineering.

**David J. Cookson** received his PhD in physics in 1989 from Monash University (Australia). After three years in industry, he joined the Australian Synchrotron Research Program in 1992 and has worked as an expatriate scientist/manager in Japan and the United States. He is now the science and beamline development manager at the Australian Synchrotron in Melbourne. His major interests are nanoscale characterization of condensed matter with elastic x-ray scattering, and the investigation of entropy and enthalpy in liquid/solid systems.

**Alison Crossley** received her PhD in surface science from the University of Liverpool. Since then she has managed the Materials Characterisation Service for AEA Technology plc. In 2002, she was appointed senior research fellow in the Department of Materials, University of Oxford, where she is managing BegbrokeNano—Oxford Materials Characterisation Services—as a commercial interface with industry for other groups within the Department of Materials. She has published more than 55 papers and is a chartered chemist, a member of the Royal Society of Chemistry (RSC), committee member for the RSC Solid Surfaces Group, a fellow of the Royal Microscopical Society and honorary chair of the EM group, and a member of the Institute of Physics Materials and Characterisation Group Committee.

**Christophe Donnet** received his PhD in analytical chemistry from the University of Lyon, France, in 1990. He has been an associate professor in the French engineering school École Centrale de Lyon up to 2000 and is now a full professor of material science and chemistry at University Jean Monnet, Saint-Etienne, France. He is also member of the University Institute of France. His principal research interests include thin-film deposition (pulsed laser deposition) and characterization, including tribological properties. Recent research has focused on superlow friction of MoS<sub>2</sub> films and diamond-like carbon (DLC), in collaboration with groups at the IBM Research Division (Yorktown Heights, United States) and Argonne National Laboratories (United States). He has recently edited a book dedicated to the tribology of DLC films (Springer, 2008).

**Lara J. Gamble** is the assistant director of the National ESCA and Surface Analysis Center for Biomedical Problems (NESAC/BIO) at the University of Washington (an NIH-NIBIB-funded biomedical technology resource center). She is also a member of the faculty in the Department of Bioengineering at the University of Washington. Her major interests are in the XPS and ToF-SIMS of biological materials. She received her PhD in physical chemistry from the University of Washington in 1996.

**Andrea R. Gerson** is the director of the Applied Centre for Structural and Synchrotron Studies (ACeSSS) at the University of South Australia. Her first degrees were from the University of Canterbury (New Zealand) followed by a PhD (1992) from the University of Strathclyde (Scotland).



Andrea completed a postdoctoral fellowship at Kings' College, London University. ACeSSS specializes in the development of advanced techniques for applied applications. Andrea's areas of interest focus on the role of surface and bulk structure in determining reactivity and physical properties.

**Daniel Graham** received his BS in chemical engineering from Brigham Young University and his PhD in bioengineering from the University of Washington. His PhD thesis work focused on the interpretation of TOF-SIMS spectral fragmentation patterns using multivariate analysis techniques. He has over 10 years of experience in surface modification and characterization. He has worked with a wide range of materials using various analysis techniques including XPS, ToF-SIMS, FTIR, and contact angle. He is currently a founder of, and principal scientist in charge of research and development at, Asemblon Inc in Redmond, Washington.

**Hans J. Griesser** is professor of surface science at the University of South Australia and deputy director of its Ian Wark Research Institute. He received his PhD in physical chemistry from the Swiss Federal Institute of Technology (ETH) Zürich, Switzerland in 1979. He has been involved in the fundamentals and applications of surface science while employed in industry, in a government laboratory, and in academia. His current research interests are in the areas of surface modification, low-temperature plasma methods, and surface analysis, particularly for bio-interfaces such as protein-resistant and antibacterial coatings.

**Thomas Gross** received a diploma in 1974 and a Dr. rer. nat. in 1979, both in chemistry, from the Humboldt University, Berlin, Germany. He was a research associate at the Institute of Physical Chemistry of the Academy of Sciences in Berlin, from 1979 to 1991. He then joined the Federal Institute for Materials Research and Testing (BAM), Berlin, in 1992, where he is a scientist in the Surface and Thin Film Analysis Working Group. He is domain expert of the DACH for XPS and the DAP for XPS and ToF-SIMS and was the vice chairman of ECASIA '03. His major interests are electron spectroscopy, secondary ion mass spectrometry, adsorption science applied to catalysis by zeolites, as well as being committed to advances in standardization of surface chemical analysis techniques.

**Birgit Hagenhoff** received her PhD in 1993 from the University of Münster in Germany. Since then she has worked for the Centre for Manufacturing Technology at Philips in the Netherlands before returning to Münster where she is now the president and CEO of Tascon GmbH. Her principal research interests are in the area of secondary ion mass spectrometry (SIMS), where she has worked closely with the pioneering group of Benninghoven. She is now fully engaged with applications of SIMS, and with problem solving for industry.

**Gar B. Hoflund** received his PhD in chemical engineering from the University of California at Berkeley in 1978. He has been a professor of chemical engineering at the University of Florida in Gainesville since 1977. His major interests involve chemical reactions at solid surfaces with applications relating to heterogeneous catalysis and nanotechnology, semiconductor materials and processing, electrochemistry, polymer erosion by oxygen atoms, and UV radiation and tribology. He has contributed to the development of instrumentation, such as atom sources, and methodologies for surface and interface analysis.

**Marek Jasieniak** has an MS in chemistry and chemical technology from Cracow University of Technology, Poland. Over a number of years at tertiary institutions, he has used extensively a number of instrumental techniques with a major focus on XPS and ToF-SIMS. He is now a staff member of the Ian Wark Research Institute at the University of South Australia. His current interest is in the application of surface analysis to the characterization, development, and performance evaluation of biomedical devices.

**Colin Johnston** received his PhD in surface science and catalysis in 1987 from the University of Dundee. Since then he has worked at AEA Technology plc in various areas including materials characterization and development of electronic materials, and within the corporate structure. Currently, he is a senior research fellow in the Department of Materials at Oxford University where he is the director of Faraday Advance—the transport node of the materials knowledge transfer network—and coordinator of the Institute of Industrial Materials and Manufacturing, part of the Department of Materials. He is director of HITEN—the network for high-temperature electronics—where he has established a pan-European strategy for high-temperature electronics, and the co-chair of the US High Temperature Electronics biennial conference series. He has published over 80 scientific papers and has edited several books on high-temperature electronics.

**Reinhard Kersting** received his PhD in 2003 from the University of Münster in Germany. His principal research interests are in applications of ToF-SIMS, with particular focus on organic materials. Since 1997 he has worked with Tascon GmbH, where he does analytical consulting and has responsibilities for customer support and business development.

**Peter Kingshott** is an associate professor at the Interdisciplinary Nanoscience Centre at the University of Aarhus in Denmark. He has a BSc with honors in chemistry from Murdoch University in Perth, Australia, and a PhD from the University of New South Wales, Sydney. His PhD focused on developing new biomaterial surfaces and on understanding and developing new methods for investigating protein adsorption phenomena. After completing postdoctoral appointments at CSIRO in Melbourne, NESAC/BIO at the University of Washington, and RWTH Aachen, Germany, he became a senior scientist at the Danish Polymer Centre, Risø National Laboratory, where his work has focused on surface functionalization and advanced surface analysis of materials, including medical materials, composites, and materials used in food processing.

**Jean-Michel Martin** is a graduate in chemistry (1972) and obtained his PhD from the University of Lyon in material science and engineering in 1978. He is presently a full professor at École Centrale de Lyon, France, and a member of the University Institute of France. He has 30 years of extensive experience in fundamental and applied research in tribology of thin films, diamond-like coatings, boundary lubrication, antiwear and extreme-pressure additives, and surface analysis. Along with his colleagues, Christophe Donnet and Thierry Le Mogne, he discovered experimentally the superlubricity of pure MoS<sub>2</sub> in ultrahigh vacuum. He is currently implementing new additive formulations for metal forming and engine applications, and developing new analytical techniques for tribofilm analyses (XPS/AES/ToF-SIMS, XANES, etc). He has authored or coauthored 130 articles in peer-reviewed journals, 8 patents, 4 book chapters, 195 contributions in conference proceedings, and about 100 oral presentations, including 30 invited talks.

**Kevin C. Prince** is a research group leader at the Italian National Synchrotron Elettra in Trieste. He received his first degrees from Melbourne University and his DPhil from the Department of Metallurgy and Materials Science (now Department of Materials), University of Oxford, in 1978. He has held posts at Flinders University, the Fritz Haber Institute (Berlin), and the KFA Jülich in Germany before moving to Italy. His interests are in the application of synchrotron work to the understanding of the electronic structure of surfaces, molecular adsorbates, and free molecules.

**Derk Rading** received his PhD in 1997 from the University of Münster in Germany. His principal research interests are with interactions of energetic particles with surfaces. Since 1998 he has worked with ION-TOF GmbH, where he has responsibilities for analytical customer support, training, and instrument demonstration.

**François Reniers** received his PhD in chemistry from the Université Libre de Bruxelles (ULB), Belgium, in 1991. He has been professor at ULB since 1999. His main research interests are the areas of modification of surfaces using plasma techniques, and the application of surface analysis techniques (AES and XPS) for the characterization of surfaces, coatings, and buried interfaces. He gave advanced courses on surface characterization at the Chinese University in Hong Kong in 2000 (Croucher Foundation), and was the chairman of the European Conference on the Applications of Surface and Interface Analysis (ECASIA'07), held in Brussels in September 2007. He is currently officer of the IUVESTA, and vice-rector for research at the ULB.

**Peter M. A. Sherwood** received his PhD in chemistry from Cambridge University in the United Kingdom in 1970. He subsequently worked at Cambridge and at the University of Newcastle-upon-Tyne in the United Kingdom and Kansas State University in the United States before joining the faculty at Oklahoma State University in 2004 where he is currently dean of the College of Arts and Sciences and a Regents professor of physics. He has headed an active and productive research program concerned with inorganic solids and surfaces with particular emphasis on electrode surfaces, corrosion, and carbon fiber surfaces. Many of the projects have been undertaken in response to problems of direct relevance to industry and emerging technologies. He has served with the U.S. National Science Foundation and held several visiting appointments. His contributions were acknowledged by the award of a Regents professorship at Oklahoma State University in 2007, and a university distinguished professorship at Kansas State University in 1997 (where he currently has emeritus status), and the conferring of ScD by the University of Cambridge in the United Kingdom in 1995.

**Roger St. C. Smart** received his PhD in surface chemistry from the University of East Anglia (United Kingdom) in 1967 and has since worked at Flinders University (Adelaide), University of Papua New Guinea, and Griffith University (Brisbane). At the University of South Australia, he founded the SA Surface Technology Centre in 1987 and was deputy director of the Ian Wark Research Institute from its inception to 2002. Since August 2004, he has been deputy director of a new Applied Centre for Structural and Synchrotron Studies (ACeSSS) at University of South Australia (UniSA). His research interests over 35 years have encompassed surface chemistry and reactions of oxides, sulfides, minerals, ceramics, glasses, polymers, salts, and metals; surface spectroscopy; materials and biomaterials science; leaching and dissolution; nuclear waste disposal; solid-state reactivity; and adsorption in soil mineral systems. In recent years, he has been closely involved with industry in the areas of surface chemistry and modification of mineral and material surfaces in processing.

**Craig R. Tewell** obtained a PhD in physical chemistry from the University of California, Berkeley in 2002. He is a staff member at Sandia National Laboratories (SNL) in Livermore, California. Prior to joining SNL in 2004, he was a staff member at Los Alamos National Laboratories in New Mexico for two years. His main research interest is understanding helium bubble nucleation and growth in metal tritides.

**John Titchmarsh** received his PhD from the Department of Materials at Oxford University, where he subsequently carried out postdoctoral work on the development of field-emission scanning transmission electron microscopy and the characterization of defects in III–V semiconductor devices. In 1975, he joined the Fracture Studies Group at the UKAEA Harwell Laboratory where he worked on the development and application of imaging and analytical electron microscopy to studies of nuclear reactor materials, including temper embrittlement, void swelling, irradiation-induced transformation, and corrosion. He returned to academia in 1994 as the Philips professor of analytical techniques at Sheffield Hallam University until 1998, when he returned to the materials department at Oxford University as a Royal Academy of Engineering professor where he continued work on materials problems in the nuclear power field.

**Sven Tougaard** received his PhD (1979) and Dr. Scient (1987) in theoretical and experimental surface physics at the University of Southern Denmark (SDU), and did his postdoctoral work in the United States and Germany (1978–1984). He has been professor at SDU since 1984, where he founded QUASES-Tougaard Inc. (1994), which develops and sells software for chemical analysis of surface nanostructures by electron spectroscopy. His current research is in experimental and theoretical studies of phenomena induced by the electron–solid interaction at surfaces and in nanostructures, and in the development of practical experimental methods to determine the chemical composition and electronic properties of nanostructures by electron spectroscopy. He has conducted several EU-supported international projects on these subjects, published more than 160 scientific papers, and presented more than 50 invited talks at international conferences and workshops. He serves on the editorial board for *Journal of Electron Spectroscopy, Surface and Interface Analysis*, *Journal of Surface Analysis*, and *Surface Science Spectra*.

**Wolfgang E. S. Unger** is the head of the Surface and Thin Film Analysis Working Group at the Federal Institute for Materials Research and Testing (BAM), Berlin, Germany. He is the chairman of the Surface Analysis Working Group at CCQM/BIPM, the German National Representative of the VAMAS Technical Working Area on Surface Chemical Analysis, a convener of ISO Technical Committee 201 on Surface Chemical Analysis, and was the chairman of ECASIA '03. After studying physics at the Humboldt University in Berlin, he received a PhD in physical chemistry from the Academy of Sciences in Berlin in 1986. His major interests are nanoscale characterization of surfaces by x-ray photoelectron and absorption spectroscopy and by secondary ion mass spectrometry.

**John F. Watts** is a professor of materials science and director of the Surrey Materials Institute within the Faculty of Engineering and Physical Sciences at the University of Surrey. Applications of XPS, AES, and ToF-SIMS to investigations in materials science have been his principal research interests for more than 30 years. He received his PhD (1981) and DSc (1997) from the University of Surrey for his contributions to fundamental studies of adhesion phenomena using surface analysis methods. He is editor-in-chief of *Surface and Interface Analysis* and is a member of the organizing committees of the biennial ECASIA and SIMS conferences. He has published more than 300 papers in applied surface analysis and is a frequent lecturer in Europe, the Americas, and Asia.

**Matthias Werner** received his PhD in electrical engineering from the Technical University of Berlin, Germany in 1994. Since then he has acted as a technical consultant for the German engineering foundation VDI/VDE, in the general area of microsystem technologies, and has been the director of the Microtechnology Innovation Team of Deutsche Bank AG. In 2004, he became the managing director of NMTC (a consulting company on nano- and microtechnologies) and has advised many of the leading German players on the exploitation of nanomaterial-related products. He is the author and coauthor of approximately 100 scientific papers, book chapters, and books and has given numerous invited talks. He is coeditor of *mstnews*, the international microsystems magazine, and is a fellow of the Institute of Nanotechnology (IoN), United Kingdom, as well as a member of the National Strategy Group for the UK Micro/Nano Manufacturing Initiative.

**Robert K. Wild** received a PhD in physics from Reading University in England in 1966. After a brief period at the University of Virginia, Charlottesville, he returned in 1968 to the Research Laboratories of the Central Electricity Generating Board at Berkeley in England. Many of the activities were subsequently transferred in 1992 to the Interface Analysis Centre at the University of Bristol. His principal professional interests are in applying AES, XPS, and SIMS to the study of corrosion of steels, and effects of grain boundary segregation on iron- and nickel-based alloys for which he was awarded a DSc in 1990. He has published texts on the microstructural characterization of materials and the properties of grain boundaries. He was the chairman of the UK Surface Analysis Forum for 10 years from 1985, and in 1993 became secretary of the ISO Technical Committee 201 on surface chemical analysis SC7 XPS.

**Vaneica Y. Young** received her PhD in analytical chemistry in 1976 from the University of Missouri-Kansas City. She is now a member of the faculty in the Department of Chemistry at the University of Florida. Her major interests are the use of XPS to characterize ion-selective electrode corrosion, the structure of ion-beam-modified surfaces, and the structure of supported rigid rod polymer films.

**Zhaoming Zhang** received a PhD in applied physics from Yale University in 1993, after which she joined the research staff at the Australian Nuclear Science and Technology Organisation (ANSTO) in Sydney. Since then she has conducted a wide range of research activities, ranging from fundamental studies in surface science and bulk crystallography to more applied topics such as the development of nuclear waste form materials. She is now a principal research scientist in the Institute of Materials Engineering at ANSTO.

---

# 1 Introduction

*John C. Rivière and Sverre Myhra*

## CONTENTS

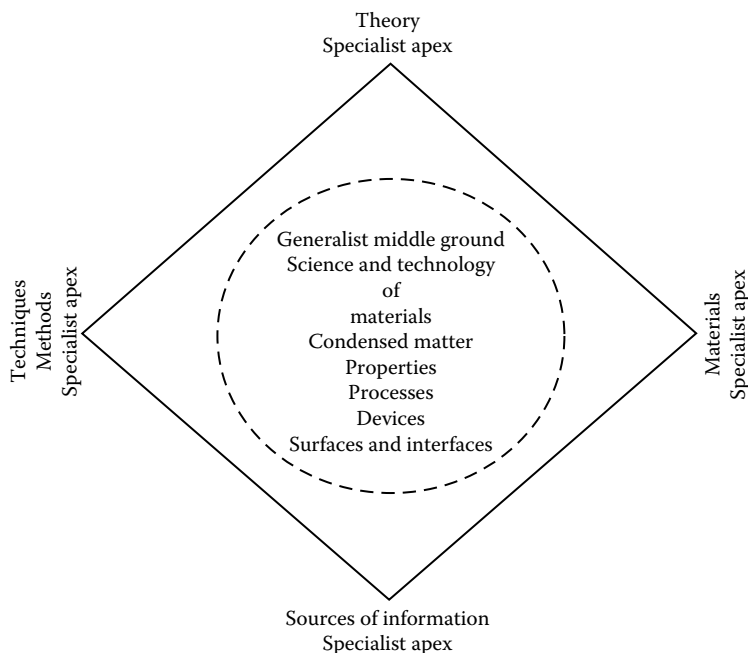
1.1	Spectrum of Practitioners and Activities .....	1
1.2	Trends in Surface and Interface Science.....	3
1.3	Intended Audience .....	4

In order to be able to describe the objectives of this book and the audience at which it is aimed, it is first necessary to consider the current situation in surface and interface science and technology.

### 1.1 SPECTRUM OF PRACTITIONERS AND ACTIVITIES

As in other mainly experimental fields, so in surface and interface science, there is a broad spectrum of approaches and activities. At one end of this spectrum are those whose sole purpose is either the development of new instruments and methods or the improvement of existing ones. Next to them, one finds another group of practitioners who have become expert in the operation and theory of a particular technique, or group of closely related techniques, and their expertise includes application of the techniques to almost any material problem. Moving to the middle, there is a wide and heavily populated band including all those who probably regard themselves more as material scientists than as surface scientists. They would be concerned either with the physical and chemical properties of a class of materials (e.g., polymers, high-tensile steels, etc.) or with a particular class of surface reaction (e.g., catalysis, corrosion, etc.), or with a particular type of application (e.g., nuclear fuel cladding, semiconductor interfaces, etc.). Those techniques would be chosen, which were known or believed to provide the required information and they would not necessarily be restricted to surface-specific techniques. Still further along the spectrum is another sizeable group investigating all types of reactions at interfaces between combinations of vacuum, gas, solids, and fluids, using model systems (e.g., single crystals or other well-characterized surfaces) and carefully controlled experimental variables. An increasingly important subset of that group is concerned with biomaterials and bio-interfaces. Within this group could be included those that are concerned with the development and testing of devices and products. Finally, at the other extreme, are those rare individuals who have managed to achieve a position in which they can devote their entire scientific career to the study of the properties of a single material or group of materials, at the most fundamental levels. They will need to deploy, as appropriate, all the available techniques, and even to invent new techniques to obtain specific information not otherwise forthcoming. The emergent group that falls under the broad heading of nanotechnology will need both to invent new techniques and methods, and to control experimental variables carefully.

As in all continuous spectra, there are no sharp boundaries between the categories listed above, and their activities merge into one another imperceptibly. Such categorization does not carry with it any value judgment. Those working in any one type of activity have much to learn from those in others, and all are necessary for the progress of surface science.



**FIGURE 1.1** Schematic compass-point representation of the generalist versus specialist description of the groups of practitioners that are concerned with, and contribute to the knowledge base of surfaces and interfaces. The broken line indicates a region of permeability for two-way flow of information and dialogue. Specialization in analysis and methods, materials, theory, and information reside at the four extreme points of the compass.

For many years now, the majority of those using techniques and methodologies for investigation of surfaces and interfaces have occupied the middle ground of the above spectrum. In Figure 1.1 is shown a compass-point schematic of the potential interactions between the specialists at the four cardinal points, that is, those working at or near the extremes of the above-described spectrum, and the generalists whose expertise, particularly on materials, is much broader than that of the specialists, but which is not as deep on many individual aspects. Thus, on the horizontal axis, information flows into the middle ground from the specialists concerned with techniques and materials, while on the vertical axis, the flow contains information arising from theory and gleaned from sources. The position of the purpose of this volume is therefore on the horizontal *E–W* axis, to the west, or left of the vertical *N–S* axis: that is to say, at the point where those specializing in techniques for the characterization of surfaces and interfaces are communicating with those generalists in the broad area of the science and technology of materials. While the principal aim of this volume is to inform the group of practitioners that occupy the middle ground, it is believed that it will also be of considerable value to audiences that reside to the north and the east of the middle ground. Unfortunately, it is often the case that the theoreticians produce outcomes to calculations that cannot be tested experimentally, while the experimentalists tend to produce data for systems that cannot readily be modeled with any degree of confidence. It is also the case that many “specialist” experimentalists prefer to work on model systems under ideal conditions (e.g., ultrapure single crystal Cu at liquid He temperature), while the “generalist” material scientist/technologist has to contend with less ideal and more complex systems under real conditions. The point of these observations is that a secondary objective of this volume is to bridge the gap between the specialist and the generalist. In this sense, the specialist might find the volume useful.

## 1.2 TRENDS IN SURFACE AND INTERFACE SCIENCE

There are other trends in surface science that need to be considered and accommodated. They can be described loosely as instrumentation, commercialization, and rationalization, and they are all highly interdependent.

Virtually all practitioners in surface and interface science now rely on the instrumentation packages supplied by the manufacturers, although over a period of time, minor in-house modifications and additions will put an individual stamp on any one instrument. This is certainly the situation for the mature surface-specific techniques (e.g., x-ray photoelectron spectroscopy [XPS], Auger electron spectroscopy, and secondary ion mass spectrometry) and the well-established electron-optical microscopies (transmission electron microscopy [TEM], scanning electron microscope [SEM], and the ancillary analytical attachments). Even the more recent scanning probe microscope (SPM) techniques are now based on instrumentation from commercial sources. An important additional trend is that many techniques are located elsewhere at large international facilities (e.g., synchrotron radiation and neutron diffraction sources). Such facilities are becoming increasingly important due to improved access for outside users, their high productivity, and their routine availability of techniques that cannot be supported by local facilities (e.g., extended x-ray absorption fine structure [EXAFS]).

With this achievement of maturity, the technical simplicity has been lost, but there has been a gain in safety, ruggedness, reliability, and automation. For instance, the latest generation of dedicated XPS instruments requires few other experimental skills than being able to load the specimen and use the software. Indeed, some instruments (e.g., SEM and atomic force microscope) can now be made accessible to all-comers, within reason, rather than being under the control of an operator. An important consequence of this is that day-to-day operation of a major instrumental facility may require only the occasional presence of a senior and experienced specialist staff member. Most of the activities can be either under the direction of an operator with background and expertise closer to the technical level, or in the hands of a generalist user of techniques. Intervention by the specialist is then more with matters of interpretation and of the generation of ideas, whenever appropriate. However, the user, who may know very well how to run the instrument, cannot also be expected to know how to deal with every single type of sample that is presented for analysis, in terms of initial preparation and handling, precautions to be taken, range of techniques to be used, and operational parameters for data acquisition. The specialist may not always be available, or may in some laboratories be nonexistent, and in any case, his/her experience is not likely to be encyclopaedic. The user needs a guide that will explain the procedures to be followed when confronted with an unfamiliar material or requirement, based on the experience of others in dealing with such materials, rather than a textbook on techniques *per se*.

The trend toward the deployment of fewer specialists at the operational and instrumental fronts has been given even greater impetus by commercial pressures. With the increasing maturity and sophistication of the techniques, in particular the now-taken-for-granted power of software packages for instrument control, data acquisition, and analysis, has come the possibility of using them in rapid turn-around modes, for troubleshooting and even for online quality control. To be effective in such modes of operation, which become basically part of a production line, the cost per analysis must be minimized. This implies not only high reliability, since both the capital outlay and the cost of maintenance are great, but also low operational costs; thus, the salary and attached overheads of the operator, which form a significant fraction of such costs, need to be kept down. Hence, the increasing reliance on multiskilled generalist staff in the R&D environment. The requirement for budgetary flexibility is another factor. It is becoming increasingly rare that research budgets can underwrite the cost of maintaining permanent staff. It is rather more common that the bulk of the staffing is funded by soft money. Consequently, there will be high turnover of personnel, and less capacity to build up and retain expertise in depth and breadth.

Yet another factor in the cost-and-time-effective equation comes from the need for the rational deployment of techniques and personnel. The growing and desirable tendency to pursue a holistic



approach in general material analysis means that analytical activity of sufficient significance, be it a technological research program or an online facility, requires access to a range of techniques in order to obtain complementary information. Decisions then have to be made about which techniques should be used, and whether any or all of them should be available in-house. The delicate balance to be struck is between purchase and operating costs on the one hand, and the cost of subcontracting analysis to one or other of the various fee-for-service analytical centers on the other. Such rational decision-making can be carried out only by those with a basic understanding of a broad range of techniques if an effective choice is to be made. However, also woven into the matrix of this choice is the matter of human resources. The desired minimization of operating costs, as already mentioned, means that the earlier luxury of having an expert attached to each technique or instrument can no longer be afforded. As a result, the available personnel must become multiskilled, that is, able to move from one technique or instrument to another as the analysis requires. There is a price to pay for multiskilling, in that the operator is unlikely to have the deep expertise of the dedicated expert in any one technique, but against that can be set much greater flexibility in deployment over a range of disciplines. Further benefits are that the likelihood of making a correct decision over choice of technique is much enhanced, and that the crossing of disciplinary boundaries will result in improved cross-fertilization of ideas.

Finally, the demographic situation within the broad field needs to be considered. Most of those scientists who grew up with the development of surface analysis and SEM/TEM in the 1960s have either retired or have moved into managerial/executive positions. Hence, there is a generational transition in which a new cadre is entering an already mature field, but is subject to entirely different imperatives. In addition, a new generation has embraced SPM and synchrotron techniques. Part of the rationale for this book is in the area of information transfer from one generation to another. The intention is to speak to members of an audience at the early stages of their careers, rather than to the founding fathers and mothers.

### 1.3 INTENDED AUDIENCE

The upshot of the foregoing is that there is a large group within the surface science community consisting of those working mostly in industrial laboratories or in analytical service centers, whose job it is to provide reliable and relevant answers to problems involving surfaces and interfaces with rapid turn-around and at relatively low cost. They will know enough about the nature of the information obtainable from some techniques, surface-specific and otherwise, to be able to decide which ones to use or not to use, and will know how to deploy them to best effect. They will not in general have sufficient in-depth background, and certainly not the time, to be able to engage in long-term basic research. Although many might well have expertise in one or more areas of materials science, the nature of their work is such that they are liable to meet at any time a material or a problem from a totally unfamiliar area. It is the members of this group at whom this book is aimed, in an effort to provide them with a guide to the strategies to be adopted when they do come up against something unfamiliar.

Tertiary education institutions are no longer immune to the dicta of efficiency, productivity, and flexibility. Not so long ago, it could be assumed that senior academic staff would devote most of their time and energy to research and the two-way teaching and learning process. As a consequence, research students and postdoctoral researchers would gain insight through lengthy one-to-one interactions in the laboratory with an academic supervisor. Regrettably, most academic supervisors are now increasingly preoccupied with fund-raising, administrative duties, and responding to corporate imperatives. This book is thus intended also as a complement and, in some cases, an alternative to traditional methods of learning for researchers at the formative stages of their careers.

The general thrust of this volume will be a description of the technical, methodological, and phenomenological aspects of surface and interface analysis, in the course of which an attempt will be made to chart the most efficient paths from an initial question to a credible answer, for a series of

generic problem areas. There will be less concern with the many techniques as ends in themselves and more as a means to an end. Since this approach is an inversion of the more usual one of first describing a technique and then giving examples of its application, it can be thought of as a top-down approach, which has been shown to be effective in many other areas. In view of the ways in which an increasingly large number of workers in the field operate, the structural inversion seems logical.

From the above, it may be deduced that the structure of the volume is reminiscent of that of an expert system. Starting with some of the most general materials science questions that could arise in surface/interface science and technology, the user is guided to ever more detailed and specific levels of questions, the choice of path between them being based on the experience of experts. There are descriptions of the principal techniques, but not in nearly such great detail as may be found elsewhere; the intention is simply to help the user toward a preliminary choice of techniques. The reader is directed to whichever chapters are appropriate to the particular problem, and find there much essential information, a recommendation for the most productive methodologies, and an indication of the likely answer, in phenomenological terms. Throughout there is an emphasis on the multiskilling approach, by the demonstration in each chapter of how the information provided by one or more of the traditional surface-specific techniques is complemented and reinforced by that either from some of the less common techniques or from the so-called bulk techniques.

The chapters fall neatly into a set of three modules. This and the next chapter are introductory, one to the aims and objectives of the book and the other to the principles of analytical problem-solving. Chapters 3 through 9 describe the tools of the trade, how to use them, when and when not to use them, what information they provide, how to quantify that information, etc. Finally, Chapters 10 through 19 represent an authoritative distillation of the expertise and experience of authors, each of whom is a specialist in the application of surface analytical and complementary techniques to a particular subject area.

Some readers may wish to consult Chapter 2, in order to inform themselves about the strategy and tactics of problem solving. Some may wish to skip the introduction module and go straight to Chapters 3 through 9, others, perhaps of less experience, will benefit from some introduction. Those who already have significant instrumental (i.e., tool-kit) experience will no doubt bypass the tool-kit module and proceed directly to the specialist module. Several variations are therefore possible. Whatever the level of experience, however, and whatever the route chosen, the objective is to provide a practical guide to methods of the solving of problems of surfaces and interfaces. The authors hope that this book will fill the need that they have perceived for such a guide.



---

# 2 Problem Solving: Strategy, Tactics, and Resources

*Sverre Myhra and John C. Rivière*

## CONTENTS

2.1	Introduction .....	7
2.2	Materials, Size Scales, and Dimensions .....	8
2.3	Strategy and Tactics of Problem Solving .....	9
2.3.1	Identification of the Problem and Formation of an Initial Hypothesis .....	10
2.3.2	Identification of the Essential Variables .....	10
2.3.3	Reduction of the Problem as far as Possible without Losing Essential Information .....	10
2.3.4	Selection of the Techniques Likely to Provide the Crucial Information by the Most Reliable and Economic Route.....	11
2.3.5	Choice of Methodologies Consistent with the Selection of Techniques.....	11
2.3.6	Acquisition and Processing of Data of Adequate Quantity and Quality .....	11
2.3.7	Interpretation of the Data.....	12
2.3.8	Review and Evaluation, and Iteration If Necessary.....	12
2.3.9	Presentation.....	12
2.4	Tactical Issues in Problem Solving for Surfaces and Interfaces .....	12
2.4.1	Specimen Handling, Preparation, and Configuration.....	13
2.4.1.1	<i>Ex-Situ</i> Preparation .....	13
2.4.1.2	<i>In-Situ</i> Preparation .....	13
2.4.1.3	Specimen Configuration.....	15
2.4.2	Technique Destructiveness .....	16
2.4.2.1	Functionality Criterion.....	16
2.4.2.2	Market Value Criterion .....	16
2.4.2.3	Sequential Analysis Criterion .....	16
2.4.2.4	Information Volume Criterion .....	16
2.4.3	Quality Assurance, Best Practice, and Good Housekeeping.....	17
2.5	Notes on Acronyms and Jargon .....	17

## 2.1 INTRODUCTION

The approach taken in this book assumes that while some readers will already be expert in many aspects of problem solving, others will either be novices or at an early stage on the learning curve. For the latter readership, this chapter sets out the strategic and tactical issues of problem solving, with the focus mainly on traditional surface and interface analysis, but with additional emphasis on the emerging and important field concerned with science and technology on the nanoscale. The successive stages that go to make up the problem-solving route are described together with the associated thought processes, many of which are intuitive for the more experienced practitioners.

## 2.2 MATERIALS, SIZE SCALES, AND DIMENSIONS

In the interrogation of any system in any scientific discipline to obtain information about that system, at least three components are necessary: a stimulus, an interaction volume in the system that responds to the stimulus, and a means of gathering the information generated within that volume as a result of the stimulus. Since not all the information will necessarily be able to be gathered, there is also an information volume, by definition equal to or smaller than the interaction volume. The shape and size scale of the information volume define the lateral and the depth spatial resolutions, over which there will be some averaging of information. For instance, imaging x-ray photoelectron spectroscopy collects information with microscale lateral resolution, but with a depth resolution of only a few interatomic distances, while scanning transmission microscopy has a lateral resolution in the nanometer range and a depth resolution limited by the thickness of the specimen foil. At one extreme is scanning tunneling microscopy performed in ultrahigh vacuum (UHV) where the information volume approaches that of a single atom in the surface.

In practice, all condensed matter objects, irrespective of the size scale, are bounded by a surface. This surface acts also as an interface due to something else being contiguous. (A number of permutations are possible and relevant, such as solid–solid, solid–liquid, solid–gas, liquid–gas, etc.) Any interactions at the boundary are usually defined by the physical and chemical conditions at the interface. As the size reduces progressively toward the nanoscale region, the interactions are dominated increasingly by surface and interface effects and in the limit converge to those characteristics purely of a surface. With these thoughts in mind, it is instructive to consider the dimensionality of objects in the context of the size scale (Table 2.1).

An important additional category is that of two-dimensional (2D) structures whose overall sizes are on the micro- or mesoscale, but whose surfaces exhibit lateral order on the nanoscale. Examples include arrays of quantum wells, crystalline polymers, zeolites, Langmuir–Blodgett films, etc. A subset includes bio-membranes, which are sometimes referred to as being para-ordered (due to the contiguity of biopolymer chains). The analysis problem is then that of needing to describe lateral differentiation, and structure, on the nanoscale, even though the surface/interface is meso/micro in lateral extent.

In some situations, mostly in basic research, it is the information generated only within the quasi-2D volume itself, for example, a surface layer or an embedded nanoparticle, that is of interest; that is, the analysis is concerned with conditions in that volume in isolation, as it were. When dealing with solids, however, it is not often that the properties of a surface layer, or an embedded

**TABLE 2.1**  
**Dimensionality and Size Scale**

Dimensionality	Size Scales <sup>a</sup>	Analytical Implications and Context
3D	All micro/macro	Bulk analysis of a solid
2D	One nano, two meso/micro/ macro	Traditional methods of thin film, and surface and interface analysis/characterization
1D	Two nano, one meso/micro/ macro	Traditional techniques require extension and adaption Examples include nano-wires, nanotubes, biomolecular strands, etc.
0D	All nano/(meso?)	Novel techniques are required. Examples include nanoparticles and single quantum wells

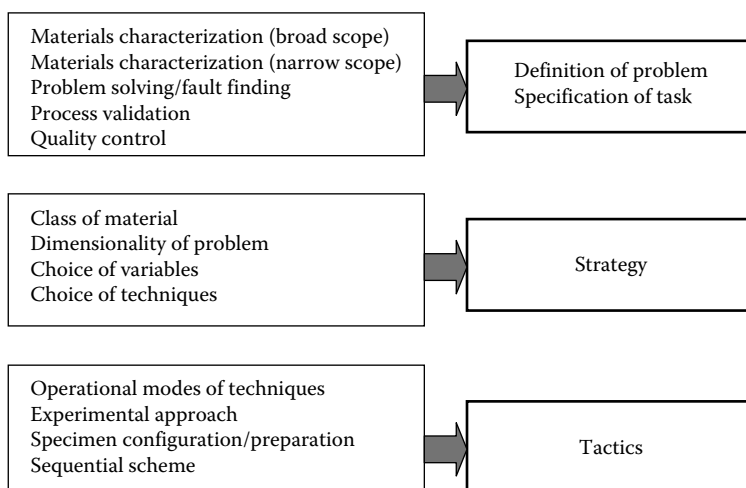
<sup>a</sup> The boundaries between regimes of size scales are ill-defined; that is, there is no general rule as to when one departs the micro-regime and enters the nano-regime. Thus, it is useful to use the term “meso” to describe the gray area between nano and micro.

particle, can be considered without reference to the same properties of regions further away, such as a substrate or a surrounding matrix, that is, beyond the shortest (atomic scale) dimension of the information volume. This is so because some properties of the surface depend on what is happening, or has already happened, in those remoter regions, generally termed the “bulk” of the solid. Even in homogeneous solids, there may be internal interfaces of many types such as phase boundaries, grain boundaries, artificially created compositional and structural interfaces, etc. In principle, it is clear that the presence of a surface must imply the existence of an interface, even if the latter is only with the UHV or other environment. The attributes of interfaces are of crucial importance to the behavior of the solid from both surface and bulk aspects, and need to be accessible for analysis. Since the interfaces are themselves effectively quasi-2D volumes, analysis of their attributes should ideally be undertaken by surface-specific methods, or by cross-section electron microscopy. However, they are of course internal and therefore, in current jargon, buried; how to gain access to them for analysis without at the same time causing perturbation leading to ambiguity is still a central question in surface and interface analysis problem-solving. (For purposes of the present discussion, the term “attributes” is being used to describe such things as topography, composition, structure, crystal-chemistry, etc, as opposed to the term “properties”, which is reserved for more intrinsic characteristics, such as density, resistivity, etc. There is a gray area between the two terms.)

It should be clear from the above that the traditional surface and interface analysis for 2D objects can be considered to be a mature field, as evidenced by a rich literature and by reasonably well-established codes of best practice and quality assurance. Likewise, the state of the art for 3D objects on the macro- and microscales is well established and proven. The situation is much less satisfactory for lower dimensional objects on the sub-microscales, because in order to attempt to study them, traditional techniques are being pushed beyond their agreed limits of utility. In the limit, on the meso- and nanoscales, new techniques are being explored and practitioners are still feeling their way along the learning curves.

### 2.3 STRATEGY AND TACTICS OF PROBLEM SOLVING

The logical sequence described below, and summarized in Figure 2.1, is not specific to problem solving by any particular technique or for any particular material, but could be applied to problem



**FIGURE 2.1** Schematics of sequence for problem solving.

solving in any branch of material science. In general, it is assumed that material characterization is concerned principally with attributes, as defined above, which may then provide the basis for determination of property.

The block diagram describes the general problem-solving process in a sequential manner. The schematics suggest a linear progression. In most cases, however, it is important to engage in quality control of the process itself, by asking appropriate questions. It might be necessary to backtrack through one or more iterations until one is satisfied that the correct sequence is being followed. The details of the process may differ if the focus is on problem solving as an activity for which a narrowly defined outcome is desired, as opposed to a broader program of investigation, dealing holistically with a particular material, device, or process. There are obviously many common elements, and also some significant differences. Some of the most important issues, alluded to in the block diagram in Figure 2.1, are discussed below. A hypothetical example, assuming a traditional surface analytical approach, has been used for illustration.

### **2.3.1 IDENTIFICATION OF THE PROBLEM AND FORMATION OF AN INITIAL HYPOTHESIS**

A typical example of a problem might be the peeling of Teflon from a pan, for which the initial hypothesis might be failure at the interface. When a technological problem occurs, it will normally be up to the person or the organization suffering the consequences of that problem to identify its nature and to initiate a process of remedy. To do that they, as customers, need to commission one or more analysts to provide both relevant and reliable analytical data to enable them to reach a resolution of the problem via the building up of an overall picture. Preliminary consideration of the nature of the problem may have suggested a hypothesis as to the reasons for its occurrence, and the types of analysis initially chosen are then based on that hypothesis. On the other hand, there may have been no clues arising from the way that the problem first occurred, and a working hypothesis in that case has to wait for the results from analysis used in either shot-in-the-dark or intuitive manners. With increasing experience, intuition can become surprisingly accurate. Experts in problem solving develop the ability to propound successful hypotheses based either on intuition or on very scant information.

Often the analysts are merely providers of data and it is the customer who works toward the solution. More interesting for the analyst, and usually more rewarding for the customer, are those instances in which the analyst is allowed to play an interactive role in the entire problem-solving sequence. Such interaction can often lead to short cuts, and therefore savings in cost, in the sequence.

### **2.3.2 IDENTIFICATION OF THE ESSENTIAL VARIABLES**

An example of this is the composition at the Teflon/pan interface. Once the problem has been identified and a preliminary hypothesis set up, the nature of the information required, based on that hypothesis, can also be identified. From that, it is a short step to deciding what can actually be measured experimentally to provide that information, that is, the essential variables. Practicalities enter here, and indeed at many other points in the sequence, in that the customer will naturally be seeking the maximum amount of information at minimum cost.

### **2.3.3 REDUCTION OF THE PROBLEM AS FAR AS POSSIBLE WITHOUT LOSING ESSENTIAL INFORMATION**

Examples of this are: disregard bulk composition of substrate, and concentrate on interface composition. Although in basic research on model systems there is usually complete freedom of experimental design, in the real world the problems are too complex to be able to solve in the same complete sense. Life is too short and available finance is strictly limited. In any case, the materials

associated with problems, and often the problems themselves, may be ill-defined, with possible hidden variables. It is vital at this stage in the sequence to avoid the temptation to start analysis at once, since the result may simply be to end up with a mass of irrelevant or even misleading data. The most important step in the art of problem solving is pinning down what is the crucial experimental variable that must be measured, and to that end all relevant background information on the system giving rise to the problem should be used. Such information might include the bulk compositions of constituents, any chemical or physical pretreatments, dopant concentrations, ambient atmosphere, etc. It is necessary for the customer and the analyst to have full discussions so that no pieces of the information jigsaw are overlooked.

### **2.3.4 SELECTION OF THE TECHNIQUES LIKELY TO PROVIDE THE CRUCIAL INFORMATION BY THE MOST RELIABLE AND ECONOMIC ROUTE**

For example, x-ray photoelectron spectroscopy (XPS) might be a good choice, but Auger electron spectroscopy (AES) and static secondary ion mass spectrometry (SSIMS) would be poor choices. Not many institutes or organizations can offer the full range of analytical instrumentation and expertise, and most only a subset of that range. Where there are only a few techniques available in-house, there is an understandable tendency not only to try to apply them regardless of suitability or otherwise, but also to push individual techniques beyond their limits of reliable and efficient function. That tendency must be resisted. In the long run, uncritical application of the same few techniques to the attempted solving of every analytical problem that comes along is counterproductive, in that for many problems the information and data produced are quite inappropriate to the solution. The techniques must be matched to the crucial information, or the whole process becomes nonsensical; if the necessary technique is not available in-house, then it must be sought elsewhere.

### **2.3.5 CHOICE OF METHODOLOGIES CONSISTENT WITH THE SELECTION OF TECHNIQUES**

Examples of this are: use large sample area for XPS, avoid obscuring contamination, and comparing data from failed components with those from control specimens. Once the choice of necessary techniques has been made, then details such as the way in which the techniques must be used to produce the crucial information, and any precautions that must be taken to avoid ambiguity in interpretation, have to be decided. In many problems, vital clues can be extracted from good vs. bad or before vs. after analytical comparisons, which require control specimens. There is also the ever-recurring and vexed question, referred to earlier, of how to access buried information. Here practicalities enter again. The customer may decide that solution of the problem can be achieved only by such access, but he/she must then be made aware not only that extra time, and therefore money, are involved but also that the mechanics of obtaining access, typically by ion bombardment to removal material, may change the nature of the information irretrievably. There is no firm and final answer to that situation; every sample and problem has to be considered individually, and the pros and cons weighed up.

### **2.3.6 ACQUISITION AND PROCESSING OF DATA OF ADEQUATE QUANTITY AND QUALITY**

Some examples of this are: energy resolution, signal-to-noise ratio, scan widths required for background subtraction, etc. At this point, the analysis can actually be started. Unless the data are of a minimum quality necessary for correct interpretation, they will not help toward solution of the problem. By this is meant that they must be good enough to disprove a preliminary hypothesis if necessary, and lead to alternative hypotheses, rather than being of just sufficient quality to support the preconceived hypothesis. The level of quality required is a function of the nature of the crucial information sought, and will vary from problem to problem.



### **2.3.7 INTERPRETATION OF THE DATA**

In the interpretation of data typical questions to be asked are: are the results consistent with hypotheses and with other experimental evidence, are they credible, are they reproducible, and if so, at what confidence level? In an ideal situation, there would be abundant data of high quality obtained from several complementary techniques, requiring fairly minimal and straightforward interpretation. In practice, the situation may be constrained to be far from ideal and interpretation must be undertaken carefully and realistically. The more direct and transparent the interpretation, and the greater the extent to which it is compatible with prior information about the problem, the more likely it is that the conclusions from it will be of use to the customer. The main hazards at this stage are that the interpretation is wrong, or irrelevant to the problem.

### **2.3.8 REVIEW AND EVALUATION, AND ITERATION If NECESSARY**

Examples of these are that the data have been misinterpreted, or in hindsight emphasis should have been put on other variables, or the customer asked the wrong questions in the first place. This is one of the most important stages in the whole sequence, and should be taken seriously. Both individual and institutional credibility are at stake, as is perhaps the long-term viability of the institute or organization in the problem-solving field. A lifetime of carefully nurtured reputation and customer relationships can be undone so easily by one or two shoddy jobs. It is far better, if in doubt, to perform additional measurements and analyses before a report is submitted to the customer.

### **2.3.9 PRESENTATION**

To-the-point reports, false color maps, succinct and adequately descriptive captions, and easy-to-follow conclusions are more useful to the customer than lengthy explanations, particularly if the essential conclusions have to be presented to management. Of course a report must be accurate, factual, relevant, and complete, but its essential messages must be transparent to the relatively nonexpert reader without, for instance, descending into the excessive use of jargon. Nowadays, with so many excellent computer packages available, there is no excuse for submitting a report without substantial visual impact. In addition, it is perfectly possible to assemble data from several different techniques for incorporation into an overall report. With the trend toward full digitization of output, including even high-resolution images, full flexibility of composition, layout, and mode of presentation can be achieved.

The sequence described above suggests that the scope of problem solving is limited to the support of R&D in an industrial setting. However, the ambit of this book is wider than that. For instance, the emphasis in strategic research may be either on a broad characterization of a particular class of material or on the investigation of a generic variety of surface/interface reactions. In both of these, the need is for completeness, which can be achieved only by adopting an integrated approach exploiting complementary techniques and methodologies. Another area in which surface/interface analysis has much to offer is that of quality control. There the emphasis is on demonstrating that the relevant variables are indeed being controlled, and that a process technology remains constant over time. Also, it must be remembered that a significant fraction of surface/interface analysis is carried out within the tertiary education sector by central facilities providing a variety of services for academic customers. The sequence thus includes a component of technology transfer, in the sense that both providers and customers are engaged in a teaching and learning endeavor, as well as a problem-solving process.

## **2.4 TACTICAL ISSUES IN PROBLEM SOLVING FOR SURFACES AND INTERFACES**

Up to now, the discussion and description of the logical sequence of problem solving has emphasized strategic issues. What follows below are some general observations on some of the tactical

practicalities that have to be taken into account. Most of the points are described, often in greater depth and breadth, in subsequent chapters, but it is useful at this stage to provide a general overview. The examples given are illustrative, rather than exhaustive, and are framed in the context of surface analysis.

### 2.4.1 SPECIMEN HANDLING, PREPARATION, AND CONFIGURATION

Whether surface characterization is being used in the context of basic science, in which both the origin and history of the specimen are known, or whether it is applied in problem solving, where the specimen is likely to arrive in a much less well-defined state, the first essential requirement in dealing with the specimen is cleanliness. This should be obvious from the extreme surface specificity of most surface analytical techniques, but must be emphasized nevertheless. Even though specimens exposed to the ambient atmosphere or subjected to various pretreatments carry surface contamination, it is vital not to add to or alter that contamination by manual contact or by any other contact that might cause transfer of material onto the surface. For the same reason, the environment in which the analysis is performed should be such that it cannot contribute to the contamination, that is, the ambient should be oil-free and in the UHV region of pressure.

One of the reasons for avoidance of any alteration to the existing contamination layer is that there will be instances where some or all of the information needed for solving a problem may actually reside in the nature of the contamination itself. These instances might arise, for example, in tribology, adhesion, or corrosion. It is in any case essential to carry out an analysis of the specimen in the as-received condition, if for no other reason than to establish the extent of the contamination and therefore to be able to decide on subsequent procedures.

Specimen preparation and treatment can take place either outside the vacuum envelope of the analysis system, that is, *ex situ* or, within the system, *in situ*. *Ex-situ* preparation could be either in the uncontrolled laboratory ambient or in a controlled atmosphere, while *in-situ* preparation and treatment could be either in the analysis position itself or in an associated chamber.

#### 2.4.1.1 *Ex-Situ* Preparation

In surface and interface problem solving, most specimens will have originated from an external source, that is, the customer, and therefore by definition they will have had some *ex-situ* preparation or treatment, if only as a result of transfer from their original environment to that of analysis. However, that is not what is really meant by *ex-situ* preparation. Many analytical techniques in materials science, those that can be classified as providing bulk analysis, require preparation of the specimen by methods such as polishing, abrasion, and sectioning. These can also be used in the preparation of specimens for certain types of surface analysis, but of course the cleanliness requirements are much stricter than in preparation for bulk analysis. For example, lubricating or cutting liquids cannot be used, because they will leave residues on the surface, while exposure to polar fluids may degrade the surface. In addition, any debris left on the surface after such *ex-situ* methods have been used should be removable by ultrasonic cleaning in a bath of high-volatility solvent. The usual reason for employing such aggressive methods is to expose a buried interface located at a depth too great to be reached by *in-situ* methods.

#### 2.4.1.2 *In-Situ* Preparation

Once inside the analytical system there are many types of preparation or treatment of the specimen that might need to be carried out in the course of any one problem-solving procedure. They fall into the approximate categories of cleaning, depth profiling, interface exposure, and surface treatment.

The most common method of removing surface contamination is by ion beam erosion, normally with energetic  $\text{Ar}^+$  bombardment. By adjusting the ion energy and by using a low ion dose (roughly

equivalent to about one incident ion per surface site), it is possible to remove just the first one or two atomic layers, which usually consist of contamination. The cycles of alternate erosion and heating to achieve perfect cleanliness of a specimen, used in basic research, are clearly inappropriate to specimens involved in problem solving since the information content would be lost immediately. However, cleaning by gentle ion beam erosion (without heating) is convenient and reliable, and is the most widely used method largely because for the vast majority of specimens there is no alternative. One or more ion guns are therefore mandatory accessories on most surface analytical installations. The principal disadvantages of a technique in which relatively heavy charged particles such as  $\text{Ar}^+$  are accelerated to impact on a surface are structural and chemical damage, mentioned in more detail below (see additional discussion in Chapter 10).

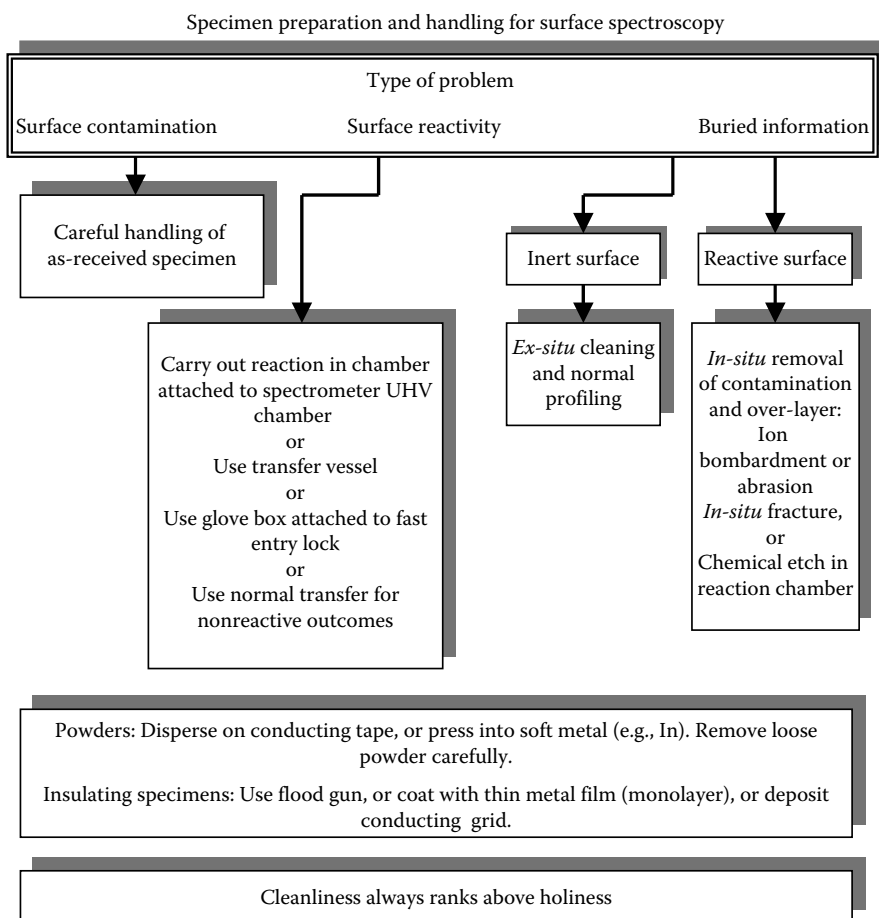
In a few special cases, *in-situ* cleaning can be performed by mechanical means. It is possible to fix special tools to the end of an auxiliary manipulator arm so that the operations of abrasion (with a diamond file) or scraping (with scalpel or razor blades), or even cleavage (with razor blade or chisel) can be carried out. When abrading or scraping, care must be taken that material from one surface is not transferred to the next.

As well as for cleaning, as mentioned above, ion beam erosion is used very extensively for the (relatively) controlled removal of material to allow analytical access to regions of the specimen beyond the surface information volume. Erosion and analysis can be either simultaneous (e.g., when using AES) or sequential (e.g., when using XPS); in both cases, the plot of elemental concentration as a function of amount removed is called a depth profile. Examples of depth profiles abound in the literature and there are several in this book. Also in this book in various places (i.e., Chapters 3, 10, 16, and 18), the deleterious effects to be expected from ion bombardment of a surface are described. The latter arise from unavoidable knock-on structural and chemical damage, which disrupts the surface crystal structure and alters the electronic structure. In addition, for a multiatomic specimen, as most are, the removal of surface species by the ion beam is selective, so that some species are enriched and others depleted as the eroded face progresses into the specimen. As a result, there may be selective desorption, interlayer mixing, and the appearance of sub-valent species and non-stoichiometry. For more details, see the above-mentioned chapters. Unfortunately, there is as yet no realistic alternative to ion beam depth profiling, particularly in the realm of problem solving, and the best that can be done is to be aware of the effects and to attempt to account for them in a semiquantitative way. In the case of transmission electron microscopy, focussed ion beam milling is now becoming a widely used tool for preparing specimens (see Chapters 5 and 9).

If internal interfaces are also regions of structural weakness, they can often be exposed for analysis by mechanical methods. The classical example is that of grain boundaries in polycrystalline metals that have been weakened as a result of impurity segregation to them following heat treatment. The boundaries can be exposed by fracture of the metal, usually at low temperatures, but any attempt to measure the nature or level of the impurity by fracture *ex situ* will always be unsuccessful because of the reaction of the impurity with ambient air and of the accumulation of contamination. Thus, there are many available designs of fracture stage for use *in situ*, mostly for impact fracture but some for tensile fracture. The stages can also be used for ceramic fracture, since there are instances in which ceramic materials also lose cohesion through the presence of grain boundary impurities.

In special cases, for example, in adhesion and in thin oxide film studies, it may be possible to expose the interface of interest by peeling techniques (see Chapters 18 and 19). Devices designed to do that are usually constructed individually and are not normally available commercially, unlike fracture stages.

Finally, *in-situ* preparation includes also all those treatments used from time to time to try and create on a specimen the same surface condition as might be found after some technological treatment or other. Since it is normally undesirable to carry out such treatments in the analysis chamber itself, many instruments have an additional chamber, communicating with but isolatable from the analysis chamber, in which the treatments can take place. Indeed, it is increasingly common to incorporate analytical techniques into processing lines, such as those used for chemical vapour deposition (CVD)



**FIGURE 2.2** Overview of specimen handling and preparation for surface specific analysis.

and multilayer epitaxial deposition. According to what is required, the additional, or reaction, chamber might therefore be equipped with the means of heating or cooling the specimen, or of exposing it to a gas or mixture of gases via a metered gas handling system, or of depositing thin films of one or more materials on its surface, or of causing alterations in its surface by ion implantation or plasma discharge. Many of these treatments are described in various places in this book.

The main points of specimen handling and preparation for surface-specific analytical techniques are summarized in Figure 2.2. Similar flowcharts of greater or lesser complexity can be constructed for other techniques and types of applications.

### 2.4.1.3 Specimen Configuration

Just because in some techniques (e.g., scanning tunneling microscope) the quasi-2D interaction volume is exceedingly small does not mean that the specimen configuration itself has to be small. Since specimens have to be positioned and oriented with the naked eye, and handled in so doing with, for example, clean high-quality tweezers, it follows that they are all macroscopic. In addition, many of the surface analytical techniques, when used in routine fashion, are macroscopic in two of the three dimensions of the interaction volume; SSIMS and XPS in their nonimaging forms are good examples.

Despite the above statement, the analyst engaged in problem solving is not infrequently presented with nonstandard specimen configurations, which require ingenuity and inventiveness if a representative analysis is to be achieved. Examples of such difficult specimens are powders, carbon and polymer fibers, biomaterials, and microelectronic circuits; again, these are mentioned in this book in the appropriate chapters, where ways of presenting them for successful analysis are described.

### **2.4.2 TECHNIQUE DESTRUCTIVENESS**

According to basic physics, any measurement process is irreversible; in that very fundamental sense, then, no measurement technique can claim to be nondestructive. In the world of practical problem-solving, however, such a limitation can be set aside as being too rigid. Given that all the surface analytical techniques can be destructive to greater or lesser extents, a pragmatic approach must be adopted. Depending on the constraints applicable to any particular problem or to a particular type of specimen, a set of functional criteria can be set up to classify techniques and procedures in terms of their potential destructiveness as follows:

#### **2.4.2.1 Functionality Criterion**

If the intended functions of a specimen or material are unaffected by the problem-solving process, then the techniques and methodologies required to solve the problem can be said to be nondestructive.

#### **2.4.2.2 Market Value Criterion**

Using “market” here in its broadest sense, if the market value of an object is not reduced by the problem-solving process, then the process can be said to be nondestructive. There might even be a gain in value as a result of the analytical procedure, which would be offset against any loss arising from possible destructiveness. Further, if there is a set of nominally identical items, it is possible that the loss in value of those that are analyzed and perhaps irretrievably damaged would be more than made up by the gain in value of the remainder as a result of the information acquired (e.g., due to demonstrable quality control).

#### **2.4.2.3 Sequential Analysis Criterion**

When using a multi-technique approach to problem solving, care must be taken that the application of one technique to a specimen does not jeopardize the validity of subsequent analyses by other techniques. Under this criterion, if that validity is unaffected, then the technique first applied can be said to be nondestructive. The criterion puts obvious constraints on the sequence in which techniques should be used, beginning with the least destructive and ending with the most. A corollary of this criterion is that in cases where there are continuing *ex-situ* or *in-situ* specimen treatments requiring periodic analysis then the analytical procedure should not itself affect the course of the treatments.

#### **2.4.2.4 Information Volume Criterion**

There is a direct relationship between the quality and quantity of information retrievable from the information volume and the fluence of the stimulus being used. The greater the fluence, the larger will be the number of interactions per unit time, and therefore the better will be the signal-to-background quality of the information. On the other hand, it is the direct, and sometimes indirect, effects of the stimulus that cause destructiveness. Among these effects, for example, might be the rate of energy deposition, or the rate of momentum transfer, or the type of interaction mechanism, or the

duration of the analytical procedure. Thus, a balance has to be struck between the quality of information and the level of damage. In practical terms, this may mean having to take longer over an analysis than normal, in order to maintain the rate of energy deposition below a certain critical level, or using an energy of the stimulating probe different from normal, to avoid or minimize a particular interaction mechanism. Where damage is unavoidable, the analysis may reduce simply to having to accept whatever information can be collected before the specimen surface is altered to a predetermined extent.

There are instances in which concerns over destructiveness override all others, as where an object is either irreplaceable or of great value, for example, archaeological artifacts, national treasures, objets d'art, etc. At the other extreme, there are objects that can be replaced at essentially zero cost, compared with the cost of the analysis, for example, mass produced consumables, waste products, common naturally occurring products, etc. Even before analysis starts, it might be the specimen preparation itself that has to be considered because of its destructiveness, for example, if a large item has to be sectioned because it cannot be accommodated in the analysis position.

It is clearly difficult from the above discussion to give fixed criteria for taking destructiveness into account. There is generally a degree of uncertainty with respect to a particular specimen or problem. The most important rule is always to tell the customer beforehand what the potential effects on the specimen might be and to have complete agreement on the procedure to be adopted.

### **2.4.3 QUALITY ASSURANCE, BEST PRACTICE, AND GOOD HOUSEKEEPING**

In an ideal world, the quality of an analytical process, and its outcome, would be guaranteed automatically by scrupulous adherence to the scientific method, independent of the intention of the analysis. That is, it should not matter whether the end user of the information is a research scientist or a customer, nor whether the results are to be used to generate new basic knowledge, improved techniques, better products, or financial gain. In the ideal situation, the quality would indeed be assured, without the need for further formality.

When it comes to the type of contractual relationship that is now commonplace between the supplier of the analytical service and the customer, a more formal guarantee basis is needed. The customer will not necessarily be familiar with the in-principle merits of the scientific method, but will understand a published set of guidelines to which the supplier must adhere. Such a set will include both rules for best practice in all aspects of handling, preparing, and treating specimens, and instructions as to how an analysis must be carried out so that its results have been quantified in an approved way and are traceable back to an agreed international standard. The latter proviso is essential in order that all results from any laboratory using the same technique are intercomparable. Only by general adherence to the same set of guidelines and instructions can quality assurance in an analysis be guaranteed. In many countries, there are now standard organizations that assess analytical supplier laboratories for accreditation in quality assurance, and the number so accredited is growing steadily.

No analytical service can operate efficiently without the internal procedures that can be lumped together under the heading of "good housekeeping". Such procedures are basically commonsense routines that ensure that both personnel and instruments function smoothly and reliably, that proper records are kept and maintained up to date, that specimens are not mislaid, mishandled, or cross-contaminated, that reports are compiled and sent on time, that customers are always fully informed, that safety standards are being met, etc. This book has much to say about the esoteric aspects of surface and interface analysis. It must always be borne in mind, however, that attention to detail is at least as important to the final outcome

## **2.5 NOTES ON ACRONYMS AND JARGON**

Communications within any field of human endeavor, whether it be skateboarding or brain surgery, will sooner or later be conducted with specialized terminology, which to the uninitiated is either just

so much alphabet soup or incomprehensible and confusing jargon. The field of surface and interface analysis and characterization is no different. Even to an insider the acronyms and abbreviations may sometimes present barriers to understanding rather than be a means of efficient communication. Regrettably, they have to be used, if for no other reason than for brevity. Other complications arise from redundant terminology where several acronyms are in common use, but refer to essentially the same technique or methodology (e.g., EDS = EDX = EDAX = EDXS). During the editorial process, all reasonable efforts have been made to ensure that acronyms are defined in each chapter when they first appear. Likewise, as far as possible, the use of jargon has been avoided, whenever it is unlikely to be comprehensible to a general scientific audience.

---

# 3 Photoelectron Spectroscopy (XPS and UPS), Auger Electron Spectroscopy (AES), and Ion Scattering Spectroscopy (ISS)

*Vaneica Y. Young and Gar B. Hoflund*

## CONTENTS

3.1	Introduction .....	20
3.2	Physical Processes .....	20
3.2.1	Photoemission .....	20
3.2.2	Auger Emission .....	22
3.2.3	Ion Scattering .....	23
3.3	Spectral Features .....	25
3.3.1	PES/XPS .....	25
3.3.2	PES/UPS .....	27
3.3.3	AES .....	29
3.3.4	ISS .....	30
3.4	Depth Specificity .....	30
3.4.1	PES/XPS/UPS .....	30
3.4.2	AES .....	31
3.4.3	ISS .....	32
3.5	Compositional Information .....	33
3.6	Elemental Sensitivity .....	34
3.7	Chemical-State Information .....	34
3.8	Spectral Resolution .....	39
3.9	Depth Profiling .....	41
3.10	Modular Instrumentation .....	41
3.10.1	Excitation Sources .....	41
3.10.1.1	UV Sources .....	41
3.10.1.2	X-Ray Sources .....	42
3.10.1.3	Electron Sources .....	44
3.10.1.4	Ion Sources .....	45
3.10.2	Energy Analyzers .....	46
3.10.3	Detectors .....	56
3.11	Special Applications of XPS .....	58
3.11.1	High Pressure XPS .....	58
3.11.2	Automated XPS .....	59
3.11.3	Dedicated XPS .....	60
3.11.4	Multi-Technique Instruments .....	61



3.12	AES Configurations .....	61
3.12.1	Dedicated Instruments.....	61
3.12.2	Other Instruments.....	61
3.13	ISS.....	61
3.13.1	Dedicated Instruments.....	61
References	.....	62

### 3.1 INTRODUCTION

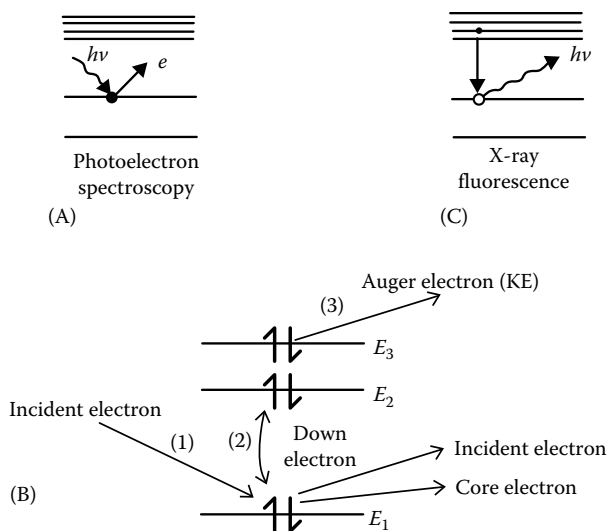
The most commonly used surface spectroscopic techniques are x-ray photoelectron spectroscopy (XPS), ultraviolet photoemission spectroscopy (UPS), Auger electron spectroscopy (AES), and ion scattering spectroscopy (ISS). XPS and UPS are similar techniques and can be grouped under photoemission spectroscopy (PES). All four techniques are used widely for the study of solid surfaces both in fundamental scientific studies and in applied studies of polymers, ceramics, heterogeneous catalysts, metals and alloys, semiconductors, nanoparticles, biomaterials, etc. They can provide information about composition, chemical state, electronic structure, and geometrical structure. Detailed reviews have been presented previously [1,2].

### 3.2 PHYSICAL PROCESSES

In this section, the underlying physical processes are outlined and the nature of the information provided by the resultant spectra is discussed.

#### 3.2.1 PHOTOEMISSION

In PES, either x-rays (XPS) or UV photons (UPS) strike the surface of a sample in an ultrahigh vacuum (UHV) environment. Electrons are emitted as shown schematically in Figure 3.1A. The emission process has been described by Berglund and Spicer [3] in a three-step model, in which the first step involves absorption of an x-ray or UV photon and promotion of an electron from its ground state to the final state above the fermi level. The final state lies within the potential field of the solid



**FIGURE 3.1** Schematic diagrams of the (A) photoemission, (B) Auger, and (C) fluorescence processes.

and satisfies the Schrödinger equation for that field. The second step is transport of the electron to the surface, and the third step is escape of the electron into the vacuum. Since the electron is generated within the potential of the solid, its wave function contains contributions from the solid even after it has escaped into the vacuum. In PES, the kinetic energies (KEs) of the emitted electrons are measured using an electrostatic charged-particle energy analyzer, from which their electron binding energies (BEs) can be calculated from the following equation:

$$E_b = h\nu - E_k + \Delta\phi \quad (3.1)$$

where

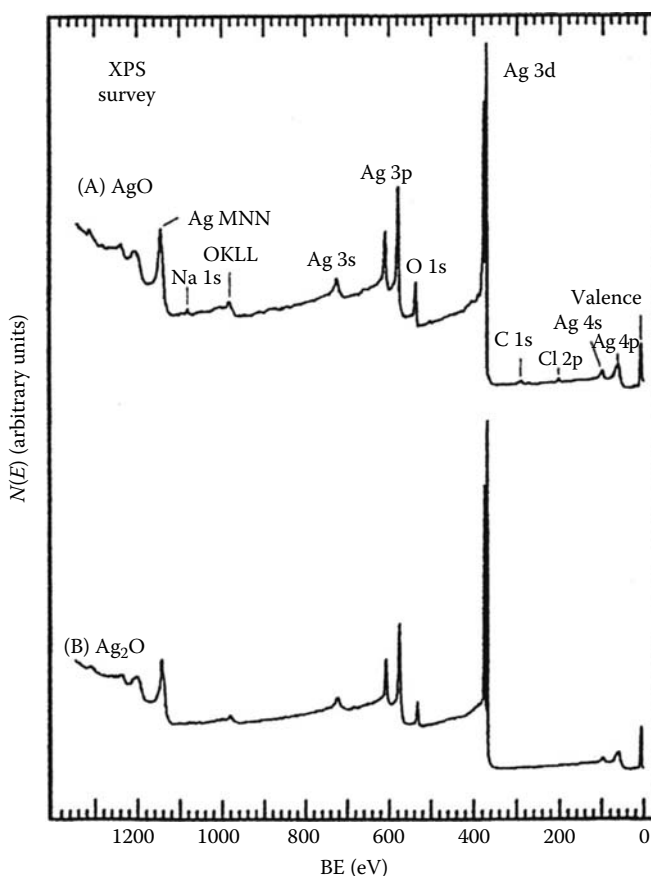
$E_b$  is the electron BE in the solid

$h\nu$  is the energy of the incident photon

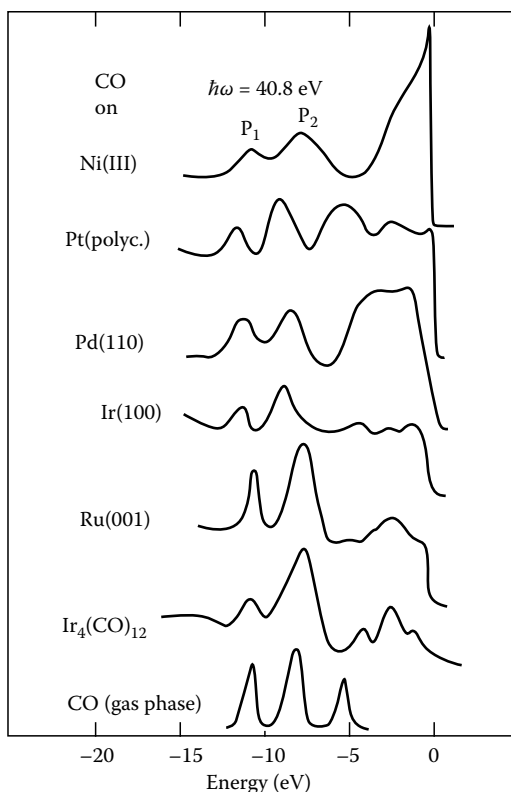
$E_k$  is the electron KE

$\Delta\phi$  is the difference in work function between the sample and the detector material assuming that there is no charge at the sample surface

Typical XPS and UPS spectra are shown in Figures 3.2 and 3.3, respectively. The characteristics of these spectra are discussed below, as are the photon sources and energy analyzers used to perform PES.



**FIGURE 3.2** XPS survey spectra obtained from (A) an AgO sample after a 130°C anneal for 30 min and (B) an Ag<sub>2</sub>O sample after a 300°C anneal for 30 min. (From Hofflund, G.B., Hazos, Z.F., and Salaita, G.N., *Phys. Rev. B*, 62, 11126, 2000.)



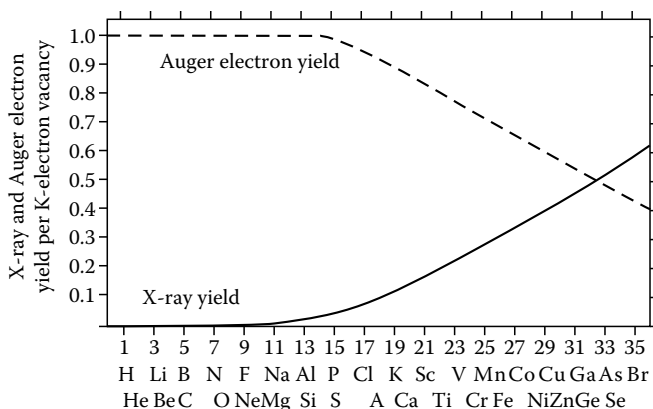
**FIGURE 3.3** HeII UPS spectra of CO adsorbed on transition metals. The two peaks below 8 eV, in the group labeled  $P_2$ , are induced by CO adsorption. The structure above 8 eV,  $P_1$ , which varies from metal to metal, is due to emission mainly from the metal d-orbitals. For comparison, the photoelectron spectra of  $\text{Ir}_4(\text{CO})_{12}$  and gas-phase CO are shown. (From Gustafsson, T. and Plummer, E.W., *Photoemission and the Electronic Properties of Surfaces*, John Wiley & Sons Ltd., Chichester, U.K., 1978.)

### 3.2.2 AUGER EMISSION

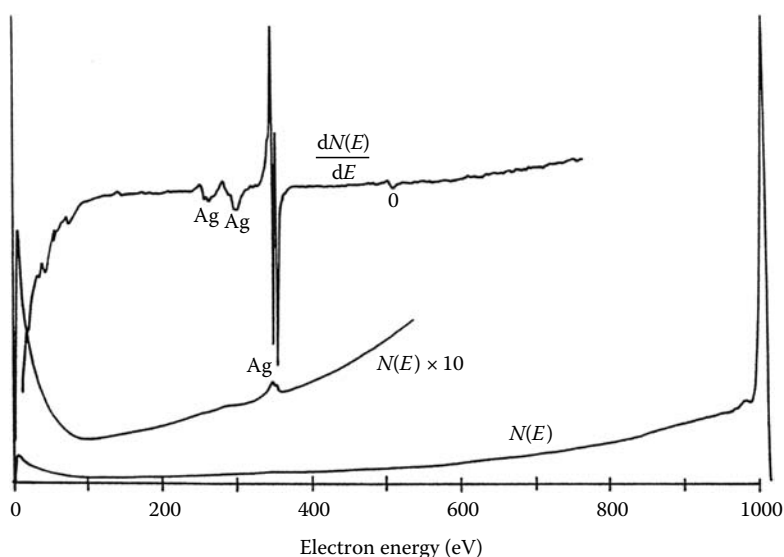
The process of Auger emission is multistep, as shown in Figure 3.1B. The first step is the production of a core hole by ejection of a core electron as a result of interaction with either incident electrons or photons. The second step involves an electron in a shallower energy level undergoing a transition to fill the core hole. The energy difference is then available to a third electron, which is ejected as the Auger electron. Thus, the AES process involves three different electrons in two or three different energy levels, and the KE of the Auger electron produced from, for example, K,  $L_1$ , and  $L_2$  electrons is given by

$$E_{\text{AE}} = E_{\text{K}} - E_{L_1} - E_{L_2} - \Delta \quad (3.2)$$

where  $E_{\text{K}}$ ,  $E_{L_1}$ , and  $E_{L_2}$  are the BEs of electrons in the K,  $L_1$ , and  $L_2$  energy levels, respectively, and  $\Delta$  is a complicated term containing both the sample and spectrometer work functions, as well as many-body corrections that account for energy shifts during the Auger process and other electronic effects. The  $\Delta$  term is usually small ( $<10$  eV) and varies with chemical state. The initial core hole can also decay by x-ray fluorescence, in which an electron in a shallower level drops into the core hole with emission of an x-ray photon as shown in Figure 3.1C. The probability of decay via an Auger



**FIGURE 3.4** Auger electron emission and x-ray fluorescence yields for K-shell electron vacancies as functions of atomic number. (From Somorjai, G.A., *Principles of Surface Chemistry*, Prentice Hall, Englewood Cliffs, NJ, 1972.)

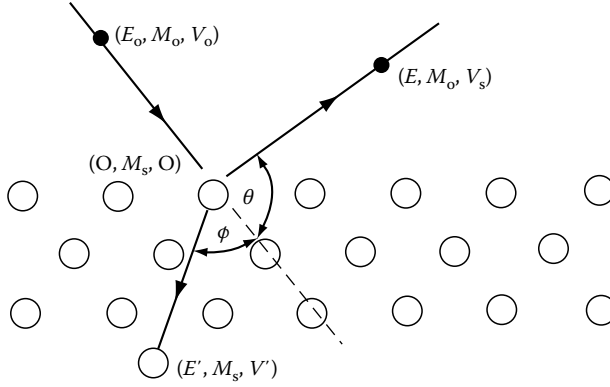


**FIGURE 3.5**  $N(E)$  and  $dN(E)/dE$  electron energy distributions recorded from Ag with a 1 keV primary electron beam. (From Joshi, A., Davis, L.E., and Palmberg, P.W., in Czanderna, A.W. (Ed.), *Methods of Surface Analysis*, Elsevier, Amsterdam, 1975.)

process is greater for light elements than that via fluorescence, as shown in Figure 3.4 for K-shell electrons [6]. Auger processes occur for all elements except hydrogen and helium, which have no or insufficient outer electrons. As can be seen from Equation 3.2, the Auger KE does not depend on the primary beam energy, and the threshold energy for the transition is that required to produce the core-level hole. A typical Auger spectrum in both the  $N(E)$  and  $dN(E)/dE$  modes, recorded from a polycrystalline Ag surface, using 1 keV primary electrons, is shown in Figure 3.5 [7].

### 3.2.3 ION SCATTERING

In ISS, an incident flux of monochromatic inert-gas ions (typically of energies 500–2000 eV) impinges on a solid surface, followed by energy analysis of the ions scattered from the surface at



**FIGURE 3.6** Schematic representation of the ISS process. The primary ion has energy  $E_o$ , mass  $M_o$ , and velocity  $V_o$  before scattering, and energy  $E$ , mass  $M_o$ , and velocity  $V_s$ , after scattering. The scattering angle is  $\theta$ .

some preselected angle, as shown schematically in Figure 3.6. The ion–solid interactions can be approximated as elastic binary collisions between the ions and the individual atoms in the solid. This approximation works quite well because the collision times are short ( $10^{-15}$  to  $10^{-16}$  s) compared to the time constant of a characteristic lattice vibration ( $10^{-13}$  s). The ion therefore strikes a surface atom and leaves the surface region before the recoiling atom has time to interact with the solid. The conservation of energy and momentum in the binary scattering process can be written as

$$E_o = E + E' \quad (3.3)$$

$$M_o V_o = M_o V_s \cos \theta + M_s V' \cos \phi \quad (3.4)$$

$$0 = M_o V_s \sin \theta - M_s V' \sin \phi \quad (3.5)$$

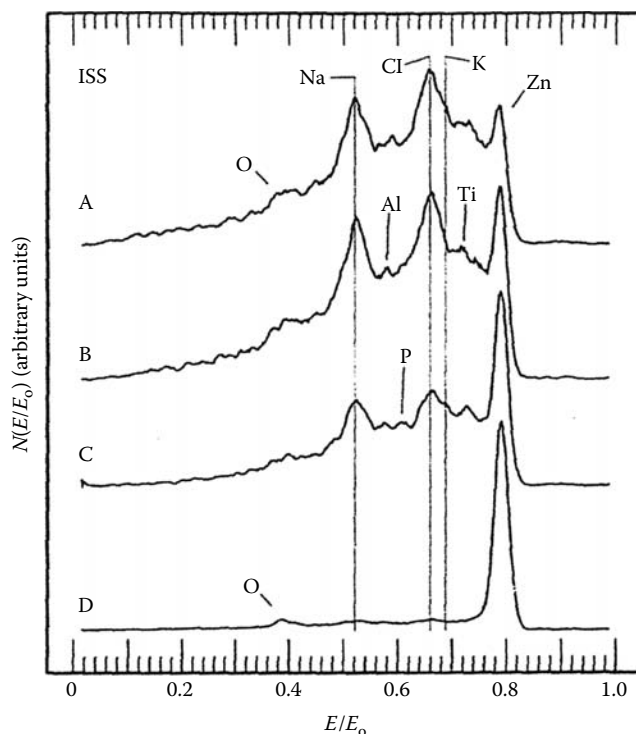
and combined to yield

$$\frac{E_s}{E_o} = \left( \frac{M_o}{M_o + M_s} \right)^2 \left\{ \cos \theta \pm \left[ \left( \frac{M_s}{M_o} \right)^2 - \sin^2 \theta \right]^{1/2} \right\}^2 \quad (3.6)$$

The symbols in these equations are specified in Figure 3.6. In Equations 3.3 through 3.6,  $E_o$  is the KE of the incident inert-gas ion (set by the ion source),  $E$  is the KE of the scattered ion measured with an electrostatic energy analyzer,  $M_o$  is the mass of the primary ion (selected by the choice of inert gas), and  $\theta$  is the scattering angle determined by the experimental geometry. The variables are all known so that  $M_s$ , the masses of the surface atoms, can be determined from the positions of the peaks in the ISS spectrum. If  $M_s/M_o > 1$ , then only the plus sign in Equation 3.6 applies and each target mass gives rise to a single peak in the spectrum of scattered intensity as a function of  $E/E_o$ . If  $M_s/M_o < 1$ , then both signs apply, subject to the constraint

$$\frac{M_s}{M_o} \geq \sin \theta \quad (3.7)$$

and each target mass gives peaks at two energies in the above spectrum. ISS spectra obtained from a higher alcohol synthesis catalyst are shown in Figure 3.7 [8].



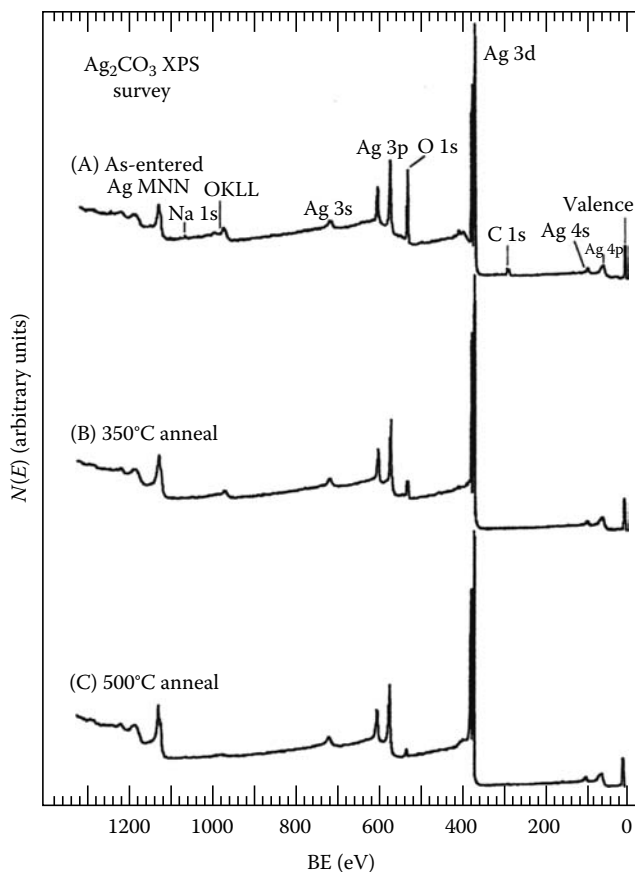
**FIGURE 3.7** ISS spectra obtained from an aged catalyst after (A) insertion into the analysis chamber and after sputtering with 1 keV  $\text{He}^+$  for (B) 5 min, (C) 10 min, and (D) after a further 15 min using a 1:1  $\text{He}^+$  and  $\text{Ar}^+$  gas mixture. (From Hoflund, G.B., Epling, W.S., and Minahan, D.M., *J. Elect. Spec. Rel. Phenom.*, 95, 289, 1998.)

### 3.3 SPECTRAL FEATURES

#### 3.3.1 PES/XPS

XPS survey (also called wide scan) spectra obtained from  $\text{Ag}_2\text{CO}_3$  before (a) and then after annealing at (b)  $350^\circ\text{C}$ , and (c)  $500^\circ\text{C}$ , each for 10 min in vacuum, are shown in Figure 3.8 [9]. In (A), many peaks are present, including the 3s, 3p, 3d, 4s, and 4p Ag peaks, as well as those of O 1s and C 1s. All these peaks arise from direct photoemission processes from core levels as shown in Figure 3.1A. A very small Na 1s peak can also be seen due to a low level of Na contamination. Tables of the BEs of core-level electrons are given in several references [10–12], so if an unknown peak is apparent at a particular BE, it can be identified. Ag and O Auger peaks are also present in Figures 3.2 and 3.8, produced by the process shown in Figure 3.1B, because core holes created by x-rays can also decay by an Auger process. Since the principal electronic shells usually contain electrons of different energies due to multiplet splitting, an Auger feature arising from the ionization of a particular core level consists of multiple peaks. Another feature in Figures 3.2 and 3.8 can be seen at and just above a BE of 0 eV. This is the valence band (VB) photoemission spectrum, due to the valence electrons of each element present. Its position and shape result from the chemical interactions (bonding) of the various elements.

Unmonochromatized x-ray sources contain several x-ray lines, each of which can cause core-hole ionization, giving rise to satellite peaks in an XPS spectrum. These satellite peaks can be removed using a monochromator, but this reduces the x-ray flux and, hence, the photoemission



**FIGURE 3.8** XPS survey spectra recorded from an  $\text{Ag}_2\text{CO}_3$  sample (A) as-entered, and after annealing for 10 min at (B) 350°C and (C) 500°C. (From Salaita, G.N., Hazos, Z.F., and Hoflund, G.B., *J. Elect. Spec. Rel. Phenom.*, 107, 73, 2000.)

signal strength. The satellite features appear at BEs lower than those of the primary peaks and are of considerably lower intensity (<10%) [10]. Structure is also apparent at BEs slightly higher (0–50 eV) than those of primary features, due to two types of electron energy loss processes: (1) excitation of plasmons and (2) production of inter- and intra-band transitions.

According to Equation 3.1 for a conductor, a raw spectrum should be shifted in energy by  $\Delta\phi$  in order to be able to plot  $N(E)$  versus BE. If  $\Delta\phi$  were to be known from the work functions of the sample and detector material, then the process would be simple. Where  $\Delta\phi$  is not known, which is invariably the case, the calibration shift can be made using a peak that corresponds to a given (known) chemical state. Most samples exposed to air accumulate hydrocarbon contamination resulting in a significant C 1s peak. The magnitude of the shift required is then often determined by assigning the BE of this C 1s peak to a value of 285.0 eV, but it is essential that this assignment be checked against the BEs of other peaks in the spectrum, to ensure they make sense chemically. If they do not, then differential charging is probably occurring, and the data must be retaken using charge compensation techniques. For insulating samples, the surface may charge to some arbitrary potential, which cannot be correlated with any physical or chemical variables.

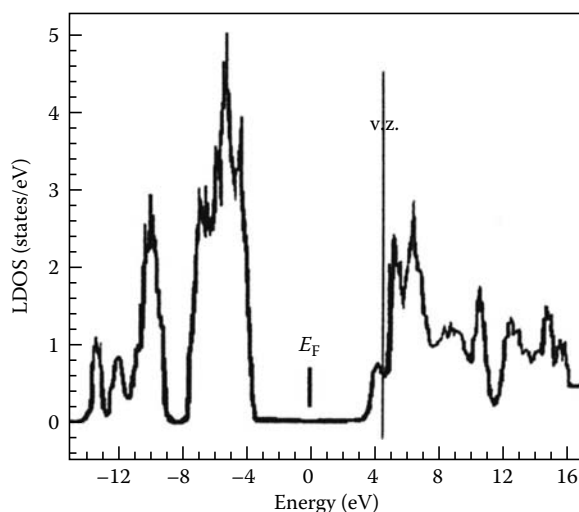
Damage phenomena must always be considered when using surface techniques. XPS produces the least damage because x-rays interact weakly with a solid, but in conventional XPS, the close proximity of the sample to the source itself can cause thermal damage. Damage can occur by several

processes including bond breakage, and emission of particles by photon-stimulated desorption. The possibility of damage can be established by recording sequential spectra as a function of irradiation time. If the spectra change during the sequence, then damage has occurred, and the data collection parameters need to be changed to minimize it.

### 3.3.2 PES/UPS

In UPS, UV photons, rather than x-rays, are used as the excitation source. In many laboratories, UV sources at fixed energies, for example, HeI and HeII at 21.21 eV and 40.82 eV, respectively, are still used, but more information can be obtained with the help of the variable photon energy provided by a synchrotron (see also Chapter 7). As in XPS, the KEs and signal strengths of the photoelectrons are measured. Similar features are observed using either XPS or UPS to examine the VB, but their relative intensities differ due to variations in the ionization cross-section with photon energy. Another important difference is that the overall intensity of the VB photoemission signal is much greater in UPS than in XPS, because in the former the photon energy is of similar magnitude to that of the energy required for the excitation process (i.e., the Einstein Golden Rule). Since photoelectrons are initially elevated from a filled to an unfilled level, the structure of the density of states (DOS) influences the UPS signal; thus, although UPS occurs by the process shown in Figure 3.1A, and obeys Equation 3.1, the photoemission signal is modulated by the DOS of the unfilled levels just above the fermi level. The UPS VB spectrum therefore reflects a joint DOS. Since the unfilled DOS is much extended at energies far above the fermi level, and is essentially continuous there, such modulation is not a consideration in XPS.

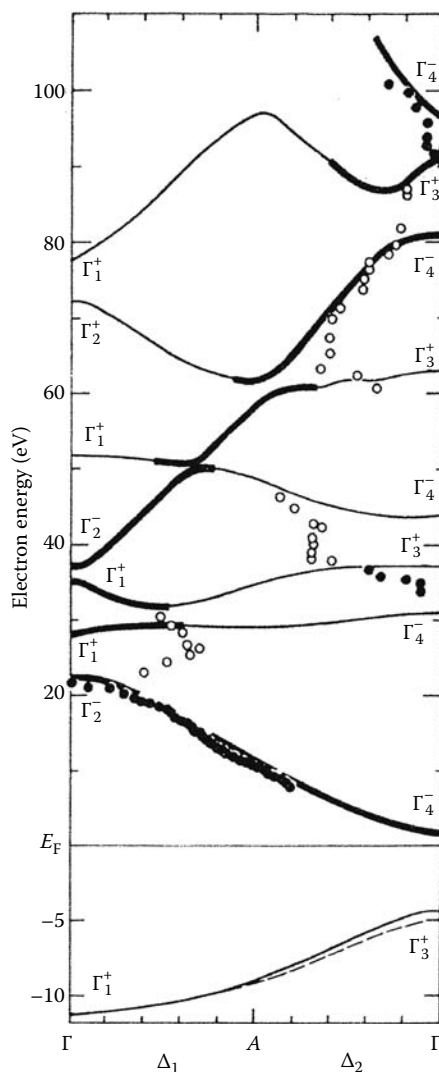
In a synchrotron, the photon energy can be scanned using a monochromator. The initial (i.e., filled) DOS can be recorded by choosing a particular unfilled level (i.e., at a fixed KE) and by scanning the photon energy. The final (i.e., unfilled) DOS, on the other hand, can be obtained by scanning both photon and KE. Figure 3.9 shows the filled and unfilled DOS from the surface of  $\alpha$ -quartz [13], recorded in this way. If 21 eV photons had been used, the feature at  $-10$  eV would have been significantly reduced due to the low population of the unfilled DOS at 11 eV. The nature of the orbitals and their related selection rules also influence the intensities in the joint DOS.



**FIGURE 3.9** Filled (below  $E_F$ ) and unfilled (above  $E_F$ ) DOS, recorded from an  $\alpha$ -quartz surface. (From Garvie, L.A.J., Rez, P., Alvarez, J.R., Busick, P.R., Craven, A.J., and Brydson, R., *Am. Mineral.*, 85, 732, 2000.)



UPS can be used to obtain various types of information, the most obvious being VB electronic structure, as described above. Valence electrons are responsible for the chemical bonding that holds atoms together to form a solid; various quantum mechanical methods can be used to calculate the bonding structure, in particular the VB DOS, thus providing a direct means of comparison of calculated results with experimental data. Both crystalline and amorphous solids can be studied. Using angle-resolved UPS and synchrotron radiation, the complete band structure of single-crystal surfaces can be mapped along different crystal directions. An illustration of this approach is given in Figure 3.10, in which the band structure of a Be(0001) surface has been mapped out in the  $\Delta$  direction [14]. Comparison is shown with the results of a calculation using an *ab initio* self-consistent pseudo-potential method in the local-density formalism. The agreement between the calculated and experimental results is quite good except near the plasmon threshold. Another important application



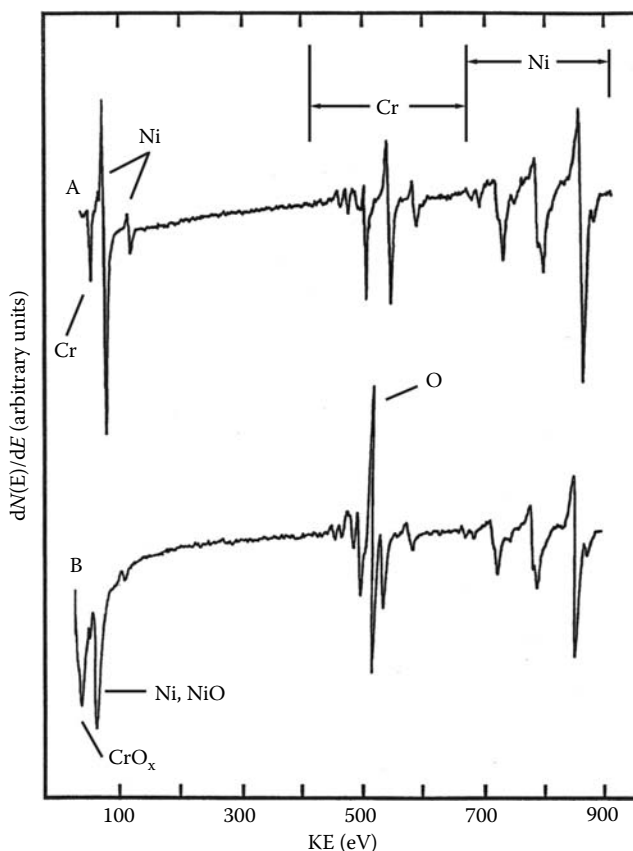
**FIGURE 3.10** Calculated and experimental band structure of Be(0001) along  $\Delta$ . The thicker lines denote final states, which have large plane-wave components along  $\Delta$ . The dashed line is the corrected initial state used to determine the final state. Note that the vertical scale changes at  $E_F$ . (From Jenson, E., Bartynski, R.A., Gustafsson, T., Plummer, E.W., Chou, M.Y., Cohen, M.L., and Hoflund, G.B., *Phys. Rev. B*, 30, 5500, 1984.)

of angle-resolved UPS, using synchrotron radiation, is the determination of bonding orientation of adsorbates on single-crystal surfaces [5,15].

### 3.3.3 AES

An Auger spectrum, in the derivative,  $dN(E)/dE$ , mode, recorded from a sputter-cleaned Ni/Cr alloy foil, is shown in Figure 3.11 [16]. In the integral mode, Auger features appear as small peaks riding on a large background of inelastically scattered electrons, as seen in the lower two spectra in Figure 3.5. Differentiating the  $N(E)$  spectrum either electronically or numerically accentuates the Auger features relative to the background, which, as can be seen in Figure 3.5, is of much greater intensity. Ni and Cr features are present in Figure 3.11 at both low (<200 eV) and high KEs (>400 eV). The low KE features involve one or two valence levels in the Auger process, while those at high KE arise from three core levels. As with XPS, AES peaks can be identified from their KEs, using reference manuals [12,17–19]. When assigning a particular peak to an element, it is vital to check that all the other Auger peaks belonging to that element are present in the spectrum and with the correct relative intensities.

Damage is a very important consideration in AES since many types of sample are susceptible to electron-beam damage by a variety of processes. Such damage can be minimized by using a low



**FIGURE 3.11** Auger spectra obtained from (A) cleaned Ni/Cr surface and (B) after room temperature exposure to 100 L of oxygen. (The Langmuir [L] is not an SI unit, but remains in common usage. 1 L is defined as a dose corresponding to one monolayer coverage for a sticking coefficient of unity.) (From Hoflund, G.B. and Epling, W.S., *Chem. Mater.*, 10, 50, 1998.)

electron-beam flux coupled with pulse counting. For a homogeneous sample, the electron beam may be rastered across the surface to minimize beam exposure. As with XPS, damage can be detected in AES by recording sequential spectra and looking for differences, as a function of electron-beam exposure.

### 3.3.4 ISS

ISS spectra recorded from an higher alcohol synthesis (HAS) catalyst are shown in Figure 3.7. They exhibit a variety of peaks arising from different elements including O, Na, Cl, Zn, Al, P, K, and Ti. Each peak lies at an  $E/E_0$  value close to that predicted by Equation 3.6.

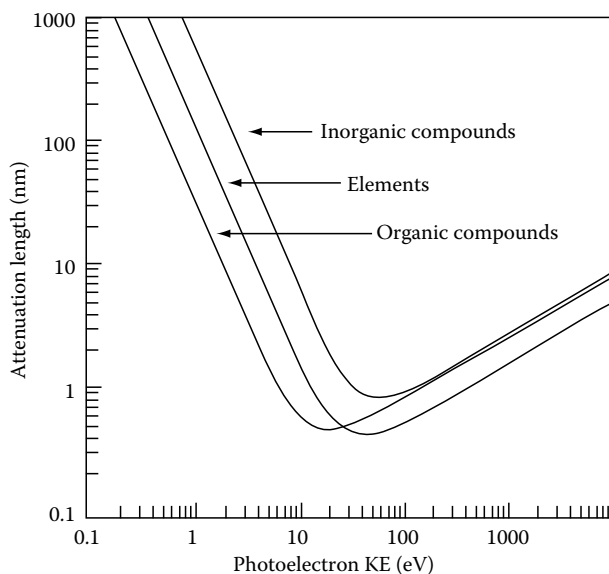
Under the usual operating conditions, that is, light incident ion ( $\text{He}^+$ ), relatively low incident ion energy (1–2 keV), and low incident ion current (10–50 nA), damage in ISS is negligible. However, when heavier ions are used, for example,  $\text{Ar}^+$ , often at higher energies, then there is a real danger of surface damage, which should be checked in a manner similar to that suggested for XPS and AES.

## 3.4 DEPTH SPECIFICITY

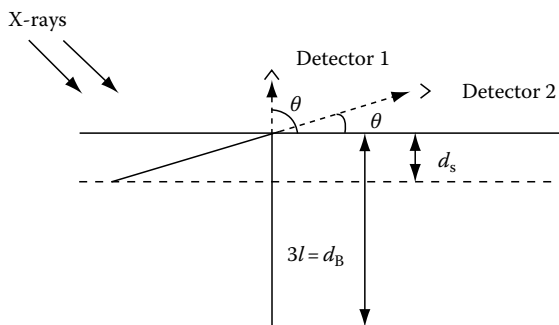
### 3.4.1 PES/XPS/UPS

Both XPS and UPS are surface-specific techniques in that the information obtained originates within the outermost 6 nm. In both techniques, the incident photons penetrate deeply, and do not govern the depth specificity. The deciding factor is the attenuation length ( $\lambda$ ) of the photoelectrons. The attenuation length is shown in Figure 3.12 as a function of photoelectron KE for elements, inorganic compounds, and organic compounds [20]. The probability of an electron traveling a given distance  $x$  in a solid without scattering inelastically is given by

$$P(x) = ke^{-x/\lambda} \quad (3.8)$$



**FIGURE 3.12** Dependence of the attenuation length on the photoelectron KE for elements, inorganic compounds, and organic compounds. (From Seah, M.P. and Dench, W.A., *Surf. Interface Anal.*, 1, 2, 1979.)



**FIGURE 3.13** Schematic diagram illustrating how the collection angle affects XPS depth specificity. If  $\lambda$  of a photo-emitted electron is  $\lambda$ , then 90% of the photoelectrons detected by detector 1 are emitted within a distance of  $3\lambda(d_B)$  beneath the surface. However, moving the detector to position 2 results in an equivalent detection of electrons emitted within a depth  $d_s$ , that is, reduction of the information depth by a factor  $\sin \theta$ . (From Hoflund, G.B., in Rivière, J.C. and Myhra, S. Eds.), *Handbook of Surface and Interface Analysis*, Marcel Dekker, Inc., New York, 1998.)

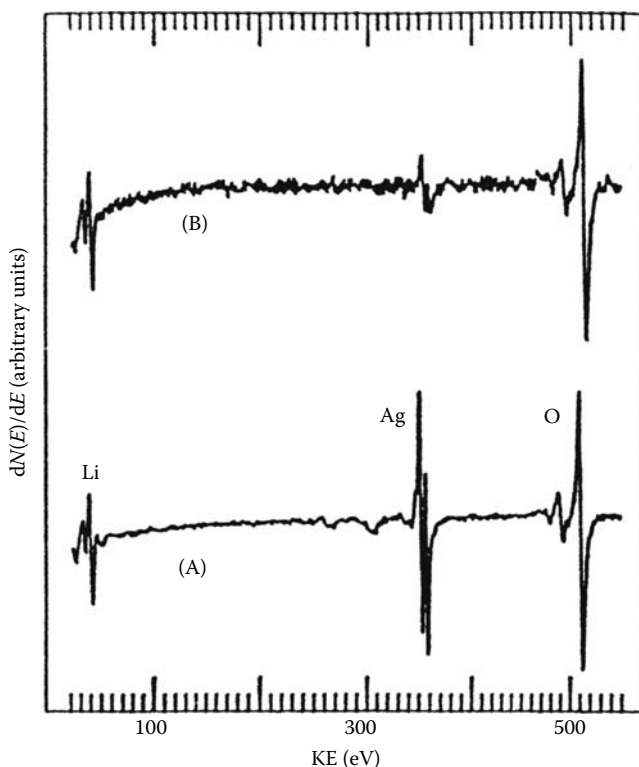
where  $k$  is a normalization constant. This equation and Figure 3.12 can be used to calculate the contributions to a given elemental peak for varying depths of the element beneath the surface. For any given element, the associated XPS peaks have different KEs and consequently different information depths. Over 90% of photo-emitted electrons originate from a depth less than  $3\lambda$ , which defines roughly the depth specificity for a particular peak. The spectral features that have the greatest surface specificity are those with KEs near the minimum  $\lambda$  in Figure 3.12. For organic compounds such as polymers, this would be at about 18 eV, where  $\lambda$  is about 0.4 nm and the information depth about 1.1 nm, that is, between 5 and 8 atomic layers for most materials. For photoelectrons at higher KEs, around 1000 eV, from elements or inorganic compounds,  $\lambda$  is about 2.5 nm so that the information depth would be about 7.0 nm. Note that photoelectrons at very low KEs have low depth specificity. Photoelectrons emitted from the outermost atomic layers have the lowest probability of scattering inelastically so that they make the largest contribution to a peak. This contribution decreases exponentially with depth according to Equation 3.8.

XPS and UPS can be performed in angle-resolved modes in order to vary the information depth. For these modes, the only parameter that can be varied is the collection angle, as shown in Figure 3.13. If this collection angle is changed from normal to grazing by rotating the specimen (typically up to  $80^\circ$  off normal), a compositional profile can be obtained, with the help of various numerical procedures [21–23]. In UPS, variation of the collection angle can reveal differences in electronic structure and composition between the surface and the bulk. These differences include band bending and accentuation of some surface electronic states not allowed in the bulk electronic structure.

### 3.4.2 AES

The Auger electrons generated in AES obey the same scattering rules as do photoelectrons in XPS and UPS, and the Auger electrons in XPS. The difference in the technique is that both the KE and angle of incidence of the primary beam can influence the surface specificity. As the KE of the primary beam is decreased, the beam penetrates less deeply into the surface, thereby increasing the surface specificity. Also, if the incident angle of the primary beam is decreased from normal to grazing, the surface specificity is again increased, because although a grazing beam travels the same distance through a solid as would a normal beam, Auger electrons would then be originating nearer the surface, and the information depth decreases.

As in XPS and UPS, AES can also be used in the angularly resolved mode. There is more flexibility available in AES, because both the incidence and collection angles as well as the primary

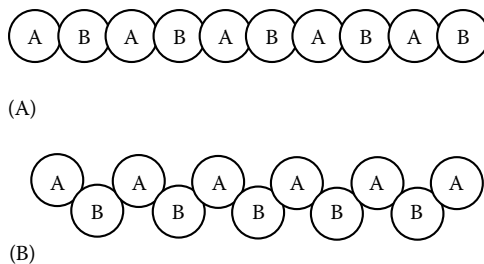


**FIGURE 3.14** Angle-resolved AES (ARAES) spectra from a Li-contaminated, polycrystalline, Ag sample after annealing in  $O_2$ . Spectrum (A) was recorded using the conventional AES geometry (normal incidence and  $42^\circ$  off-normal collection angle), and spectrum (B) with an angle of incidence of  $45^\circ$  and a collection angle of  $7^\circ$ . (From Davidson, M.R., Hoflund, G.B., and Outlaw, R.A., *J. Vac. Sci. Technol. A*, 9, 1344, 1991.)

beam energy can be altered, and all these influence the surface specificity [24]. An example is shown in Figure 3.14 [25]. The spectra shown there were collected, using a cylindrical mirror analyzer (CMA), from a Li-contaminated Ag sample after annealing in  $O_2$ . Spectrum (A) contains three prominent features due to Li, Ag, and O, and was collected in the conventional manner using a primary electron beam at normal incidence and a collection angle of  $42^\circ$  off normal. Spectrum (B) was recorded in a surface-specific mode using angles of incidence and collection of  $45^\circ$  and  $7^\circ$ , respectively, with respect to the surface plane. The Li and O peaks were unchanged but the Ag peak size decreased greatly, indicating that the  $Li_2O$  was present as a film covering the Ag.

### 3.4.3 ISS

Atomic scattering cross sections are in fact larger than indicated schematically in Figure 3.6, which means that a primary ion scattered from an atom in the second atomic layer cannot easily escape without being scattered again by a surface atom. This and the fact that any ion penetrating beneath the surface has a very high probability of being neutralized imply that ISS is almost entirely specific to the outermost atomic layer. However, the situation is not always clear-cut. Figure 3.15 shows two possible atomic configurations of the outermost layer. In Figure 3.15A, ISS spectral features will be present for both elements A and B, regardless of incidence angle or collection angle. On the other hand, in Figure 3.15B features will be present for both A and B only if near-normal incidence and collection angles are used. For any other angles, there will appear a peak only for element A.



**FIGURE 3.15** Two schematic models of the outermost atomic layer of a solid.

### 3.5 COMPOSITIONAL INFORMATION

Since quantification is the subject of Chapter 8, it will not be dealt with here in any detail. In any case, UPS does not provide direct compositional information even though the shapes of features in a UPS spectrum do depend upon composition. XPS and AES can provide good compositional information, as pointed out in Chapter 8, but that usually involves making the assumption that the sample is homogeneous. Except for pure metals, relatively few samples have homogeneous near-surface regions, and the matrix effect (i.e., the spatial distribution of elements in the near-surface region of a homogeneous sample) can have a very large effect on peak intensities [26]. Therefore, any quantification based on the assumption of homogeneity must be viewed with great caution. XPS and AES equipment manufacturers make the homogeneous assumption when programming their software, without providing detailed information, which means that the compositions calculated using the software may be quite far from reality. However, as also described in Chapter 8, study of the shape of the inelastic background under spectra can provide useful information about elemental distributions in subsurface layers in inhomogeneous samples, so the situation is not as difficult as it might seem.

Deriving compositional information from ISS spectra is also challenging for two reasons. The first is that accurate cross-sections are not available for elements as functions of the type of scattering ion and its energy, and the cross sections increase significantly as elemental mass increases [27], so that heavy elements give rise to larger relative peaks than do light elements. The second difficulty involves the neutralization probability, that is, the percentage of ions colliding with an element, that is neutralized, which is very high, ~99%. Thus, small variations from one element to another in this probability can have large effects on quantification. Studies of neutralization using a combination of ISS and the measurement of the scattering of neutrals would be useful, but have not been performed, so the usual assumption is that the neutralization probability is the same for all elements.

Since absolute quantification of XPS, AES, and ISS is not easy, another approach is to use relative quantification, that is, to compare spectra from related surfaces. This could take the form of preparing a number of samples in which just one parameter was varied systematically, and then collecting and comparing spectra. Even small differences in the spectra would then be significant and interpretable. A similar approach would be to subject a sample to various treatments in UHV, and again collect and compare spectra. The treatments could be oxidation, reduction, ion sputtering, annealing, etc., and the sample might oscillate between two distinct states as a result of these treatments. In a study of  $\text{TiO}_2(001)$  [28], sequential reduction, oxidation, and sputtering was applied, with analysis after each treatment by XPS, AES, and ISS, and it was found that the chemical state at the surface changed systematically and reproducibly with the various treatments, in a cyclical manner. The study demonstrated that very small changes in features or lineshapes in spectra can be significant.

A useful way of reporting comparative XPS, AES, and ISS data is by way of peak-area ratios (in the case of AES, in the undifferentiated  $N(E)$  vs.  $E$  spectra). Such ratios contain both compositional and matrix effects, of course, but the use of ratios tends to minimize those effects, and the resultant relative compositions are more accurate than those based on the assumption of homogeneity.

### 3.6 ELEMENTAL SENSITIVITY

The question often arises as to what are the elemental sensitivities in XPS, AES, and ISS. The answer is complex because the elemental sensitivity depends upon the technique, the element, the nature of the sample, including compositional and matrix effects, the instrument used, and the parameters used for data collection. Each of these is discussed below.

The three techniques XPS, AES, and ISS have different information depths, dependent in the first two on experimental conditions. ISS collects information from the outermost surface layer only, while in AES the information depth is governed by the incident and collection angles, and the primary beam energy; in XPS, it is determined by the incident photon energy and the collection angle. Thus, the observed sensitivity of a technique to any one element will depend on the spatial distribution of that element. If an element is not located in the outermost couple of layers, but is distributed in the immediate subsurface layers, then it will not appear in ISS spectra, but may yield large XPS and AES features. Again, an element spread uniformly over a surface will give rise to a larger signal for all three techniques compared to the same amount of that element present as clusters [26]. In a multielement sample, there may be overlapping peaks, which would affect sensitivity, since less prominent, but well-separated, peaks might have to be used.

The relationship between elemental sensitivity and the nature of the physical process is also different in each of the techniques. It is simplest for ISS, in that the scattering cross section increases monotonically with mass. In AES, the Auger electron yield per K-electron vacancy is higher than the x-ray yield for lighter elements, but becomes lower for heavier elements [6]. Relative sensitivity factors are provided by equipment suppliers for XPS and AES since the factors will depend on the analyzers used, and can vary by factors of 30–100. Thus, some elements are easier to detect than others. Using both AES and XPS can be advantageous because a given element may have a large sensitivity factor in one technique and a small one in the other. Carbon is an example, having a relatively high sensitivity factor in AES but a low one in XPS. Thus, a C-contaminated surface may appear to be relatively clean when using XPS but not when using AES.

Hydrogen is an element that is virtually impossible to detect with these methods. This is unfortunate because surface hydrogen is often present and can determine the chemical behavior of a surface. Surface hydrogen has been observed directly using ISS [29,30] but only at extremely small scattering angles that are not accessible with most ISS systems. Hydrogen has no core-level electrons so it cannot be observed directly with either XPS or AES, but it can sometimes be observed indirectly by XPS because of its presence as part of a surface group. For example, hydroxyl groups on oxide surfaces yield O 1s peaks at higher BEs than the oxide O 1s peaks. If it is necessary to establish that hydrogen, or an H-containing molecule, is definitely present, then either one of the SIMS family of techniques, or electron stimulated desorption (ESD), must be used.

All the various instruments available for XPS and AES produce different signal intensities for a given element for reasons such as differences in sample area analyzed, in electron optics and analyzer transmission function, and in type of electron detection. These topics are discussed in detail later in this chapter. The data collection parameters used can also have a great influence on elemental detectability. Elemental detectability can always be improved via the data collection parameters; for example, a small peak can be amplified by making multiple ( $N$ ) scans over the energy range around the peak for a long time. The number of counts increases with  $N$ , but the background noise increases with  $\sqrt{N}$ . Using a lower energy resolution setting also increases the signal strength, but at the cost of poorer spectral resolution.

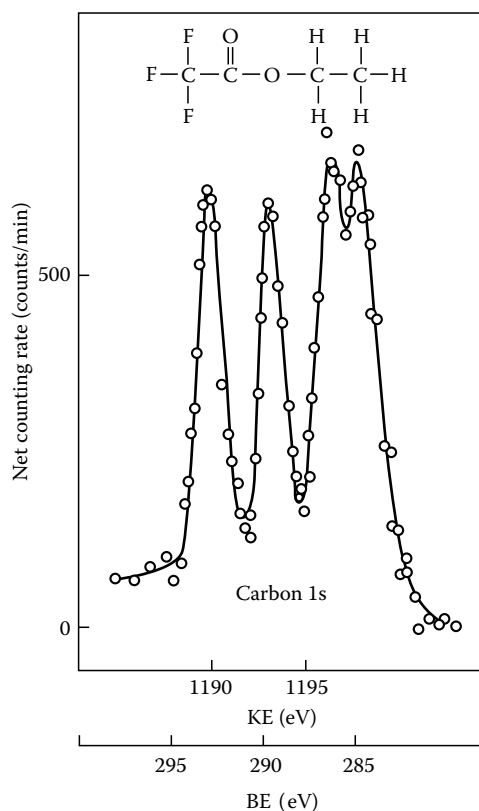
### 3.7 CHEMICAL-STATE INFORMATION

Of these techniques, XPS offers the best ability to provide chemical-state information. In this context, chemical state is often taken to mean that of an element in one or other of its known various valence states. What XPS actually measures is the influence on the BE of a given orbital of the

electronic structure surrounding an element, whether the element is in a well-defined valence state or not. This is a more general definition of chemical state that is appropriate to the interpretation of XPS data. For example, on a completely oxidized surface, the metallic constituent may indeed be in one well-defined valence state. However, bombardment with energetic inert-gas ions will remove selectively oxygen atoms and ions, leaving an oxygen-depleted surface (i.e., a sub-valent oxide, see Chapter 10). The metallic element may then be reduced to a range of intermediate valence states, which is usually reflected in the XPS spectra [31].

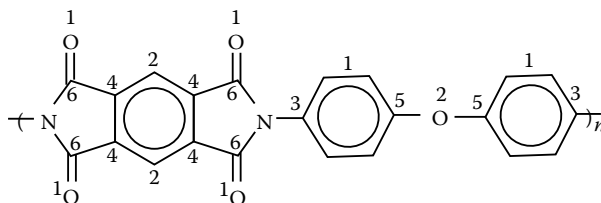
Following their discovery in 1954 [32] that photoemission spectra could be used for elemental identification, Siegbahn et al. went on to demonstrate [33] that spectral shifts could be used to provide chemical-state information. Their classical example [34] is that of ethyl trifluoroacetate, whose C 1s spectrum is shown in Figure 3.16. Each of the four carbon atoms in this molecule has a different chemical environment, resulting in four different C 1s BEs, as seen in Figure 3.16. In most cases, however, BE shifts are not as obvious as in Figure 3.16 and may be difficult to detect.

This point is illustrated by the high-resolution spectra recorded from Kapton (a polyimide polymer used for coating spacecraft in orbit at altitudes of 200–700 km) [35]. The structure of Kapton is shown in Figure 3.17; it can be seen that the C atoms are in six different chemical positions and the O atoms in two. Survey spectra taken before and after exposure to atomic oxygen (AO) and to air give the compositions (calculated on the basis of a homogeneous distribution) shown in Table 3.1.



**FIGURE 3.16** C 1s XPS spectrum recorded from ethyl trifluoroacetate, whose molecular structure is shown at the top. The four C atoms are each in a different chemical environment, giving rise to peaks at four different BEs. (From Siegbahn, K., Nordling, C., Fahlman, A., Nordberg, R., Hamrin, K., Hedman, J., Johansson, G., Bergman, T., Karlson, S., Lindgren, I., and Lindberg, B., *Electron Spectroscopy for Chemical Analysis—Atomic, Molecular and Solid-State Structure Studies by Means of Electron Spectroscopy*, Almquist & Wiksells, Stockholm, 1967.)





**FIGURE 3.17** Molecular structure of poly(ether imide) (Kapton HN) with labeled atomic sites. The C atoms are in six different chemical environments, and the O atoms in two. (From Grossman, E., Lifshitz, Y., Wolan, J.T., Mount, C.K., and Hoflund, G.B., *J. Spacecraft Rockets*, 35, 75, 1999.)

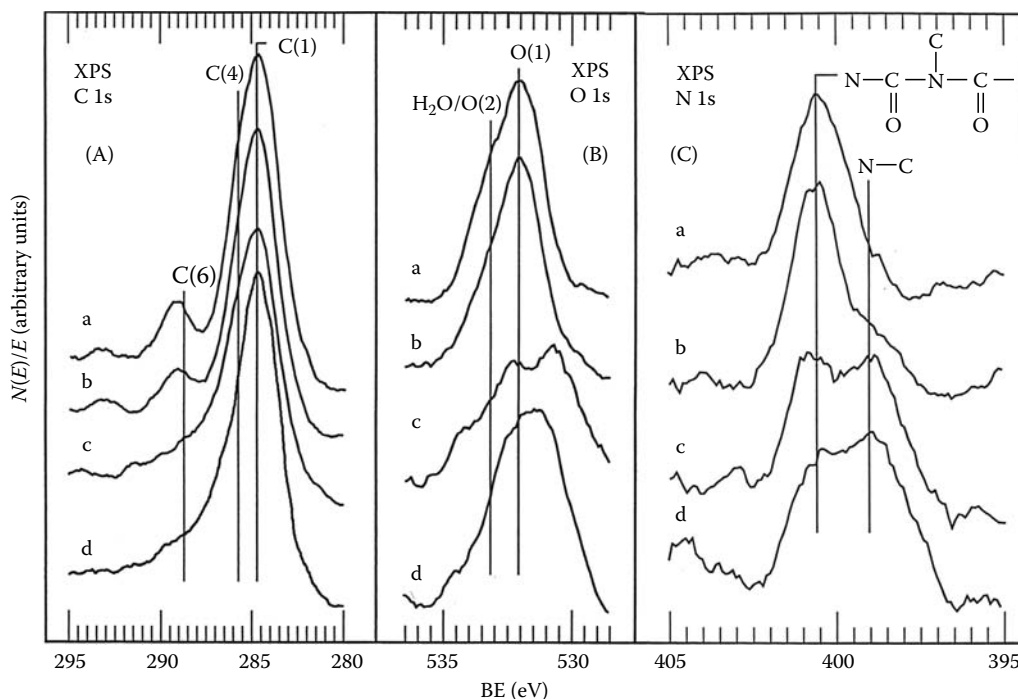
**TABLE 3.1**  
**Near-Surface Composition Determined from XPS Spectra**  
**from Solvent-Cleaned, O-Atom, and Air-Exposed Kapton**

Surface	Composition (%)		
	O	C	N
Sample treatment			
Theoretical	17.2	75.9	6.9
Solvent cleaned	18.1	77.7	4.2
20 min O-atom exposure	14.4	78.4	7.2
24 h O-atom exposure	9.2	83.0	7.8
3 h air exposure following	17.9	78.2	3.9
24 h O-atom exposure			
RF plasma	28.4	64.9	6.7
Low-earth orbit environment	22.2	70.8	7.0

Source: Grossman, E., Lifshitz, Y., Wolan, J.T., Mount, C.K., and Hoflund, G.B., *J. Spacecraft Rockets*, 35, 75, 1999.

The as-received Kapton surface had a composition close to the theoretical, while on AO treatment, the O 1s peak intensity decreased significantly compared to that of the C 1s. However, the high-resolution C 1s, O 1s, and N 1s spectra in Figure 3.18 provide much more information. In the as-received state (a), the C 1s spectrum contains one large and rather broad peak, corresponding to unresolved peaks due to the C atoms labeled 1–5 in Figure 3.17, and a smaller peak at higher BE that can be attributed to the C atom in position 6, bonded to carbonyl. With increasing AO exposure, the smaller peak diminished, thought to be a result of surface reaction to form CO<sub>2</sub>, which desorbed. At the same time, the peak in the O 1s spectrum due to carbonyl also decreased, but to a greater extent than the C(6) peak, so that the O/C compositional ratio also decreased. If this interpretation is correct, then the N 1s spectrum should also have altered, since all the N atoms in Kapton are bonded to carbonyl groups, and indeed that is what was found, as can be seen from the N 1s spectrum. With AO exposure, the predominant N 1s peak diminished as a new one formed at a lower BE and increased in intensity.

In some previous studies on Kapton [36,37], it was found that the surface oxygen content increased with AO exposure, contrary to the above observations. In those studies, the samples were exposed to air after the AO exposure and before taking XPS data. After the 24 h AO exposure, the sample described above was exposed to air for 3 h and then analyzed again, whereupon the O content was found to have nearly doubled. This demonstrates that it is important to carry out such experiments *in situ* in order to understand the processes occurring during AO exposure, since air exposure alters the results.

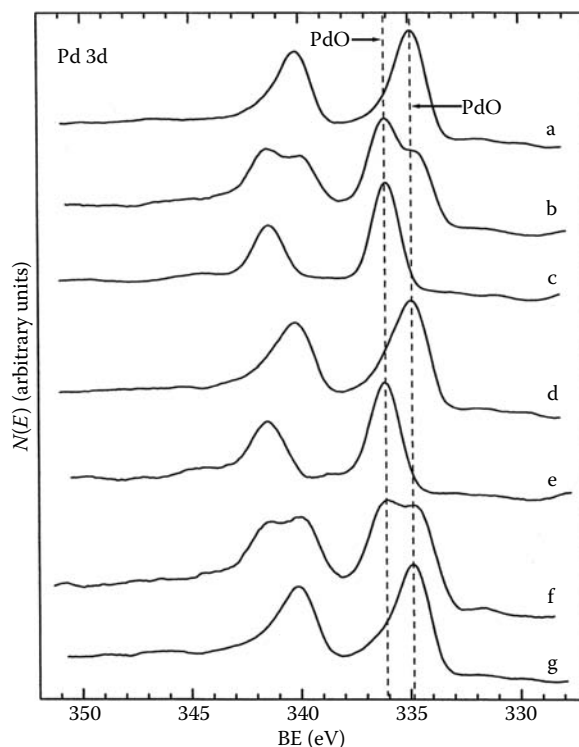


**FIGURE 3.18** High-resolution C 1s (A), O 1s (B), and N 1s (C) XPS spectra from a solvent-cleaned Kapton film after (a) insertion into the vacuum system, (b) 20 min, (c) 24 h exposure to the hyperthermal O-atom flux, and (d) 3 h air exposure following the 24 h O-atom exposure.

In some cases, air exposure between treatment and XPS analysis does not affect the results, but this should always be tested and never assumed. An example is shown in Figure 3.19 [38]. In this study, Pd metal, anhydrous PdO, and hydrous PdO powders were given various treatments in a catalytic reactor operating at 1 atm, exposed to air, and then analyzed. The spectrum shown in (a) was taken from Pd metal powder that had been reduced in hydrogen in the reactor, and consisted of only the metallic Pd 3d features, indicating that the reduction was complete, and that air exposure at room temperature did not result in oxidation of Pd. Spectrum (b) was recorded after exposing the reduced Pd metal powder to methane oxidation conditions in the reactor, transferring the sample in air to the XPS system, and then collecting XPS data. Features due to both Pd metal and PdO were clearly present, which is interesting because the reaction mixture consisted of methane, which is a reducing species, and oxygen, an oxidizing species. This spectrum thus indicates that a layer of PdO had formed over the Pd metal, showing that PdO was the catalytically active species under the conditions.

The spectra shown in (c) and (d) were from fresh anhydrous PdO before and after reduction, respectively, in hydrogen in the reactor. The treatment converted the near-surface PdO back to metallic Pd, but there was peak broadening on the high-BE side due to the presence of subsurface PdO. A similar treatment on hydrous PdO gave similar results, as shown in (e) and (f). A mild sputter treatment with Ar ions also reduced hydrous PdO to Pd metal as shown in (g).

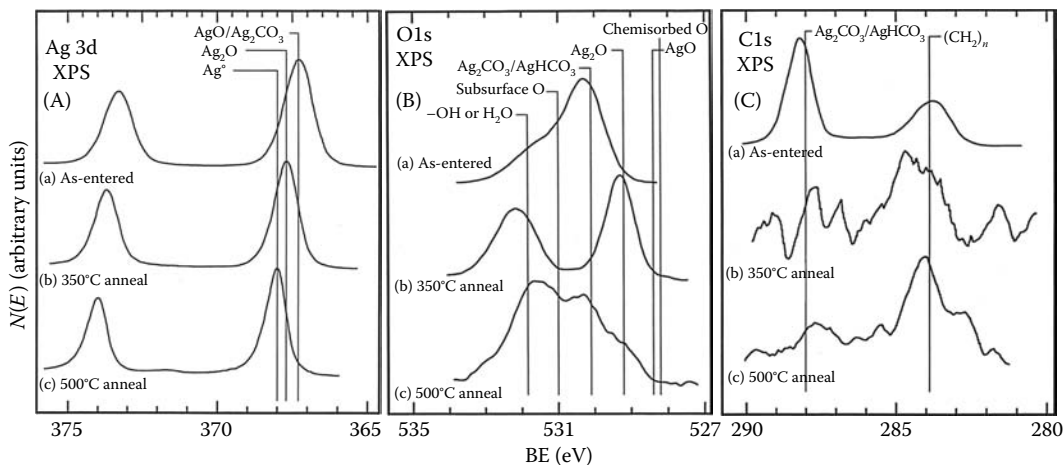
In order to understand the behavior of a complicated system, the different elemental spectra from all the elements involved should be compared, and consistency attained. Analysis of the spectrum from just one element may give a partial explanation, but a more complete explanation can be found only by analysis of all of the relevant peaks. This also provides a check on the consistency of the analysis, since if it is found that changes in all the spectra are not self-consistent, then the interpretation must be rethought. For example, consider the thermal decomposition of silver carbonate ( $\text{Ag}_2\text{CO}_3$ ) as studied by XPS [9]. A fresh silver carbonate powder sample was analyzed before and



**FIGURE 3.19** High-resolution Pd 3d XPS peaks from (a) and (b) Pd powder after hydrogen and methane/oxygen oxidation, respectively, (c) and (d) anhydrous PdO before and after reduction, respectively, (e) and (f) hydrous PdO before and after reduction, respectively, and (g) PdO after ion sputtering. The specimens were exposed to air between each treatment. (From Hoflund, G.B. and Hagelin-Weaver, H.A.E., to be published.)

after annealing at 350°C and then at 500°C (survey spectra shown in Figure 3.8). The resultant Ag 3d spectra are shown in Figure 3.20A, in which the peaks recorded from the fresh sample exhibited a single peak at a BE characteristic of either  $\text{Ag}_2\text{CO}_3$  or  $\text{AgO}$ . Although the sample was nominally  $\text{Ag}_2\text{CO}_3$ , the presence of  $\text{AgO}$  could not be eliminated. After annealing at 350°C, another single peak was present with a BE characteristic of  $\text{Ag}_2\text{O}$ , suggesting that  $\text{Ag}_2\text{CO}_3$  decomposes by losing a  $\text{CO}_2$  molecule to form  $\text{Ag}_2\text{O}$ . Annealing at 500°C resulted in another single Ag 3d peak at the BE characteristic of Ag metal, due to desorption of  $\text{O}_2$ .

Now consider the corresponding O 1s and C 1s spectra shown in Figure 3.20B and C, respectively. Again, the spectra labeled (a) in these figures were obtained from fresh  $\text{Ag}_2\text{CO}_3$ . The predominant O 1s peak was due to either  $\text{Ag}_2\text{CO}_3$  or  $\text{AgHCO}_3$ . The presence of a significant shoulder due to hydroxyl groups or possibly water suggests the presence of bicarbonate. No O 1s features due to  $\text{Ag}_2\text{O}$  or  $\text{AgO}$  were present, which indicates that these species were absent and the Ag was present as  $\text{Ag}_2\text{CO}_3$ . The corresponding C 1s spectrum exhibits two well-defined and well-separated peaks due to carbonate/bicarbonate species and adsorbed hydrocarbons, respectively, the latter being present on all air-exposed surfaces. Annealing at 350°C produced the spectra shown in (b). A C 1s peak was not positively identifiable in the survey spectrum, and the O 1s peak was reduced by a factor of about 3 as the  $\text{Ag}_2\text{CO}_3$  was converted to  $\text{Ag}_2\text{O}$ , consistent with the O 1s spectrum (b) in Figure 3.20B, which exhibits a well-defined  $\text{Ag}_2\text{O}$  feature as well as a feature due either to hydroxyl groups or to adsorbed water. The spectrum in the C 1s region was essentially noise. After annealing at 500°C, the O 1s peak in the survey spectrum decreased greatly, while the



**FIGURE 3.20** High-resolution Ag 3d, O 1s, and C 1s XPS spectra from an  $\text{Ag}_2\text{CO}_3$  sample (a) as-entered, and after annealing at (b)  $350^\circ\text{C}$  for 10 min and (c)  $500^\circ\text{C}$  for 10 min. (From Salaita, G.N., Hazos, Z.F., and Hoflund, G.B., *J. Elect. Spec. Rel. Phenom.*, 107, 73, 2000.)

high-resolution O 1s spectrum indicated that the low level of oxygen remaining was present as hydroxyl groups/water, subsurface dissolved oxygen, and  $\text{Ag}_2\text{CO}_3/\text{AgHCO}_3$ . The C 1s feature was consistent in that a small amount of  $\text{Ag}_2\text{CO}_3/\text{AgHCO}_3$  was present as well as some hydrocarbons. This group of spectra demonstrates that the chemical behavior of the system was much more complex than that indicated by the Ag 3d spectra on their own.

In principle, chemical-state information can also be derived using AES, by observing changes in peak shapes and positions, but the complexity of the Auger process means that interpretation is usually too difficult. No chemical-state database has yet been formulated for AES. There are, however, special cases where AES can provide useful chemical-state information.

### 3.8 SPECTRAL RESOLUTION

It can be seen in the above examples that peaks recorded at high resolution often overlap. Ideally, peaks would be very narrow and well separated. In practice, they are broadened by three factors: (1) the full width at half-maximum (FWHM) of the x-ray line,  $\Delta E_x$ , (2) the width of the analyzer energy window,  $\Delta E_A$ , and (3) the natural line width of the orbital in the atom,  $\Delta E_2$ . The overall energy resolution ( $\Delta E$  in units of eV) is given by

$$\Delta E = (\Delta E_x^2 + \Delta E_A^2 + \Delta E_2^2)^{1/2} \quad (3.9)$$

$\Delta E_2$  cannot be altered, while the analyzer energy window width can be set so that it does not limit resolution. Thus, it is the x-ray line-width that usually limits the overall energy resolution in XPS, which is the critical factor in the unambiguous extraction of chemical-state information. Mg  $K_\alpha$  x-rays have a natural line-width of 0.70 eV, while line widths from other possible anode metals can be as broad as several electron volts (Table 3.2). Reduction in x-ray line-width, and hence improvement in resolution, can be achieved by the use of a monochromator. For example, the Mg and Al  $K_\alpha$  widths can be reduced to about 0.35 eV. Monochromatization also removes the x-ray satellite lines and most of the Bremsstrahlung background, leading to cleaner spectra. The disadvantage of a monochromator is that the incident x-ray flux is reduced significantly (by as much as a factor of 40), thereby reducing the photoemission signal strength. Improvements in signal detectability, for example, multichannel detection, are beginning to overcome this problem. When a spectrum contains

**TABLE 3.2**  
**X-Ray Sources**

Source <sup>a</sup>	Energy (eV)	Line Width (eV)
Zr M <sub>ξ</sub>	151.4	0.77
Mg K <sub>α</sub>	1253.6	0.70
Al K <sub>α</sub>	1486.7	0.85
Mono-Al K <sub>α</sub>	1486.7	0.26
Mono-Si K <sub>α</sub>	1739.9	0.35
Zr L <sub>α</sub>	2042.4	1.7
Au M <sub>α</sub>	2122.9	
Ag L <sub>α</sub>	2984.3	1.3
Mono-Ti K <sub>α</sub>	4510.0	2.0
Mono-Cr K <sub>β1</sub>	5946.7	2.0
Mono-Cu K <sub>α</sub>	8047.8	2.4

Sources: Patthey, F. and Schneider, W.-D., *J. Electron Spectrosc. Relat. Phenom.*, 81, 47, 1996; Beamson, G., Haines, S.R., Moslemzadeh, N., Tsakirooulos, P., Weightman, P., and Watts, J.F., *Surf. Interface Anal.*, 36, 275, 2004; Moslemzadeh, N., Beamson, G., Haines, S.R., Tsakirooulos, P., Watts, J.F., and Weightman, P., *Surf. Interface Anal.*, 38, 703, 2006; Diplas, S., Watts, J.F., Morton, S.A., Beamson, G., Tsakirooulos, P., Clark, D.T., and Castle, J.E., *J. Electron Spectrosc. Relat. Phenom.*, 113, 153, 2001; Vargo, T.G. and Gardella, J.A., Jr., *J. Vac. Sci. Technol. A*, 7, 1733, 1989; Wagner, C.D., *J. Electron Spectrosc. Relat. Phenom.*, 15, 518, 1978.

<sup>a</sup> "Mono" refers to use of a monochromator.

several closely spaced and overlapping peaks whose separation and identification is essential for the analysis, then it is worth compromising on the loss in signal strength caused by using a monochromator.

According to Equation 3.1, only core levels with BEs less than the energy of the x-ray line can be ionized, which, with the conventional Mg and Al sources, can occasionally be a limitation. Photoelectrons from levels with higher BEs can of course be excited by x-rays of higher energy. One source that has been found useful for that application is Ti, whose K<sub>α</sub> line energy is at ~4510 eV. However, the line width is 2.0 eV, so that the energy resolution, and hence the ability to acquire chemical-state information, is much reduced. The situation is not helped by the fact that chemical shifts in core levels at higher BEs are usually small.

The cross-section for photoemission of an electron in a core or molecular level is dependent on the photon energy. An important consequence of this statement relates to the VB electrons that have large cross-sections for photoemission by UV light but very small ones for photoemission by x-rays. A good choice of anode for XPS VB photoemission is therefore Zr, for which the M<sub>ξ</sub> line has a photon energy of 151.4 eV and a line width of ~0.77 eV. With Zr M<sub>ξ</sub> radiation the VB cross-sections are large, the spectral resolution is not significantly limited by the photon line-width, and electrons in core levels with BEs between 20 and 145 eV can also be excited. The latter are not accessible with most UV sources and are useful because they are quite sensitive to chemical state, even if a compositional analysis cannot be made.

Curve-fitting techniques to separate the contributions of the various species are widely used, and manufacturers usually supply programs for them, but, caution should be exercised when using them.

It is all too easy to allow a program free rein to produce a fit involving many component peaks, some of which may have no chemical or physical meaning. If possible, it is better to have available a set of peak shapes and positions of all the species that may be present, and then to add these together in the appropriate proportions to obtain an envelope that is the best fit to the experimental one. The use of an x-ray monochromator for recording both the experimental envelope and the spectra of the standards yields the best results.

### 3.9 DEPTH PROFILING

Most samples encountered are layered, either naturally or intentionally, or are otherwise spatially inhomogeneous, over depths greater than the information depths available with these techniques. The layer structure or the inhomogeneity can in principle be uncovered by depth profiling using inert-gas ion sputtering [45]. Surface analysis performed after each sputtering dose then provides some sort of elemental depth profile. However, there are several processes that may distort the compositional profiles so obtained, and in addition there is the problem of ion-beam damage leading to chemical reduction of some species. Nevertheless, under carefully controlled conditions it can prove useful. Analysis of buried information is discussed in Chapter 10.

### 3.10 MODULAR INSTRUMENTATION

The four techniques described here generally share a similar instrumental platform and have a functional modularity, but of course the actual components used for a module vary with the technique. In this section, upgrades to existing modules, as well as new modules that have been introduced in the last 10 years, are discussed. In the following sections, the modules for each of the techniques are discussed individually, concentrating on the commercially available instruments and their figures of merit, and also on emerging developments in the types of samples analyzed and the conditions under which they can be analyzed.

#### 3.10.1 EXCITATION SOURCES

The primary excitation sources are a flux of vacuum ultraviolet (VUV) light for UPS, of x-rays for XPS, of electrons for AES, and of ions for ISS. Ideally, all the particles making up any one flux are identical, that is, the photon and the electron fluxes would be mono-energetic, and the ion flux would consist of ions of a single mass, energy, and charge.

##### 3.10.1.1 UV Sources

In conventional UPS, UV photons are produced using an inert gas, usually He but occasionally Ne, in a plasma-discharge lamp. If He is being used, then, according to the pressure of He in the discharge capillary, either the HeI line at 21.21 eV or the HeII at 40.82 eV can be selected. Control of the gas pressure in the discharge zone is crucial, particularly when trying to maximize the HeII or NeII line intensity, and it is normal to leave a lamp operating for a long time continuously once it has started, to save time. A system of differential pumping in the source housing ensures that UHV can be maintained in the experimental chamber. The line-widths of the resonant lines are narrow ( $\sim 20$  meV), so that, unlike the x-ray sources for XPS, there is negligible contribution to instrumental broadening from the UV source. The most important application of UPS is in the angle-resolved mode, in which the angular orientation of the specimen, as well as that of the analyzers, can be changed, so that all emission angles are covered.

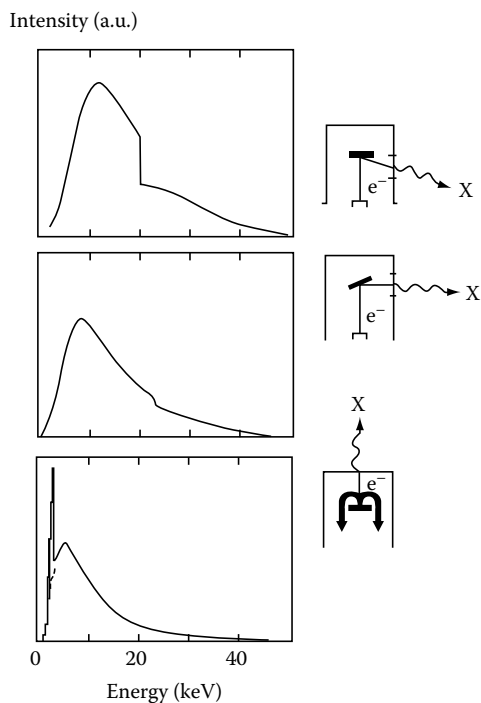
As discussed in Section 3.3.2, UPS can also be performed using radiation from a synchrotron, and indeed much additional and valuable information can be gathered by so doing. For a full description of the design of, and techniques available with, synchrotrons, see Chapter 7.

### 3.10.1.2 X-Ray Sources

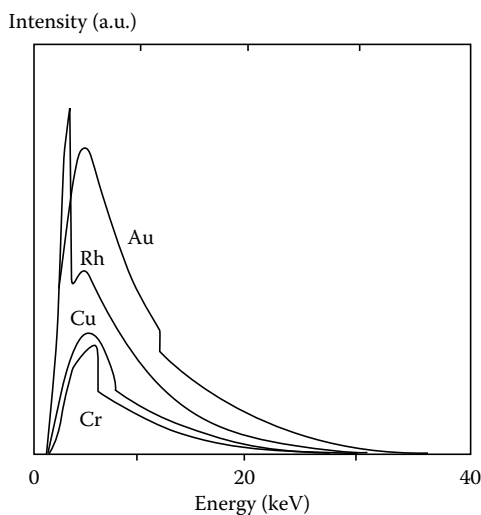
X-rays are generated by accelerating electrons emitted from a heated filament onto a metal anode with an applied voltage of 10–15 keV. The x-ray spectrum so generated consists of a continuous radiation band (Bremsstrahlung) on which discrete lines characteristic of the anode material are superimposed. For a standard x-ray source using a dual Mg/Al anode source, a thin aluminum foil is interposed between the anode and the sample, to reduce the Bremsstrahlung background, to prevent stray electrons from hitting the sample, and to maintain the UHV in the system. Since the imaginary component of the atom scattering coefficient decreases monotonically with increasing energy both before and after an absorption edge, the thin aluminum foil functions as an imperfect high-energy cutoff filter. Without monochromatization, seven different Mg or Al K-emission lines are produced: the unresolved  $K_{\alpha 1,2}$  and the  $K_{\alpha 3}$ ,  $K_{\alpha 4}$ ,  $K_{\alpha 5}$ ,  $K_{\alpha 6}$ , and  $K_{\beta}$  lines [10]. Of these, the  $K_{\alpha 1,2}$  lines are the most intense. Thus, an XPS spectrum will contain peaks excited not only by  $K_{\alpha 1,2}$  but by the other five emission lines as well. The peaks excited by the minor emission lines are called satellites. The  $K_{\alpha 3}$  and  $K_{\alpha 4}$  source satellites are of sufficient intensity (3%–8% of the principal lines) for many vendors to provide a software algorithm that allows them to be stripped from the observed spectra.

For complete removal of satellite lines, and nearly all the Bremsstrahlung radiation, coupled with a valuable improvement in line width, an x-ray monochromator should be used. It so happens that, for Al x-rays, diffraction from the (10 $\bar{1}$ 0) plane of a quartz crystal at a Bragg angle of 78.5° selects the larger component of the  $K_{\alpha}$  doublet, and rejects all other wavelengths. If then the x-ray source anode is placed at a particular point on a focussing sphere (often of diameter 0.5 m), the quartz crystal at another, and the sample at a third, x-rays will be dispersed by the crystal and refocused on the sample. In this way, the line width of the Al  $K_{\alpha}$  radiation is reduced from 0.85 to 0.35 eV. Another advantage of a monochromator is that the hot anode is removed from the near vicinity of the sample, thereby eliminating any possible degradation of the sample by heating. However, a disadvantage is that the x-ray intensity is reduced by a factor of up to 40. In principle, it is also possible to use Ag  $L_{\alpha}$ , Ti  $K_{\alpha}$ , and Cr  $\beta_1$  radiations in monochromators, since their photon line-energies are multiples of Al  $K_{\alpha}$ , which means that a quartz crystal could again be used for dispersion. The use of higher energy x-rays for special applications is becoming more common, and many vendors sell sources with anodes other than Mg and Al. Table 3.2 is a tabulation of x-ray sources in current use. They are all commercially available except for monochromated Si  $K_{\alpha}$  [39] and Cu  $K_{\alpha}$  [40,41]. The former uses a quartz crystal at a Bragg angle of 56.85°, but requires special procedures to prepare the Si anode. The latter uses an LiF(220) crystal.

Several different figures of merit can be used to characterize optical sources, and, in principle, similar ones may be used to compare XPS sources. One such figure of merit is the spectral radiance ( $L_{\lambda}$ ), defined as the radiance (power per unit area per steradian) per unit wavelength with SI units of  $\text{W m}^{-2} \text{sr}^{-1} \text{m}^{-1}$ , although the units  $\text{W m}^{-2} \text{sr}^{-1} \text{nm}^{-1}$  are usually used [46]. Since  $h\nu$ , and not  $\lambda$ , is the parameter usually used in XPS, the analogous figure of merit might be  $L_{h\nu}$ , with units of  $\text{W m}^{-2} \text{sr}^{-1} \text{eV}^{-1}$ . This would be a very useful parameter for comparing sources with different anode materials operating at the same source power, but, unfortunately, is not provided by suppliers, so that research workers simply have to make qualitative comparisons based on the source power (in W), as determined by the maximum filament current and the maximum voltage that may be applied to the anode. On output this energy appears mainly as thermal energy, which is usually removed by cycled chilled water. Only about 1% appears as spectral energy. Radiance can be calculated from the source power provided that the area of the source, the solid angle of emission, and the efficiency of conversion of supply power to photon power are known. To determine the spectral radiance, the actual spectral distribution is needed. Several factors determine the spectral distribution of the x-ray source. One is the geometry, as shown in Figure 3.21, for the x-ray photon intensity distributions of three different source geometries [47]. A second is the target material of the source for a fixed geometry and electron power, as shown in Figure 3.22 [47]. In Figure 3.23, it can be seen that the intensities of the

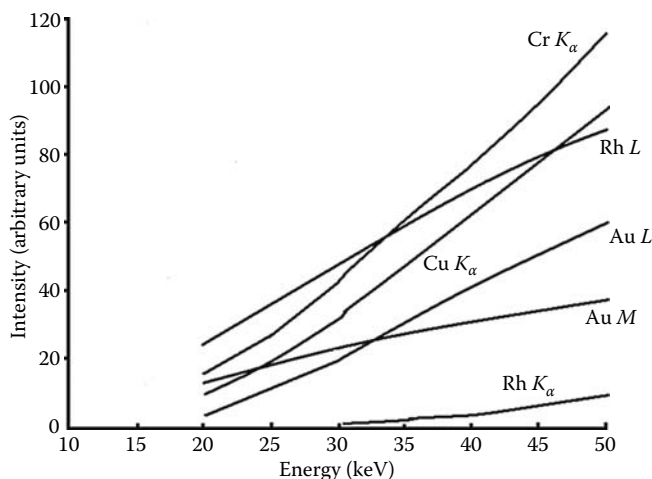


**FIGURE 3.21** Measured x-ray source spectral continuum distributions: effect of source geometry. (From Broll, N. and de Chateaubourg, P., *Adv. X Ray Anal.*, 41, 393, 1999. With permission.)



**FIGURE 3.22** Measured x-ray source spectral continuum distributions: effect of target material. (From Broll, N. and de Chateaubourg, P., *Adv. X Ray Anal.*, 41, 393, 1999. With permission.)





**FIGURE 3.23** Measured x-ray source line intensities as a function of electron power. (From Broll, N. and de Chateaubourg, P., *Adv. X Ray Anal.*, 41, 393, 1999. With permission.)

x-ray lines as a function of electron power all increase monotonically, but the slopes depend on the individual material [47]. In order to evaluate experimental differences in photoionization cross-sections for different sources, the measured intensities must be referenced to a standard level recorded using all sources.

One new source that is not yet commercially available, but has great potential, is the table-top synchrotron [48], in which the radius of the electron orbit is a mere 15 cm. Under the operating conditions described in Ref. [48], it has a spectral radiance similar to that of a rotating anode, that is, a factor of about 10 brighter than that of a fixed anode. The spectral radiance can be increased by a judicious choice of target. However, the real potential of a synchrotron lies in its ability to tune the emergent x-rays over an energy range of several keV up to 20 MeV. Furthermore, the spectral distribution function is almost flat over this range, that is, nearly ideal. Many important photoemission studies that cannot be performed with classical x-ray sources can be with synchrotron radiation. The use of radiation from large diameter (tens of meters) synchrotrons also allows chemical imaging at a lateral resolution of around 20 nm using a photoelectron microscope. Unfortunately, there are only about 50 operational synchrotron facilities worldwide, and there is greater demand than time available. Although the table-top synchrotron, at its present level of development, will not achieve 20 nm lateral resolution, it is likely to be reasonably affordable compared to large synchrotrons, thereby allowing greater numbers of research workers to carry out experiments of greater sophistication.

### 3.10.1.3 Electron Sources

Electron sources for AES and SAM consist of an emitter, either thermionic or field emission, a set of electron lenses for beam focus and transport, and an optional electron energy selector for high-energy resolution. Almost all electron guns provided by suppliers come with a four-pole electrostatic deflector, which allows the beam to be moved in any direction perpendicular to the optical axis; the deflection system for scanning Auger microscopy (SAM) is more complex. The beam stability is determined by the power supply. Figures of merit used for these electron sources are radiance, spot size, and energy spread, and a comparison of them for the various sources is shown in Table 3.3. The suppliers normally make this information available.

Field-emission sources have radiances that are similar to those of synchrotron sources; for example, a synchrotron source operated at 3 GeV and 300 mA stored beam current, an x-ray conversion efficiency of 0.01, a solid angle of  $2\pi \times 10^{-3}$  sr, and an area of  $0.1 \text{ mm}^2$ , has a radiance of

**TABLE 3.3**  
**Comparison of Electron Sources for AES/SAM**

Source	Radiance (W mm <sup>-2</sup> sr <sup>-1</sup> )	Spot Size	Energy Spread $\Delta E$ (eV)
W	$2 \times 10^7$	30–100 $\mu\text{m}$	1.0–3.0
Thoriated W <sup>a</sup>	$4 \times 10^8$		
LaB <sub>6</sub>	$2 \times 10^8$	5–50 $\mu\text{m}$	1.2
<b>Field emission</b>			
Cold	$2 \times 10^{10}$	<5 nm	0.3
Thermal	$2 \times 10^{10}$	<5 nm	1.0
Shottky	$2 \times 10^{10}$	15–30 nm	0.3–1.0

<sup>a</sup> Calculated at 1900 K using the Richardson–Dushman equation and the maximum brightness equation [49].

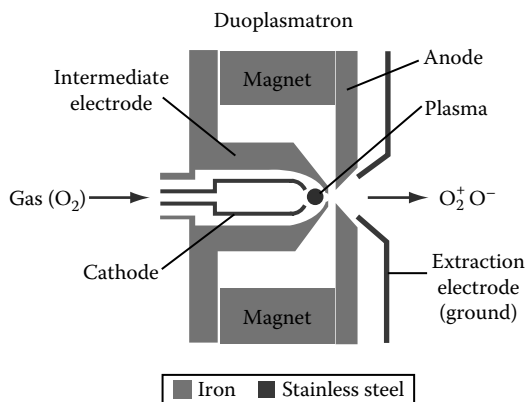
$\sim 2 \times 10^{11}$  W mm<sup>-2</sup> sr<sup>-1</sup> [50], to be compared to those quoted in Table 3.3 for field emission. The energy spread in field-emission sources rivals those of x-ray sources used for XPS. They are used in the more sophisticated SAM instruments, where lateral resolution in the nanometer range is currently the best achieved in dedicated laboratory instruments. The lifetimes of the various types of filament are determined by the material properties and the operating conditions. On the horizon is a new field-emission cathode, based on an array of carbon nanotubes. It has been demonstrated that a single carbon nanotube with a tip diameter of  $\sim 20$  nm has a brightness that is a factor of 10 greater than that of conventional field emitters [51]. Field-emission carbon-nanotube cathodes have been used to make miniature x-ray sources with brightnesses comparable to classical ones [52]. However, the x-ray line-widths are much too large for photoemission.

### 3.10.1.4 Ion Sources

Ion sources for ISS comprise a beam of ions, electrostatic lenses for focus and ion transport, an optional mass filter, and an optional energy filter/selector. They are available with or without deflectors, the latter being used mostly for sputter cleaning. The most commonly used ion is He<sup>+</sup>, but Ne<sup>+</sup> and Ar<sup>+</sup> have also been employed; the ions are generated from the gases by electron impact ionization. Alkali metal ions, that is, Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup>, produced by the surface ionization of directly heated alkali aluminosilicate plugs are also used. Figures of merit for ion sources include the ranges of beam energy, beam current, and spot size, and the spread in the beam energy; beam current and spot size are adjustable independently. Typical operating parameters for a noble-gas ion source for ISS are as follows: beam energy 10 eV–5.0 keV, beam current 1–50 nA, spot size 1–20 mm, and energy spread <5 eV at low current. For an alkali ion source, the corresponding figures would be as follows: beam energy 50 eV–5.0 keV, beam current 1–100 nA, spot size 1–10 mm, and energy spread 0.4 eV (calculated for thermal spread).

The typical energy range for primary ions used in ISS is in fact 1–2 keV, which means that the energy spreads for the sources are acceptable, and an energy selector would be an unnecessary expense. Mass filters, which actually filter according to mass/charge ratio, remove multiply charged ions from the transported beam. When using He, the most commonly used gas, multiply charged ions are not a problem, and so a mass filter is not normally required.

A less common type of ion source used in ISS is the duoplasmatron, a schematic of which is shown in Figure 3.24; it is used when negatively charged primary ions are to be scattered from surfaces. A gas discharge is generated between a cathode and an anode, and the plasma so formed



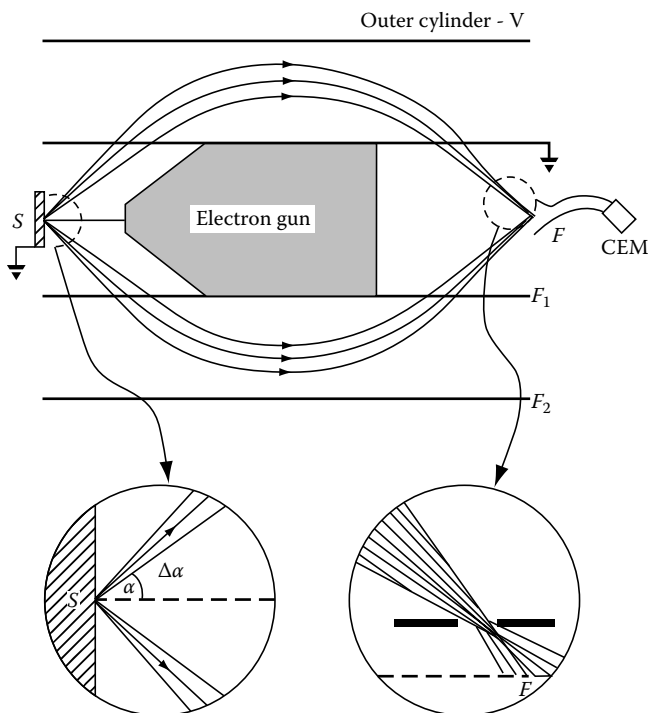
**FIGURE 3.24** Schematic diagram of a duoplasmatron ion source. (From Evans Analytical Group, Online SIMS Instrumentation Tutorial. With permission.)

contains positive ions, negative ions, and neutrals. Either positive ions or negative ions can be extracted, but neutrals with velocities parallel to the source axis and moving toward the exit will also enter the next stage. Deflection is therefore used to separate ions from neutrals, followed by a mass filter to select ions with the desired mass/charge ratio. Duoplasmatron sources are bright sources with energy spreads of the order of 15 eV, and spot sizes of 40–300  $\mu\text{m}$ . A duoplasmatron-like ion source that produces a microbeam with a spot size less than 0.1  $\mu\text{m}$  is being developed [54].

### 3.10.2 ENERGY ANALYZERS

An energy analyzer consists of an energy dispersing element, entrance and exit slits, and (optionally) entrance and exit lenses. Many commercial instruments use an entrance lens, but only a few an exit lens. In XPS,  $\mu\text{XPS}$ ,  $\text{iXPS}$ , AES, and SAM, energy dispersion is achieved by deflection in an electrostatic field. The three types of electrostatic energy analyzer commonly in use are the CMA, the double-pass CMA (DPCMA), and the concentric hemispherical analyzer (CHA). An electrostatic energy analyzer is also the commonly used method of energy dispersion in ISS, but time-of-flight (TOF) analyzers are also used, in which the primary ion-beam is pulsed, and the time taken for a scattered ion to reach a detector, at a known distance from the surface, is measured. In the DPCMA, better energy resolution is achieved by placing two CMAs in series. A schematic of a CMA is shown in Figure 3.25. The analyzer consists of a pair of coaxial cylinders with entrance and exit apertures at the front and back ends, respectively, of the inner cylinder. To reach the detector, a particle must travel along a trajectory that takes it from the entrance aperture, through the space between the two cylinders, through the exit aperture, and into the detector. An ideal CMA has a circular entrance aperture of zero width. The position of the entrance slit relative to the sample position,  $S$  in Figure 3.25, determines the entrance angle,  $\alpha$ . In the figure,  $\alpha$  is the angle between the cylinder axis and the central trajectory shown beginning at  $S$ . The distance  $L$  from  $S$  to the focal point on the axis,  $F$  in Figure 3.25, depends on  $\alpha$ . To discriminate charged particles on the basis of their energies, an electric field is set up between the two cylinders. The inner cylinder is usually grounded, and for the analysis of electrons a negative potential,  $-V$ , is used to generate an electrical field between the two cylinders. Only those electrons with energy  $E$  satisfying the condition

$$E = K_0 eV \left[ \ln \left( \frac{R_2}{R_1} \right) \right]^{-1} \quad (3.10)$$



**FIGURE 3.25** Schematic of a CMA. (From Seah, M.P., *Methods of Surface Analysis*, Cambridge University Press, Cambridge, U.K., 1989. With permission.)

are focussed at  $F$ , where

$K_0$  is a constant

$e$  is the elementary charge

$V$  is the magnitude of the applied potential

$R_1$  is the radius of the inner cylinder

$R_2$  is the radius of the outer cylinder [55]

The same equation applies for univalent positive ions (charge =  $Ze$ , with  $Z = 1$ ), but a positive potential,  $+V$ , is applied to the outer cylinder. For  $\alpha = 42^\circ 18.5'$ , the analyzer becomes a second-order focussing device, since the first-order spherical aberrations vanish, and then  $K_0 = 1.3099$ . In practice, the entrance aperture has a finite width, which allows electrons with entrance angles of  $\alpha - \Delta\alpha$  to  $\alpha + \Delta\alpha$  to enter into the space between the two cylinders. For small values of  $\Delta\alpha$  on either side of  $\alpha = 42^\circ 18.5'$ , electrons of energy  $E$  will be brought to the same focal point, therefore all CMAs are constructed using this particular acceptance angle. However, an unavoidable consequence of a finite width entrance slit is that electrons with energies slightly smaller and slightly larger than  $E$  will also be brought to focus very close to  $F$ . This leads to an uncertainty in the value of  $\Delta E$  for any given applied deflecting voltage. Notice that all the electron trajectories cross in a small region of space within the inner cylinder just before they reach the detector. This crossing region is called the circle of least confusion, and is shown magnified below the analyzer in Figure 3.25.

If there is no ring slit at the circle of least confusion, the relative energy resolution is given by

$$\frac{\Delta E}{E} = \frac{C_s (\Delta\alpha)^3}{D_E + C_c (\Delta\alpha)} \quad (3.11)$$

where

$D_E$  is the specific linear energy dispersion

$C_s$  is the spherical aberration coefficient

$C_c$  is the chromatic aberration coefficient

$\Delta\alpha$  is the in-plane half-angle of acceptance into the analyzer (in radians)

If a ring slit of width  $W$  is placed at the circle of least confusion, the relative energy resolution is then given by

$$\frac{\Delta E}{E} = \frac{0.9W}{R_1} + \frac{1}{4} \left[ \frac{C_s (\Delta\alpha)^3}{D_E + C_c (\Delta\alpha)} \right] \quad (3.12)$$

where  $R_1$  is the radius of the inner cylinder. An appropriate choice of  $W$  for any given set of concentric cylinders will result in improved resolution, but at the expense of a reduction in transmission. The ring slit is not normally adjustable by the user, which represents a consideration that must be addressed at the time of purchase. Although the energy resolution of a CMA is adequate for classical AES and ISS, it is not adequate for XPS or for lineshape analysis in AES. In order to obtain better energy resolution, the DPCMA was developed, and an example is shown in Figure 3.26A. Two hemispherical, retarding grids are placed in front of the sample. The nearer hemispherical grid is at the same potential as the sample, usually ground. When used as an electron energy analyzer, a negative potential,  $-V_1$ , is applied to the second hemispherical grid in order to decelerate the electrons to a selected pass energy  $E_p$ . The same potential is applied to the inner cylinder. A potential  $-V_2$ , such that  $V_2$  is greater than  $V_1$ , is applied to the outer cylinder, the difference  $V_2 - V_1$  determining the pass energy. A spectrum is recorded by ramping the potential on the inner cylinder while maintaining the potential difference between the outer and inner cylinders. The analyzer in Figure 3.26A has four individually selectable entrance/exit slits in the inner cylinder, and two apertures that lie in planes perpendicular to the cylinder axis, one at the midpoint and one at the end of the inner cylinder. During the first pass, electrons are focussed into a region that is smaller than the entrance region. This becomes a source for the second pass CMA, which overall has the effect of reducing  $\Delta\alpha$ . Because the pass energy is fixed, so is  $\Delta E$  throughout the spectrum. The improvement in energy resolution comes with a loss in analyzer transmission.

A CHA consists of two concentric hemispheres, of radii  $R_1$  for the inner and  $R_2$  for the outer. The trajectory along which a charged particle moves from the entrance to the exit slits of the analyzer lies on a hemispherical surface with radius  $R_0$ , between the two hemispheres.  $R_0$  is equal to  $\frac{1}{2}(R_1 + R_2)$ . An electron of energy  $E$  can move from the entrance slit to the exit slit if the condition

$$E = \left( \frac{R_1 R_2}{R_2^2 - R_1^2} \right) e(V_2 - V_1) \quad (3.13)$$

is satisfied, where  $-V_1$  and  $-V_2$  are the potentials applied to the inner and outer hemispheres, respectively, with  $V_2$  greater than  $V_1$  (i.e., the inner hemisphere is more positive than the outer hemisphere) [55]. A spectrum is recorded by scanning the applied potential difference across the concentric hemispheres. For a CHA used without a transport lens, the relative energy resolution is given by the recursive relationship

$$\frac{\Delta E}{E} = \frac{W_1 + W_2}{2} + \frac{C_s (\Delta\alpha)^2}{D_E + C_c (\Delta\alpha) + C_E \left( \frac{\Delta E}{E} \right)} \quad (3.14)$$

where

$W_1$  and  $W_2$  are the entrance and exit slit widths, respectively

$C_E$  is the nonlinear energy dispersion coefficient