MODERN TECHNIQUES OF SURFACE SCIENCE

This fully revised, updated and reorganised Third Edition provides a thorough introduction to the characterisation techniques used in surface science and nanoscience today. Each chapter brings together and compares the different techniques used to address a particular research question, including how to determine the surface composition, surface structure, surface electronic structure, surface microstructure at different length scales (down to submolecular) and the molecular character of adsorbates and their adsorption or reaction properties. Readers will easily understand the relative strengths and limitations of the techniques available to them and, ultimately, will be able to select the most suitable techniques for their own particular research purposes.

This is an essential resource for researchers and practitioners performing materials analysis and for senior undergraduate students looking to gain a clear understanding of the underlying principles and applications of the different characterisation techniques used in the field today.

D. PHIL WOODRUFF is Professor of Physics at the University of Warwick. He has more than 40 years' experience in the development and application of surface science techniques, resulting in more than 500 publications. He has also worked at Bell Laboratories in the USA and spent 13 years in collaboration with the Fritz Haber Institute in Berlin. He is the recipient of several prizes and awards in the UK, USA and Germany, and in 2006 became a Fellow of the Royal Society.

"For more than three decades, the first two editions of Phil Woodruff's text have been a key reference for surface scientists: simple, comprehensive, authoritative, and extremely helpful as a first step for graduate students and junior researchers. The fast evolution of the field required a general update, and this was done in a masterful way. But this new edition goes well beyond: the strategy of the presentation has changed radically to reflect the present situation of the field, becoming a "user-oriented" instrument. As such, it is even more useful than the past editions, and therefore highly recommended."

Giorgio Margaritondo, EPFL

"This is an excellent textbook for introducing students and new researchers to the most important characterization techniques used in surface analysis and adsorption studies, which are of ever-increasing importance in a wide range of chemistry, materials science and nanotechnology research. It is logically organized and very well written for facile understanding by non-experts, yet refers to the best literature sources with more detailed information when needed for the next level of mastery of each method. It is impressive in its in-depth and up-to-date coverage of the most important aspects of this broad range of techniques, all within a moderate-size text. The author is a true expert and pioneer in this field, and it shows in this valuable new contribution."

Charles Campbell, University of Washington

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CAMBRIDGE UNIVERSITY PRESS

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UNIVERSITY PRESS

University Printing House, Cambridge CB2 8BS, United Kingdom

Cambridge University Press is part of the University of Cambridge.

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www.cambridge.org
Information on this title: www.cambridge.org/9781107023109

First published 1986
Second edition 1994
Third edition 2016

Printed in the United Kingdom by TJ International Ltd. Padstow Cornwall

A catalogue record for this publication is available from the British Library

Library of Congress Cataloging-in-Publication Data
Names: Woodruff, D. P., author.
Title: Modern techniques of surface science / D. Phil Woodruff, University of Warwick.
Description: Third edition. | Cambridge, United Kingdom : Cambridge University Press, 2016. | 2016 | Includes bibliographical references and index.
Identifiers: LCCN 2016012974 | ISBN 9781107023109 (hardback ; alk. paper) | ISBN 1107023106 (hardback ; alk. paper)
Subjects: LCSH: Surfaces (Physics)–Technique. | Surface chemistry–Technique. | Spectrum analysis.
Classification: LCC QC173.4.S94 W66 2016 | DDC 530.4/17–dc23 LC record available at http://lccn.loc.gov/2016012974

ISBN 978-1-107-02310-9 Hardback

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Cambridge University Press
978-1-107-02310-9 — Modern Techniques of Surface Science
D. Phil Woodruff
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Preface to First Edition

Since the early 1960s or so there has been a virtual explosion in the level of research on solid surfaces. The importance of understanding surface processes in heterogeneous catalysis had been recognised since the early part of the twentieth century but it was not until the 1960s, with the introduction and development of ultra-high-vacuum techniques, that real advances could be made, even using the 'old' techniques such as low energy electron diffraction (1927) and field emission (1936). The subsequent development of materials science and the growth of the semiconductor industry have added further surface problems for investigation while, at the same time, many new techniques have been introduced and exploited to study surfaces at the atomic level. For someone coming fresh to the field of surface physics or surface chemistry there seems to be a bewildering excess of different techniques, each commonly referred to by its acronym or unpronounceable string of initial letters. Much of the scientific literature in this field is occupied with technique-orientated studies of specific problems in which the strengths and limitations (particularly the latter!) of the technique or techniques used are rarely explained. Quite early in the development of surface science it became evident that surface problems should be tackled using a range of complementary techniques if a proper and complete understanding were to be obtained. Therefore, before one can appreciate the general progress being made in an area of surface science, or select a technique to investigate a particular problem, or understand the results of investigations of one's problem by other methods, it is necessary to understand the basic physical principles, strengths and limitations of the available techniques.

In this book we set out to provide the reader with just this information. The level of presentation and discussion is that appropriate to final-year undergraduates or postgraduate students although the wide scope of the book may well make it useful to many research workers, particularly those working on the periphery of surface science. This wide scope means that we have not attempted to be exhaustive in discussing every application of every technique or the results of all the wealth of published research in the field. What we have attempted to do is to cover all the techniques and to try to illustrate the way in which they can be used. We have also attempted to give some assessment of the value of each technique; these assessments must be, at least in part, subjective, but we hope that they will be seen to be balanced judgements. The presentations of the techniques also include a description of the experimental methods as these often influence or dominate the technique, and in the case of the more longstanding techniques we include some limited historical background. In these instances, where the technique is straightforward, the examples chosen may be from the pioneer workers themselves.

An expert in the field will undoubtedly detect omissions, particularly of some of the most recently developed techniques such as scanning tunnelling electron microscopy, inverse photoemission and Raman techniques. These methods are still quite new and their impact on the field has yet to be assessed. A specialist practitioner of one technique may also feel we have omitted some key application or elegant example; we apologise, but the field is vast and some things have had to be omitted to make this book manageable. We hope, however, that the reader will be able to obtain a clear 'flavour' of the techniques and their applications, and be well armed to delve into specialist review articles on specific techniques to find out more.

Many researchers have kindly given their permission to reproduce their results and in several cases have provided us with more detailed illustrations. Each is acknowledged in the relevant figure caption but we thank them all again for this help and their encouragement.

We should also add a final note on the units in this book. The normal practice in research papers in surface science, like other research fields, falls short of adopting SI units fully. We have, in order to be consistent with this wider literature, retained at least two non-SI units in this book. These are the Å unit of length (1 Å = 0.1 nm) and the torr unit of pressure (1 torr = 133.3 Pa).

D.P.W.
December, 1984 T.A.D.

Preface to Second Edition

In the eight years since the first edition was prepared there has continued to be a high level of activity in the field of surface science, but there has been something of a change in character of the field. In particular, the rate of introduction of new techniques has slowed, and the rate of exploitation of existing methods, especially in the application of multiple methods to single scientific problems, has grown. This consolidation of the field has been a major benefit to the authors of this technique-based book, who found that the task of updating it was less of a hurdle than we might have anticipated when the first edition was published. Nevertheless, there have been some very important developments during the intervening period, and some major new sections have been introduced. For example, the whole field of atomic-scale scanning probe microscopy (particularly scanning tunnelling microscopy) is entering into the mainstream of the surface scientist's armoury. At the time of the first edition this technique could clearly be seen to be very elegant, but the scale of its impact was difficult to judge; even now there is much to be done (particularly on the theory) for it to achieve its full potential, but it has already progressed far beyond the novelty stage. Another, somewhat more prosaic, development included in this new edition is that of inverse photoemission, and particularly the momentum(**k**)-resolved version of the technique, which provides less immediate visual impact than STM images but complements the unique electron band mapping capabilities of angle-resolved photoemission to explore unoccupied as well as occupied states (and might be judged to be comparably elegant by those who like to view the world through **k**-space!). A third entirely new section of this edition deals with the application of X-ray diffraction methods to the investigation of surface structures; here again, methods which were already recognised as potentially valuable eight years ago are now proved to be so and deserve discussion in the spirit of this book, which continues to aim to provide a clear description of the basic physical principles, strengths and weaknesses of the many methods of surface science currently in use.

Apart from these entirely new sections in this edition we have attempted to revise, update and in some cases expand existing treatments of various other techniques which were already included in the earlier edition. Some newer references, including those to other books and review articles, are also included, although certain early reviews continue to provide the best introductions to some techniques. We have continued, however, to restrict our discussions to techniques which have established a proven range of application. Thus, it is notable that in our earlier preface we specifically remarked on the exclusion of STM and inverse photoemission as methods too new to judge. One method which might now be judged to fall into this category is photoelectron microscopy in its various forms. Here is a field of significant instrumental development and a few (but as yet rather few) important applications; perhaps the full impact of this method will be clear in another eight years! We hope that this new edition will be as well received as the first edition appears to have been, and that it will continue to prove of value to those new to surface science research (including graduate students and senior undergraduates) as an introduction to the scientific principles of the techniques used. Our hope is that this benefit will be felt not only by those (especially experimentalists) concerned particularly with one or more of the techniques but also those seeking a complement to books concerned with the basic theory of surface phenomena, such as Zangwill's text *Physics at Surfaces,* also published by Cambridge University Press.

D.P.W.
May, 1993 T.A.D.

Preface to Third Edition

It is now more than 20 years since the second edition of this book was published, and the field of surface science and its associated techniques have matured significantly in this period. Quite a number of the techniques developed in the 1970s and 1980s, in particular, have fallen into disuse; the information they could provide was found to be accessible more easily or with higher quality by other methods. While it is probably true to say that no completely new techniques have emerged in the last two decades, there have been very significant developments in several existing techniques, in many cases due to improvements in the associated detectors and other instrumentation. As a result, the balance of technique utilisation has certainly changed. Microscopies, and particularly (but not only) scanning probe microscopies (SPMs), are now far more widely used, particularly with the growing emphasis on understanding and applying the properties of nanoscale materials. In some cases these SPM techniques are used exclusively, unlearning the lesson of many years of surface science studies that no one technique can completely characterise a surface; the failure to use complementary methods risks seriously misinterpreting the data. Nevertheless, some developments associated with SPM have greatly extended the information obtainable from these techniques in the most detailed studies.

In producing this third edition of *Modern Techniques of Surface Science* I have implemented two significant changes. Firstly, and most obviously, I have substantially updated the content. Techniques described in early editions that have fallen into disuse have mostly been removed, although in a few cases brief descriptions have been retained to provide some historical perspective to current practice. By contrast, some sections have been substantially extended to reflect more recent developments. I have also, in large part, used more recent examples to illustrate specific techniques. Sometimes it is the earliest examples of the use of a technique that most clearly illustrate the physical principles and how the data are interpreted, perhaps because these early applications involve simpler systems. For this reason some early examples are retained.

The second major change in this third edition is to completely reorganise the material. The earlier editions were organised broadly according to the nature of the incident probes: what can I learn using incident electrons, or photons or ions? This seemed to be a good scheme in the early development of these techniques, when researchers purchased or built instrumentation using one of these probes with a particular experiment in mind, but then wanted to broaden the scope of their studies within the constraints of the available instrumentation. Coming to surface science now, with a range of mature methods available, it seems more appropriate to ask a different question: what is the best method to obtain the particular information I seek, such as the surface composition, or the surface structure or the surface electronic structure? Accordingly, the chapters in this new edition are organised according to these questions. This structure does lead to somewhat more cross-references between chapters than the earlier scheme. For example, X-ray photoelectron spectroscopy (XPS) as a core level spectroscopy is firstly a technique for determining surface compositions (Chapter 2), but the 'chemical shifts' in the photoelectron binding energies that are observed, a consequence of changes in electronic structure (Chapter 5), provide a spectral fingerprint that can aid in identifying molecular character (Chapter 6). More generally, however, there *are* many interconnections in techniques and instrumentation that will lead to cross-referencing, whatever organisational scheme is used. Coincidentally, while I lectured to senior undergraduates and new postgraduates at the University of Warwick on the techniques of surface science and their underlying physics over many years, naturally using *Modern Techniques of Surface Science* as a reference text, I increasingly came to organise the material along the lines that I have now used in the book.

Although this is billed as the third edition of *Modern Techniques of Surface Science*, implying a direct continuity, a very large part of the text (and associated figures) is new. When restructuring the book it seemed easier to start afresh in many places rather than being constrained by text written to fit the old structure. I hope readers will still find the book valuable as a teaching aid, whether it is self-taught or accompanied by lectures, for young (and not-so-young) researchers coming new to the field.

As in the earlier editions, the positive responses to my requests to other researchers for (now electronic versions of) figures, in some case producing significantly modified versions of published figures, has been of great help; individual acknowledgements are included in the relevant figure captions. I have also benefitted from detailed discussions with some experts in techniques that I have never used personally; I believe that this has led to more informed judgements in several cases though any remaining faults are mine, not theirs.

December 2015 DPW

Abbreviations

2PPE	Two-photon photoemission
3DAP	Three-dimensional atom probe
AES	Auger electron spectroscopy
AFM	Atomic force microscopy
AM-AFM	Amplitude modulated atomic force microscopy
APD	Atom probe tomography
ARPES	Angle-resolved photoelectron spectroscopy
ARSPIPES	Angle-resolved spin-polarised inverse photoemission spectroscopy
ARUPS	Angle-resolved ultraviolet photoelectron spectroscopy
BIS	Bremsstrahlung isochromat spectroscopy
CAICISS	Coaxial impact collision ion scattering spectroscopy
CHA	Concentric hemispherical analyser
CI	Configuration interaction
CITS	Current imaging tunnelling spectroscopy
CMA	Cylindrical mirror analyser
CPD	Contact potential difference
DFT	Density functional theory
DLEED	Diffuse low energy electron diffraction
DOS	Density of states
EELS	Electron energy loss spectroscopy
ESCA	Electron spectroscopy for chemical analysis
ESD	Electron stimulated desorption
ESDIAD	Electron stimulated desorption ion angular distributions
EXAFS	Extended X-ray absorption fine structure
FAD	Fast atom diffraction
FEM	Field emission microscopy
FIM	Field ion microscopy

FM-AFM	Frequency modulated atomic force microscopy
FOM	Figure of merit
FSCI	Final-state configuration interaction
FTRAIRS	Fourier transform reflection absorption infrared spectroscopy
FWHM	Full width half maximum
FZP	Fresnel zone plate
GIXRD	Grazing incidence X-ray diffraction
HAS	Helium atom scattering
HAXPES	Hard X-ray photoelectron spectroscopy
HEIS	High energy ion scattering
HOMO	Highest occupied molecular orbital
HREELS	High-resolution electron energy loss spectroscopy
HRTEM	High-resolution transmission electron microscopy
IETS	Inelastic electron tunnelling spectroscopy
iHAS	Inelastic helium atom scattering
INS	Ion neutralisation spectroscopy
IPES	Inverse photoemission spectroscopy
IRAS (IRRAS)	Infrared reflection–absorption spectroscopy
ISS	Ion scattering spectroscopy
KPFM	Kelvin probe force microscopy
KRIPES	*k*-resolved inverse photoemission spectroscopy
LDOS	Local density of states
LEED	Low energy electron diffraction
LEEM	Low energy electron microscopy
LEIS	Low energy ion scattering
LER	Linear extension resonator
LOSMS	Line-of-sight mass spectrometry
LUMO	Lowest unoccupied molecular orbital
MAES	Metastable atom electron spectroscopy
MBE	Molecular beam epitaxy
MCT	Mercury cadmium telluride
MDS	Metastable de-excitation spectroscopy
MEIS	Medium energy ion scattering
MIES	Metastable impact electron spectroscopy
MQS	Metastable quenching spectroscopy
NC-AFM	Non-contact atomic force microscopy
NEXAFS	Near-edge X-ray absorption fine structure
NISXW	Normal incidence X-ray standing waves
PD	Photoelectron diffraction

PED	Photoelectron diffraction
PEEM	Photoelectron emission microscopy
PES	Photoelectron spectroscopy
PhD	(Scanned-energy mode) photoelectron diffraction
PIES	Penning ionisation electron spectroscopy
PMA	Plane mirror analyser
PSD	Photon stimulated desorption
RAIRS	Reflection–absorption infrared spectroscopy
RBS	Rutherford backscattering
REMPI	Resonant-enhanced multiphoton ionisation
RFA	Retarding field analyser
RHEED	Reflection high energy electron diffraction
RIXS	Resonant inelastic X-ray scattering
SAM	Scanning Auger microscopy
SCAC	Single-crystal adsorption calorimetry
SCLS	Surface core-level shift
SERS	Surface enhanced Raman spectroscopy
SEXAFS	Surface EXAFS (extended X-ray absorption fine structure)
SFG	Sum frequency generation
SHG	Second harmonic generation
SIMS	Secondary ion mass spectrometry
SPA-LEED	Spot profile analysis low energy electron diffraction
SP-ARPES	Spin-polarised angle-resolved photoelectron spectroscopy
SPEM	Scanning photoelectron microscopy
SPIES	Surface Penning ionisation electron spectroscopy
SP-KRIPES	Spin-polarised *k*-resolved inverse photoemission spectroscopy
SSIMS	Static SIMS
STM	Scanning tunnelling microscopy
STM-IETS	Scanning tunnelling microscopy inelastic electron tunnelling spectroscopy
STS	Scanning tunnelling spectroscopy
SXRD	Surface X-ray diffraction
TDS	Thermal desorption spectroscopy
TEAS	Thermal energy atom scattering
TEM	Transmission electron microscopy (or microscope)
TLK	Terrace-ledge kink
TOF	Time of flight

TPD	Temperature programmed desorption
TPRS	Temperature programmed reaction spectroscopy
UHV	Ultra-high vacuum
UPS	Ultraviolet photoelectron spectroscopy
VEELS	Vibrational electron energy loss spectroscopy
XAFS	X-ray absorption fine structure
XANES	X-ray absorption near-edge structure
XES	X-ray emission spectroscopy
XMCD	X-ray magnetic circular dichroism
XPD	X-ray photoelectron diffraction
XPEEM	X-ray photoelectron emission spectroscopy
XPS	X-ray photoelectron spectroscopy
XSW	X-ray standing wavefield absorption