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and Henning Bubert

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Surface and Thin Film Analysis

A Compendium of Principles, Instrumentation, and Applications

Second, Completely Revised and Enlarged Edition
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Preface to the First Edition

The surface of a solid interacts with its environment. It may be changed by the surrounding medium either unintentionally (for example, by corrosion) or intentionally due to technological demands. Intentional changes are made in order to refine or protect surfaces, that is, to generate new surface properties. Such surface changes can be made, for instance, by ion implantation, deposition of thin films, epitaxially grown layers, and other procedures. In all these cases, it is necessary to analyze the surface, the layer or system of layers, the grain boundaries, or other interfaces in order to control the process which finally meets the technological requirements for a purposefully changed surface. A wealth of analytical methods is available to the analyst, and the choice of the method appropriate for the solution of his problem requires a basic knowledge on the methods, techniques, and procedures of surface and thin film analysis.

Therefore, the goal of this book is to give the analyst—whether a newcomer wishing to acquaint with new methods or a materials analyst seeking information on methods that are not available in his own laboratory—a clue about the principles, instrumentation, and applications of the methods, techniques, and procedures of surface and thin film analysis. The first step into this direction was the chapter *Surface and Thin Film Analysis* of *Ullmann’s Encyclopedia of Industrial Chemistry* (Vol. B6, Wiley-VCH, Weinheim 2002), in which practitioners give a brief outline of various important methods.

The present book is based on that chapter. It has essentially been extended by new sections dealing with electron energy loss spectroscopy (EELS), low-energy electron diffraction (LEED), elastic recoil detection analysis (ERDA), nuclear reaction analysis (NRA), energy dispersive X-ray spectroscopy (EDXS), X-ray diffraction (XRD), surface analysis by laser ablation (LA), and ion-beam spectrochemical analysis (IBSCA). Thus, the book now comprises the most important methods and should help the analyst to make decisions on the proper choice of methods for a given problem. Except for atomic force microscopy (AFM) and scanning tunneling microscopy (STM), microscopic methods, as essential as they are for the characterization of surfaces, are only briefly discussed when combined with a spectroscopic method. Methods of only limited importance for the solution of very special problems, or without availability of commercial equipment, are not considered or
only briefly mentioned in the sections entitled *Other Electron/Ion/Photon Detecting Techniques*.

Furthermore, the objective was not to issue a voluminous book, but a clearly arranged one outlining the basic principles and major applications of important methods of surface and thin film analysis. For more detailed information on any of these topics, the reader is referred to the special literature given in the references.

The editors are gratefully indebted to all contributors who were ready to redirect time from their research, educational, and private activities in order to contribute to this book. They also wish to thank Mrs Silke Kittel for her tireless help in developing our editorial ideas.

Autumn 2001

Henning Bubert
Holger Jenett
Preface to the Second Edition

The first edition of this book was very well received on the market and, after becoming “out-of-print”, a variety of ideas was discussed to produce a second edition. It became clear to us very quickly that, instead of an unchanged reprint of the first edition, the opportunity should be taken to update the information in the book and to add new chapters based on feedback from our readers. Fortunately, all authors of the first edition immediately supported this idea, though some were no longer available to actively contribute to the revisions due to changes in their professional careers.

Almost all chapters of this book have been thoroughly revised, taking into consideration new developments on the described methods as well as valuable feedback from the First Edition. Although a complete collection of surface analytical techniques would be beyond the scope of a compendium such as this, new chapters on field ion microscopy (FIM) and atom probe (AP), sum frequency generation (SFG), and scanning near-field optical microscopy (SNOM) have been added.

With regard to Appendix B the point must be addressed that, due to a rapidly changing market that is characterized by the frequent takeover of one company (or of their subsidiaries) by another, it became rather difficult to produce a compilation that was fully consistent with regard to the names of brands, branches, and company owners. However, the given internet addresses should serve to guide readers to the desired information and contacts to their local distributors.

The editors would like to thank all authors for revising and updating their chapters from the First Edition of the book, and all new authors for writing the new chapters and for revising some of the chapters already in existence. To those authors who were unable to revise their chapters themselves, we are certainly indebted that they agreed to a revision of their chapters by new authors. Without this consent between “old” and “new” authors the revision of this book would not have been possible.

Finally, we would like to thank Dr. Manfred Köhl and Mrs. Lesley Belfit from Wiley-VCH for their continued support to move this book project forward, as well as Mrs. Bernadette Cabo for the helpful and pleasant communication during the production process.

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1
Introduction

John C. Rivière and Henning Bubert

Wherever the properties of a solid surface are important, it is also important to have the means to measure those properties. The surfaces of solids play an overriding part in a remarkably large number of processes, phenomena, and materials of technological importance. These include: catalysis; corrosion, passivation, and rusting; adhesion; tribology, friction, and wear; brittle fracture of metals and ceramics; microelectronics; composites; surface treatments of polymers and plastics; protective coatings; superconductors; and solid-surface reactions of all types with gases, liquids, or other solids. The surfaces in question are not always external; processes occurring at inner surfaces such as interfaces and grain boundaries are often just as critical to the behavior of the material. In all of the above examples, the nature of a process or of the behavior of a material can be understood completely only if information about both the surface composition (i.e., the types of atoms present and their concentrations) and the surface chemistry (i.e., the chemical states of the atoms) is available. Furthermore, knowledge of the arrangement of surface atoms (i.e., the surface structure) is also necessary.

First of all, what is meant by a solid surface? Ideally, the surface should be defined as the plane at which the solid terminates—that is, the last atom layer before the adjacent phase (vacuum, vapor, liquid, or another solid) begins. Unfortunately such a definition is impractical, because the effect of termination extends into the solid beyond the outermost atom layer. Indeed, the current definition is based on that knowledge, and the surface is thus regarded as consisting of that number of atom layers over which the effect of termination of the solid decays until bulk properties are reached. In practice, this decay distance is of the order of 5–20 nm.

By a fortunate coincidence, the depth into the solid from which information is provided by the techniques described here matches the above definition of a surface in many cases. These techniques are, therefore, surface-specific; in other words, the information they provide comes only from that very shallow depth of a few atom layers. Other techniques can be surface-sensitive, in that they would normally be regarded as techniques for bulk analysis, but have sufficient sensitivity for certain elements that can be analyzed only if they are present on the surface.
1 Introduction

Why should surfaces be so important? The answer is twofold. First, the properties of surface atoms are usually different from those of the same atoms in the bulk; and second, because in any interaction of a solid with another phase the surface atoms are the first to be encountered. Even at the surface of a perfect single crystal the surface atoms behave differently from those in the bulk, simply because they do not have the same number of nearest neighbors; their electronic distributions are altered, and hence their reactivity. Their structural arrangement is often also different. When the surface of a polycrystalline or glassy multielemental solid is considered—such as that of an alloy or a chemical compound—the situation can be very complex. The processes of preparation or fabrication can produce a material, the surface composition of which is quite different from that of the bulk, in terms of both constituent and impurity elements. Subsequent treatment (e.g., thermal and chemical) will almost certainly change the surface composition to something different again. The surface is highly unlikely to be smooth, and roughness at both the micro and macro level can be present, leading to the likelihood that many surface atoms will be situated at corners and edges and on protuberances (i.e., in positions of increased reactivity). Surfaces exposed to the atmosphere, which include many of those of technological interest, will acquire a contaminant layer that is one to two atom layers thick, containing principally carbon and oxygen but also other impurities present in the local environment. Atmospheric exposure might also cause oxidation. Because of all these possibilities, the surface region must be considered as a separate entity, effectively a separate quasi-two-dimensional (2-D) phase overlaying the normal bulk phase. Analysis of the properties of such a quasi phase necessitates the use of techniques in which the information provided originates only or largely within the phase—that is, the surface-specific techniques described in this volume.

Nearly all these techniques involve interrogation of the surface with a particle probe. The function of the probe is to excite surface atoms into states giving rise to the emission of one or more of a variety of secondary particles such as electrons, photons, ions, and neutrals. Since the primary particles used in the probing beam can also be electrons or photons, or ions or neutrals, many separate techniques are possible, each based on a different primary–secondary particle combination. Most of these possibilities have now been established, but in fact not all the resulting techniques are of general application—some due to the restricted or specialized nature of the information obtained, and others due to difficult experimental requirements. In this book, therefore, most space is devoted to those surface analytical techniques that are widely applied and readily available commercially, whereas much briefer descriptions are provided of some others, the use of which is less common but which—under appropriate circumstances, particularly in basic research—can provide vital information.

Since the various types of particle can appear in both primary excitation and secondary emission, most authors and reviewers have found it convenient to group the techniques in a matrix, in which the rows refer to the nature of the exciting particle and the columns to the nature of the emitted particle. Such a matrix of techniques is provided in Table 1.1, which uses widely accepted acronyms. The
meanings of the acronyms, together with some of the alternatives that have appeared in the literature, are provided in Listing 1.1.

A few techniques cannot be classified according to the nature of the exciting particle, because they do not employ primary particles but depend instead on the application either of heat or a high electric field. These techniques are listed in Table 1.2.

<table>
<thead>
<tr>
<th>Detection</th>
<th>Excitation</th>
</tr>
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<tbody>
<tr>
<td>e⁻</td>
<td>AES, EELS, AEFS, LEED, LEED</td>
</tr>
<tr>
<td></td>
<td>SAM</td>
</tr>
<tr>
<td>A⁺, A⁻, A⁰</td>
<td>ESD, ESDIAD</td>
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<tr>
<td></td>
<td></td>
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<tr>
<td>hv</td>
<td>EDXS, SXAPS, IPES</td>
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</table>

a) Some of the techniques in Table 1.1 have angle-resolved variants, with the prefix AR (e.g., ARUPS), or use Fourier-transform methods, with the prefix FT (e.g., FT-RAIRS).

<table>
<thead>
<tr>
<th>Detection</th>
<th>Excitation</th>
</tr>
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<tbody>
<tr>
<td>A⁺</td>
<td>TDS</td>
</tr>
<tr>
<td>A⁻</td>
<td>TDS</td>
</tr>
<tr>
<td>e⁻</td>
<td>IETS</td>
</tr>
<tr>
<td>(Displacement)</td>
<td></td>
</tr>
</tbody>
</table>
### Listing 1.1. Meanings of the surface analysis acronyms, and their alternatives, that appear in Tables 1.1 and 1.2.

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td><strong>1. Electron Excitation</strong></td>
<td>AES, Auger electron spectroscopy</td>
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<tr>
<td></td>
<td>BIS, Bremsstrahlung isochromat spectroscopy (or ILS, ionization loss spectroscopy)</td>
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<tr>
<td></td>
<td>EDXS, Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td></td>
<td>EELS, Electron energy loss spectroscopy</td>
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<tr>
<td></td>
<td>EFTEM, Energy-filtered transmission electron microscopy</td>
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<tr>
<td></td>
<td>ESD, Electron-stimulated desorption (or EID, electron-induced desorption)</td>
</tr>
<tr>
<td></td>
<td>ESDLAD, Electron-stimulated desorption ion angular distribution</td>
</tr>
<tr>
<td></td>
<td>IPES, Inverse photoemission spectroscopy</td>
</tr>
<tr>
<td></td>
<td>LEED, Low-energy electron diffraction</td>
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<tr>
<td></td>
<td>RHEED, Reflection high-energy electron diffraction</td>
</tr>
<tr>
<td></td>
<td>SXAPS, Soft X-ray appearance potential spectroscopy (or APS, appearance potential spectroscopy)</td>
</tr>
<tr>
<td></td>
<td>SAM, Scanning Auger microscopy</td>
</tr>
<tr>
<td><strong>2. Ion Excitation</strong></td>
<td>ERDA, Elastic recoil detection analysis</td>
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<tr>
<td></td>
<td>GDMS, Glow discharge mass spectrometry</td>
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<tr>
<td></td>
<td>GD-OES, Glow discharge optical emission spectroscopy</td>
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<tr>
<td></td>
<td>IAES, Ion (excited) Auger electron spectroscopy</td>
</tr>
<tr>
<td></td>
<td>IBSCA, Ion beam spectrochemical analysis (or SCANIIIR, surface composition by analysis of neutral and ion impact radiation or BLE, bombardment-induced light emission)</td>
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<tr>
<td></td>
<td>INS, Ion neutralization spectroscopy</td>
</tr>
<tr>
<td></td>
<td>LEIS, Low-energy ion scattering (or ISS, Ion-scattering spectroscopy)</td>
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<tr>
<td></td>
<td>NRA, Nuclear reaction analysis</td>
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<tr>
<td></td>
<td>RBS, Rutherford back-scattering spectroscopy (or HEIS, high-energy ion scattering)</td>
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<tr>
<td></td>
<td>SIMS, Secondary-ion mass spectrometry (SSIMS, static secondary-ion mass spectrometry) (DSIMS, dynamic secondary-ion mass spectrometry)</td>
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</tbody>
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