# Introduction

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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.

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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.

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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 guite 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 guasi-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

| Detection  | Excitation <sup>a)</sup>     |                     |                               |                              |  |                     |  |
|--|------------------------------|---------------------|-------------------------------|------------------------------|--|---------------------|--|
|  | Electrons, e⁻                |                     | Ions, neutrals, A⁺,<br>A⁻, A⁰ |                              | Photons, <i>hv</i>                               |                     |  |
|  | AES<br>EELS<br>EFTEM<br>LEED | <b>SAM</b><br>Rheed | IAES<br>INS                   |                              | XPS  | UPS                 |  |
| A <sup>+</sup> , A <sup>-</sup> , A <sup>0</sup> | ESD                          | ESDIAD              | SIMS<br>GDMS<br>RBS<br>ERDA   | SNMS<br>FABMS<br>LEIS<br>NRA |  |                     |  |
| hv   | EDXS<br>SXAPS<br>IPES        | BIS                 | GD-OES<br>IBSCA               |                              | TXRF<br>XRD<br>LA<br>RAIRS<br>SHG<br>ELL<br>SNOM | LIBS<br>SERS<br>SFG |  |

 
 Table 1.1
 Surface-specific analytical techniques using particle or photon excitation. The
 acronyms (see Listing 1.1) printed in bold are those used for methods discussed in more detail in this book.

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).

| Detection      | Excitation      |                  |                  |     |  |  |  |
|----------------|-----------------|------------------|------------------|-----|--|--|--|
|                | Heat, <i>kT</i> | High electrica   | Mechanical force |     |  |  |  |
| A <sup>+</sup> | TDS             | FIM              | AP               |     |  |  |  |
| Ā              | TDS             |                  |                  |     |  |  |  |
| e              |                 | IETS<br>STM, STS |                  |     |  |  |  |
| (Displacement) |                 |                  |                  | AFM |  |  |  |

 Table 1.2
 Surface-specific analytical techniques using non-particle excitation.

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.

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Listing 1.1. Meanings of the surface analysis acronyms, and their alternatives, that appear in Tables 1.1. and 1.2.

### 1. Electron Excitation

AES, Auger electron spectroscopy

BIS, Bremsstrahlung isochromat spectroscopy (or ILS, ionization loss spectroscopy)

EDXS, Energy-dispersive X-ray spectroscopy

EELS, Electron energy loss spectroscopy

EFTEM, Energy-filtered transmission electron microscopy

ESD, Electron-stimulated desorption (or EID, electron-induced desorption)

ESDIAD, Electron-stimulated desorption ion angular distribution

IPES, Inverse photoemission spectroscopy

LEED, Low-energy electron diffraction

RHEED, Reflection high-energy electron diffraction

SXAPS, Soft X-ray appearance potential spectroscopy (or APS, appearance potential spectroscopy)

SAM, Scanning Auger microscopy

#### 2. Ion Excitation

ERDA, Elastic recoil detection analysis

GDMS, Glow discharge mass spectrometry

GD-OES, Glow discharge optical emission spectroscopy

IAES, Ion (excited) Auger electron spectroscopy

IBSCA, Ion beam spectrochemical analysis (or SCANIIR, surface composition by analysis of neutral and ion impact radiation or BLE, bombardmentinduced light emission)

INS, Ion neutralization spectroscopy

LEIS, Low-energy ion scattering (or ISS, Ion-scattering spectroscopy)

NRA, Nuclear reaction analysis

RBS, Rutherford back-scattering spectroscopy (or HEIS, high-energy ion scattering)

SIMS, Secondary-ion mass spectrometry (SSIMS, static secondary-ion mass spectrometry) (DSIMS, dynamic secondary-ion mass spectrometry)

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SNMS, Secondary neutral mass spectrometry

# 3. Photon Excitation

ELL, Ellipsometry

LA, Laser ablation

LIBS, Laser-induced breakdown spectroscopy (or LIPS, Laser-induced plasma spectroscopy)

RAIRS, Reflection-absorption infrared spectroscopy (or IRRAS, infrared reflection-absorption spectroscopy, or IRAS, infrared absorption spectroscopy, or ERIRS, external reflection infrared spectroscopy)

SERS, Surface-enhanced Raman scattering

SFG, Sum frequency generation

SHG, (optical) Second harmonic generation

SNOM, Scanning near-field optical microscopy

TXRF, Total reflection X-ray fluorescence analysis

UPS, Ultraviolet photoelectron spectroscopy

XPS, X-ray photoelectron spectroscopy (or ESCA, electron spectroscopy for chemical analysis)

XRD, X-ray diffraction

## 4. Neutral Excitation

FABMS, Fast-atom bombardment mass spectrometry

5. Thermal Excitation

TDS, Thermal desorption spectroscopy

# 6. High-Field Excitation

AP, Atom probe

FIM, Field ion microscopy

IETS, Inelastic electron tunneling spectroscopy

STM, Scanning tunneling microscopy

STS, Scanning tunneling spectroscopy

7. Mechanical Force

AFM, Atomic force microscopy