

Electron Spectroscopy for Surface Analysis

Edited by H. Ibach

With Contributions by

J. D. Carette B. Feuerbacher B. Fitton

H. Froitzheim M. Henzler H. Ibach

J. Kirschner D. Roy

With 123 Figures

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Preface

The development of surface physics and surface chemistry as a science is closely related to the technical development of a number of methods involving electrons either as an excitation source or as an emitted particle carrying characteristic information. Many of these various kinds of electron spectroscopies have become commercially available and have made their way into industrial laboratories. Others are still in an early stage, but may become of increasing importance in the future. In this book an assessment of the various merits and possible drawbacks of the most frequently used electron spectroscopies is attempted. Emphasis is put on practical examples and experimental design rather than on theoretical considerations. The book addresses itself to the reader who wishes to know which electron spectroscopy or which combination of different electron spectroscopies he may choose for the particular problems under investigation.

After a brief introduction the practical design of electron spectrometers and their figures of merit important for the different applications are discussed in Chapter 2. Chapter 3 deals with electron excited electron spectroscopies which are used for the elemental analysis of surfaces. Structure analysis by electron diffraction is described in Chapter 4 with special emphasis on the use of electron diffraction for the investigation of surface imperfections. For the application of electron diffraction to surface crystallography in general, the reader is referred to Volume 4 of "Topics in Applied Physics". Chapter 5 discusses phonon excited electron spectroscopies and Chapter 6 is devoted to electron-loss spectroscopy. This technique has found rather important applications recently for the investigation both of electronic transitions and surface vibrations.

Specific surface systems are discussed in Chapters 3 to 6; however, only in connection with the experimental technique used and only insofar as the question of the specific information provided by the technique is addressed. For further details of the physical interpretation, the reader is referred to the literature. It is hoped that this book may serve as a guide through the embarrassing number of different electron spectroscopies that are in practical use.

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1. Introduction

H. Ibach

With 2 Figures

1.1 Electron Spectroscopy and Its Importance in Surface Science

Modern technologies frequently make use of the interaction of gases and fluids with solids and the properties of interfaces or thin films. Still our knowledge about fundamental processes at surfaces and interfaces is rather limited. The great difficulties in the understanding of heterogeneous catalysis, corrosion protection, semiconductor and thin-film technology have spurred many scientists to develop new tools for the study of surfaces and to learn more about the chemical and physical nature of the solid in its outermost atomic layers. Concurrently, the commercial availability of surface analysis instruments and the mature stage of ultrahigh-vacuum equipment in general is already beginning to have a major impact on further progress of the applied sciences.

The use of ultrahigh vacuum is in general considered as an advantage since it permits the investigation of surfaces under static and stable conditions. However, for many questions of technical importance especially those in the field of catalysis and corrosion, the high vacuum required by the surface analytical technique itself may actually be a drawback. The availability of surface analytical tools that operate while the surface is in contact with a liquid or high gas pressures remains the major need in surface science. While such a technique would allow analysis of the surface under the conditions to which they are exposed in reality, the present tools are limited to investigations under static low gas pressure conditions. Possible major differences in composition and structure of surfaces under these two conditions are the reason for a "credibility gap" between pure surface science and applied technology.

Surface analytical tools mostly make use of particles such as photons, electrons, atoms, molecules or ions. As in material science in general, the most valuable information is obtained by various kinds of spectroscopies. Surface spectroscopies, however, encounter the difficult problem of being selective to a rather small number of surface atoms compared to bulk atoms. The natural way to circumvent this problem is to reduce the number of contributing bulk atoms by using particles of appropriate energy that probe only a few Å into the solid. Still, separation between surface and bulk properties may remain difficult.

Among the available particles for surface spectroscopies electrons as the carriers of the specific information have found by far the widest application for a number of reasons:

1) Electrons have an inelastic mean free path of a few \AA depending on the energy. Energy and momentum of an electron are therefore characteristic of elementary excitations near the surface.

2) Electrons are easily focused into beams and the energy may be varied by applying appropriate potentials.

3) Electrons are efficiently detected and counted.

4) Electrons may be analyzed with respect to angular and energy distribution using electrostatic lenses and deflection systems.

5) Another major advantage of electrons which one comes to appreciate, if one has ever worked with atoms, molecules, or ions as probing particles, is that electrons disappear from the vacuum system after being used for the surface analysis.

Electrons offer a wide range of different spectroscopies with different type of information: surface structure, elemental composition, chemical bond and surface vibrations may be investigated on clean or gas-covered surfaces. Single crystal surfaces are, in general, not required however widely used in fundamentally oriented studies. The various kinds of electron spectroscopies may be divided into two subgroups. In the first group of spectroscopies, the solid is excited by an electron beam and either the backscattered electrons or secondary electrons are analyzed. In the second group, electrons are generated by photon excitation. Other sources of electron excitation are possible, however, but not in wide-spread use so far.

Although electrons have been so successfully applied in surface science and the overwhelming part of our knowledge about surfaces stems from one or the other kind of electron spectroscopy, it should not be concealed that the use of the electron as the carrier of surface information has certain inherent limitations.

As already mentioned, rather good high vacuum conditions are required for the normal operation of the electron spectroscopic methods. Unfortunately this high vacuum requirement makes electron spectroscopic studies of surfaces in technical environments impossible. Even the analysis of such surfaces *in situ* after evacuating the gas is of limited value as evacuation may change the surface condition. Nevertheless this last variant is to be preferred to the transportation of the surface in air. The requirement of good vacuum is automatically overfulfilled in fundamental surface studies because in this case the partial pressure of reactive gases as hydrogen, oxygen, carbon monoxide, and nitrogen must be kept at least in the low 10^{-10} mbar range. Because of the much lower sticking coefficient, 10^{-9} mbar may be tolerated for clean semiconductor surfaces.

Another limitation arises from the fact that electron spectroscopies are in general not nondestructive. This holds especially for those spectroscopies where e-

electron beams of high current are used as a primary source of excitation. The excitation or ionization of the surface atoms of the substrate and of adsorbed molecules or atoms provides enough energy for dissociation, desorption, and chemical reactions. Cross sections for electron-stimulated desorption of adsorbed gases range from 10^{-15} cm^2 down to unmeasurable small values [1.1]. The highest values have been found for adsorbed halides, which are therefore rather difficult to detect by electron spectroscopies. Smaller values in the 10^{-18} cm^2 range and below apply to more stable adsorption systems. These are sufficiently low to allow an electron-beam excited surface analysis, provided that one works with a moderately focused beam. Highly focused beams of a few microns diameter as used, for instance, in scanning Auger spectroscopy still may cause problems and one has to check for electron stimulated desorption effects on any particular system under investigation. Only for substrate atoms, electron-stimulated desorption may be neglected. In addition to electron-stimulated desorption, the electron beam may cause surface chemical reactions. Frequently a cracking of hydrocarbons and carbon monoxide adsorbed on the surface is observed. Light products may desorb and carbonaceous layers are deposited on the surface. Carbon deposition may proceed at a rather rapid rate in poor vacuum.

Another source of continuous concern and confusion is the information depth of electron spectroscopies, i.e., the thickness of the surface layer that is actually probed in the particular experiment. The information depth depends on the electron energy and the material; in some cases it is even difficult to define what one may consider as the information depth. This most important question warrants a more detailed discussion which is given in the next paragraph. In any case electron spectroscopies are tools for a true surface analysis only in a limited sense. Even the smallest obtainable information depth of about 5 \AA is sufficiently high so that not only true surface properties but also properties of bulk atoms are investigated simultaneously. This causes the problem of discriminating between properties of surface atoms and bulk atoms for which a general solution has not yet been found. For adsorbate systems one may consider the difference between the clean and the adsorbate-covered surface as being the property of the adsorbate layer. For the investigation of the properties of surface substrate atoms, no such method exists. Substantial confusion may arise from this fact, especially in alloy substrates where the chemical composition of the surface layer may be different from the second and deeper layers. Surface analytical techniques other than electron spectroscopies (e.g., ion backscattering) should be used to solve such questions.

1.2 The Information Depth

For most electron spectroscopies (with a few exceptions) the characteristic surface information is contained in the energy E and momentum k of the electron escaping the material. Therefore the information is lost after elastic or inelastic scattering events that the electron may encounter on its way between the point where it was generated and the surface. Inelastic scattering processes arise from electron-electron or electron-phonon interactions. With the present experimental resolution the energy loss in electron-phonon scattering is negligibly small. Large-angle phonon scattering events that would affect the angular distribution have a relatively small cross section corresponding to a mean free path of several hundred Å and are therefore not considered in the following.

For bulk material the inelastic scattering probability is proportional to the path length in the solid. The flux of electrons of certain energy and momentum, therefore, decays exponentially

$$I = I_0 e^{-x/\lambda} \quad (1.1)$$

where λ is the mean free path of the electron. The mean free path is inversely proportional to the imaginary part of the electron self-energy [1,2,3] which may be calculated from the dielectric response function $1/\epsilon(q,\omega)$

$$\lambda^{-1} = \frac{me^2}{\pi\hbar E} \int \frac{1}{q} dq \frac{1}{2} \int_0^{\omega_{\max}} d\omega \operatorname{Im} \left[\frac{-1}{\epsilon(q,\omega)} \right] \theta(E - E_{\min} - \hbar\omega) \quad (1.2)$$

with E the energy of the electron and q and $\hbar\omega$ the momentum transfer and energy involved in a transition, respectively. E_{\min} is the Fermi energy or the conduction band edge E_c in case of an insulator. The step function θ and the upper integration limit

$$\omega_{\max} = \frac{\hbar}{2m} [k^2 - (k-q)^2]$$

takes care of energy conservation. As the response function represents the electronic excitation spectrum of the solid which is different for different materials, the mean free path of the electron depends on the material under investigation. For an insulator, for example, $\operatorname{Im}[-1/\epsilon(q,\omega)]$ becomes considerable only when $\hbar\omega$ exceeds the band-gap energy E_g . Because of energy conservation (the θ function in (1.2)) the electronic contribution to λ^{-1} becomes rather small for electron energies $E < E_c + E_g$ (dashed line in Fig.1.1d). Impurity scattering may set a lower limit. Thus for low electron energies the mean free path for an insulator is much higher than for a metal.