SURFACE CHARACTERIZATION

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Summary

Characterization of a solid surface requires the use of analytical techniques which are able to detect very low quantity of material and to discriminate the information originating from the surface from that coming from the bulk. Usually, information is searched on the topography (roughness) of the surface, its structure, its elementary and chemical composition and the quantitative distribution of the elements (laterally as well as in function of depth). The improvement of ultra-high vacuum technology and the automation of data acquisition and reduction in the past four decades have lead to an explosion in the development of surface analytical probes. Four of the most widely used surface analysis techniques are described in this chapter: Auger electron spectroscopy, X-ray photoelectron spectroscopy, secondary ion mass spectrometry and atomic force microscopy. For all of them, the basic physical background is given, together with the major features of the technique and its applications.

1. Introduction

The importance of the properties of solid surfaces is crucial in many areas of science and technology which are contributing to our daily well-being, such as metallurgy, microelectronics, catalysis, adhesion science, tribology, environment, corrosion… However, even though the importance of understanding surfaces has been recognized since the early part of the twentieth century, it is only in the last four decades that the improvement of ultra-high vacuum technology and the automation of data acquisition and reduction have lead to an explosion in the development of surface analytical probes.

In most materials, the surface composition differs from the bulk. This can be intentional (e.g. in coatings) or unintentional (e.g. due to contamination) and may be either an advantage or a disadvantage. The first question which arises in surface characterization is the definition of the geometric extent of the surface layer. The surface layer is often considered as the layer from which the information is obtained using a specific analytical technique. Because the information depth can vary from one technique to another, such a definition can clearly give rise to misleading interpretation. When defined as the region where the properties differ from those of the bulk, the surface thickness depends on the application and may vary from a few tens of kilometers in geology to a few tenths of a nanometer in catalysis. In materials science the surface layer will extend from atomic dimensions (as in catalysis) to micrometers (as in coatings). Thus a major problem encountered in surface studies is to ensure that the bulk signal is small compared to the surface signal (surface specificity). Another problem is the detection limit of the technique. Detection of an element present at the one per cent level when probing the topmost layer of a sample with a surface of size 1cm^2 requires a technique sensitive to ca. 10^{13} atoms! In fact, sufficient sensitivity is easily achieved, but only a few surface analytical techniques are specific to the topmost layer of atoms. For most of the techniques, the signal comes from within a few atomic layers of the material. Such techniques are thus considered as surface sensitive, rather than surface specific, techniques.

A complete characterization of the surface must provide information on:

- the topography (roughness) of the surface
- the geometrical (structural) arrangement of the surface atoms
- the elementary composition
- the quantitative distribution of the elements
- the chemical bonding
- the lateral distribution of the elements
- the in-depth distribution of the elements

This usually requires a combination of several techniques. A huge number of techniques (microscopies, spectroscopies, spectrometries) have been developed in the past four decades based on the reflection, absorption or emission of particles. Only some of the most widely used methods will be discussed below. They are all based on the same scheme (see Figure 1): a probe is used to locally disturb the material and the characteristic signal(s) emitted from the disturbed region is analyzed.

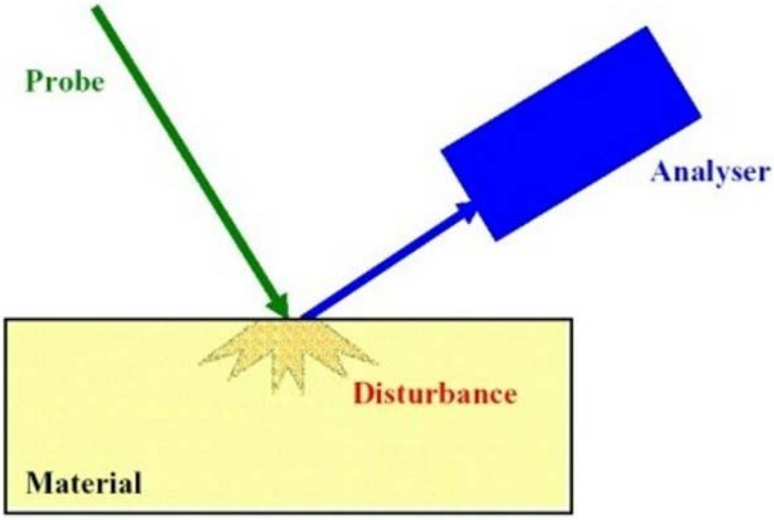


Figure 1 Schematic principle of surface characterization

The probe can be a particle beam (electrons, photons, ions, neutrals), or a mechanical probe (stylus, tip).

2. Auger Electron Spectroscopy

2.1. Physical Background: The Auger Process

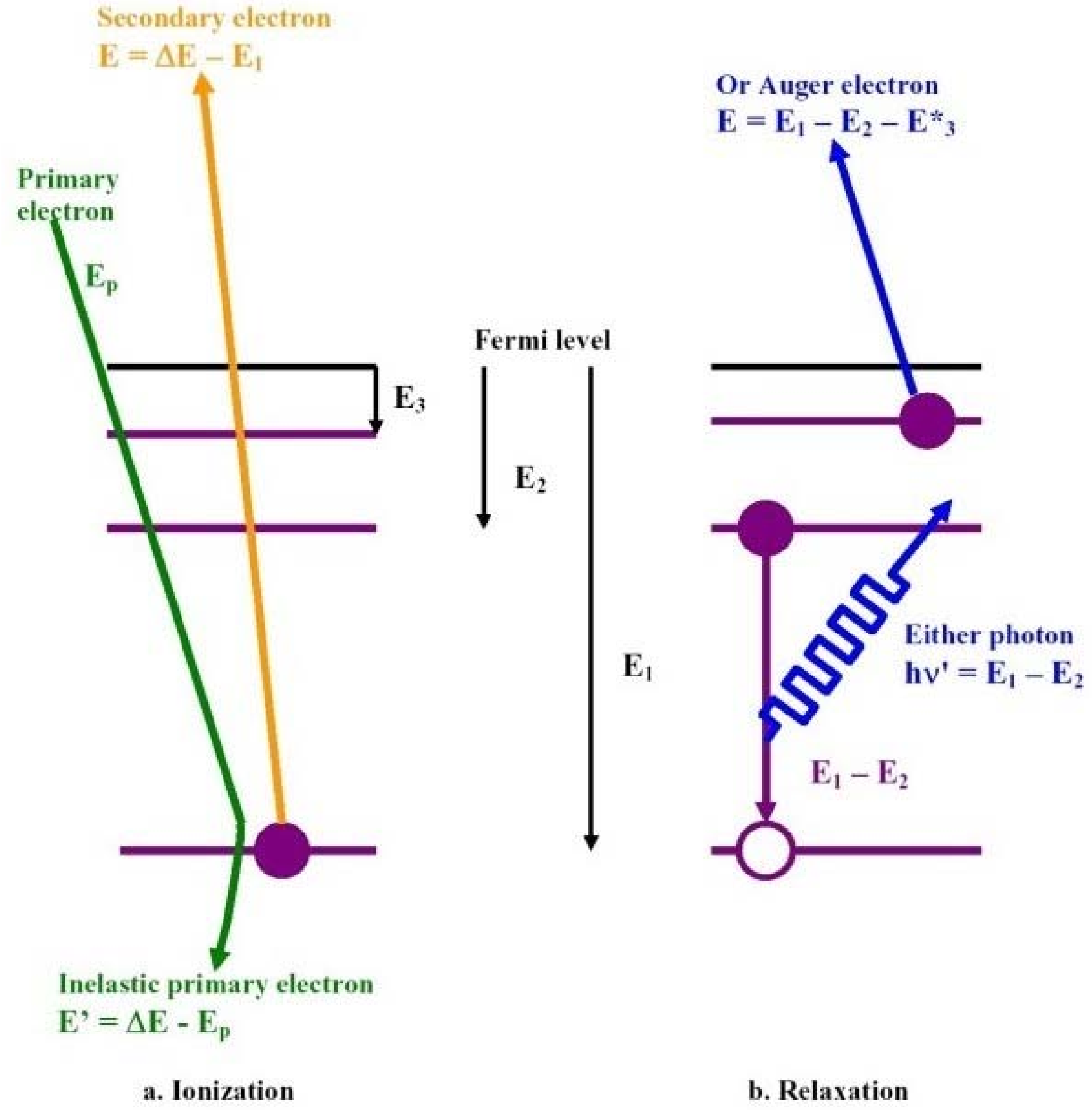
The first description of the physical phenomena giving rise to the “Auger” electrons dates back to the work of the French scientist Pierre Auger in 1923.

Irradiation of a solid surface by an incident electron beam of energy E_p (2-10 keV typically) results in ionization of a core level (binding energy E_1), creating a vacancy by ejection of a secondary electron with an energy $E = \Delta E - E_1$ corresponding to the difference between the energy loss of the primary electron and the energy of the core level involved in the ionization process, (see Figure 2a). This ionization process can be achieved using other particles (ions, neutrals, X-rays) (see X-ray photoelectron spectroscopy) and in its original work, Pierre Auger was studying X-ray induced electron emission. However, bombardment with an electron beam is the most common excitation source in Auger Electron Spectroscopy.

The resulting hole is then filled via a transition from an outer level (binding energy E_2). An excess energy (E_1-E_2) thus becomes available and the atom can relax in two ways: either a characteristic X-ray photon is emitted with the energy $h\nu = E_1 - E_2$ (X-ray fluorescence) or an outer electron (the Auger electron) is expelled from the atom with the kinetic energy E_A (see Figure 2b):

$$E_\mathrm{A} = E_1 - E_2 - E^*_3 \tag{1}$$

E^*_3 is the ionization potential of an electron in the shell 3 with respect to the fact that the atom is already ionized by the loss of one inner electron.



a. Ionization b. Relaxation

Figure 2: Illustration of the Auger process

It must be pointed out that the kinetic energy of the Auger electron is:

(a) independent of the energy of the incident electron beam and of the mechanism of formation of the initial vacancy,

(b) dependent of the binding energies of the electrons involved in the process and thus characteristic of the emitting element. Each element can give rise to a set of characteristic Auger peaks, which can be used for element identification.

The Auger transitions are conventionally described in terms of the X-ray spectroscopic nomenclature where the designation of the levels K, L, M… is derived from the value of their principal quantum number 1, 2, 3… respectively. The Auger transitions are then labeled by giving first the level of the initial vacancy location, followed by the levels involved in the relaxation process. For example, if in Figure 2, 1evels 1, 2, 3 stand for levels K, L_1 and $L_{2,3}$ respectively, the transition illustrated is a KL_1L_{23} transition.

2.2. Auger Electron Spectroscopy (AES)

2.2.1. The Auger Spectrum

Auger electron spectroscopy (AES) is based upon the measurement of the distribution of the kinetic energies of the electrons emitted by an electron bombarded surface: $n(E) = f(E)$. In a solid, this energy distribution is consisting of three contributions:

- elastically and inelastically scattered primary electrons (including loss excitations), whose energies range from E_p to 0,
- secondary electrons, whose energies range from 0 to $E_p/2$
- Auger elastic and inelastic electrons, whose energies range from their characteristic value $E_1 - E_2 - E^*_3$ to 0.

In a typical AES spectrum, the Auger peaks are thus superimposed to a background due to the sum of all electronic contributions and extracting the “Auger information” might prove difficult. Differentiating the spectrum provides a simple way to eliminate the background and improve sensitivity for detection. AES spectra are still often shown in a differentiated form, even though the reasons for this mainly historical. Figure 3 shows the direct (3a) and differentiated (3b) Auger spectra recorded from a copper specimen. Additionally to the Cu characteristic peaks, features which can be ascribed to S and C, due to contamination of the surface, are clearly visible.

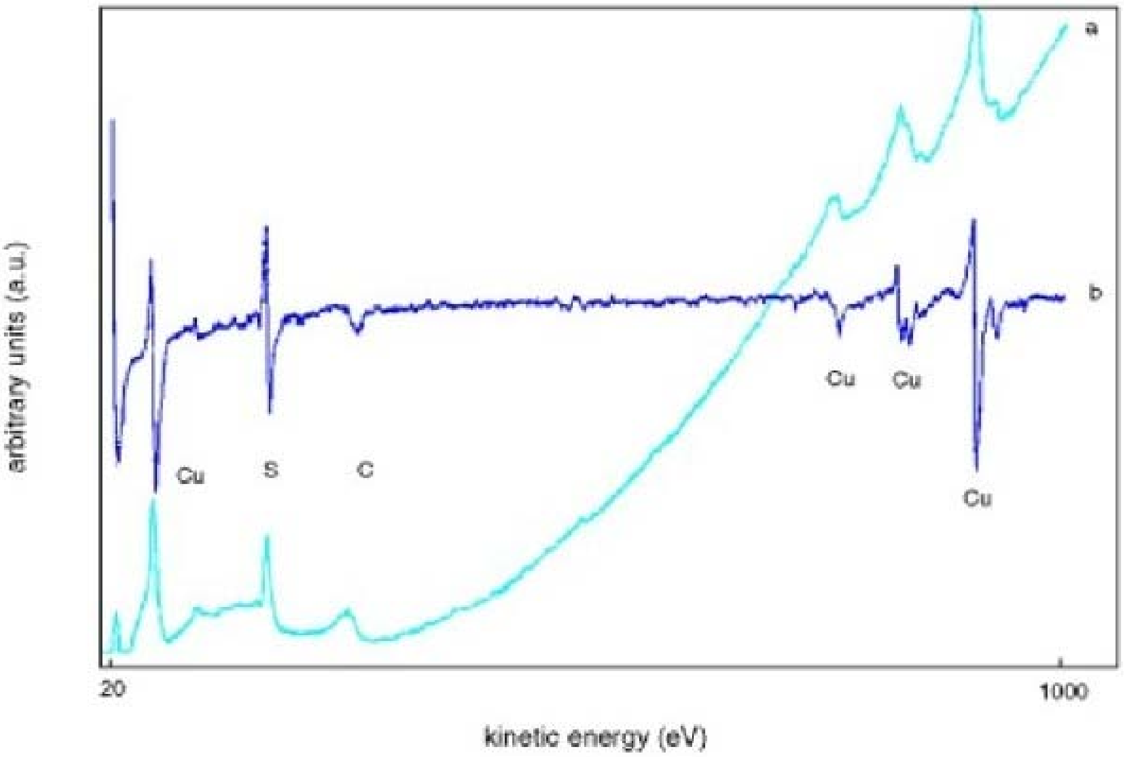


Figure 3: Direct (a) and differentiated (b) Auger spectra from contaminated copper

2.2.2. Surface Sensitivity of AES

In surface analysis, Auger electrons in the energy range 20-5000 eV are typically analyzed. The inelastic mean free path (IMPF) for such electrons in solids, i.e. the distance they can travel without undergoing inelastic scattering, varies with the sample material but remains in the range 0.5 –5 nm as shown in Figure 4. Auger Electron Spectroscopy is thus a surface sensitive technique.

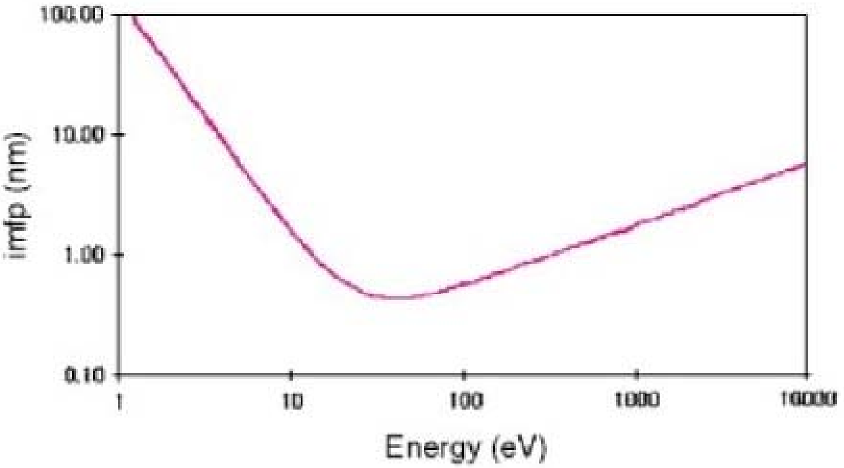


Figure 4: Variation of the inelastic mean free path (IMFP) of the electrons in solids as a function of their kinetic energy

2.2.3. Lateral Resolution in AES

The lateral resolution limit of AES is governed by the minimum spot size of the incident electron beam, i.e. in today's instruments typically a few nanometers.

2.2.4. Quantification in AES

The intensity of an Auger peak is proportional to the amount of the emitting element in the surface region. Quantification of Auger electron spectroscopy thus requires to correctly measure the intensity of the peaks and to establish the expression relating these intensities to the emitting elements concentration. Both these steps might prove difficult.

In the differentiated spectrum, the peak-to-peak height is used as a measurement of the intensity of a specific transition. However, a direct use of such a measurement is difficult because of the dependence of the Auger electron yield on the element and of instrumental parameters (analyzer transmission function, resolution, modulation voltage…).

In the direct spectrum, the Auger intensity is given by the area under the appropriate peak and the major difficulty is then to define and subtract the background due to secondary electrons which is superimposed to the Auger signal.

The relationship between the Auger intensity I_A and the atom distribution with depth z, $N(z)$, of a given element is often written in the form:

$$I_\mathrm{A} = I_0 \gamma\, \sigma(E_0) \sec\alpha \left[1 + r_\mathrm{M}\,(E_\mathrm{A},\alpha)\right] T(E_\mathrm{A}) \quad D(E_\mathrm{A}) \int_0^\infty N(z) \exp\left[-\frac{z}{\lambda_\mathrm{M}}(E_\mathrm{A})\right] \cos\theta\, dz \qquad (2)$$

where I_0 is the primary electron beam current, γ is the probability of the Auger transition, $\sigma(E_0)$ is the ionization cross section by electrons of energy E_0, α is the angle of the incident electron beam to the surface normal, r_M is the backscattering term, E_A is the energy of the Auger transition, $T(E_A)$ is the transmission efficiency of the spectrometer at energy E_A, $D(E_A)$ is the electron detector efficiency, λ_M is the attenuation length of Auger electrons in the material and θ is the angle of emission from the surface normal.

This equation is usually simplified by making a number of assumptions (e.g. sample homogeneity, no directional effects in Auger emission…). For example, in a binary compound, the relative concentration X_A/X_B of two elements A and B can be deduced from the ratio of their respective Auger signal I_A and I_B:

$$\frac{X_\mathrm{A}}{X_\mathrm{B}} = F_\mathrm{AB}\, \frac{I_\mathrm{A} / I_\mathrm{A}^\infty}{I_\mathrm{B} / I_\mathrm{B}^\infty} \qquad (3)$$

where I_A^∞ and I_B^∞ are elemental standard signals for A and B and F_{AB} takes account of the environmental dependence of factors such as attenuation lengths, backscattering factors…

2.2.5. Instrumentation in AES

In 1953, Lander was the first to realize that Auger electrons had great potential for surface chemical analysis and in the 1950s several attempts were made to perform surface analysis following electron bombardment. However, it is not before the introduction of phase-sensitive detection by Harris in 1967 that Auger electron spectroscopy became a widespread tool for surface analysis.

A typical Auger instrument usually consists of a primary electron gun, an energy dispersive analyzer working in the 0-5 keV range and a sputter-ion gun. The facilities and the sample are all located inside an ultrahigh vacuum chamber (where pressure is typically less than 10^{-8} Pa) to ensure that the surface conditions are kept constant and that the low-energy Auger electrons can reach the analyzer.

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Biographical Sketch

Marie-Geneviève Barthés-Labrousse is research director at the Centre National de la Recherche Scientifique (CNRS) in Vitry-sur-Seine (France). She received her degrees from the University of Paris (PhD in 1981). She is working in the field of surface characterization, surface reactivity and thin films. Her research interests were first devoted to the study of growth modes and properties of ultrathin metallic films. At the present time, she is interested in adhesion processes, including characterization of chemical bonding at interfaces. She has published approximately 50 scientific papers in international scientific journals. She was awarded the 1981 CNRS bronze medal and has received the 1986 award of the Société Française de Chimie Physique. She is involved in international advisory committees of conferences and workshops. She is currently completing a two year term (1999-2001) as President of the French Vacuum Society and a three year term (1998-2001) as President Elect of the International Union for Vacuum Science, Technique and Applications (IUVSTA).