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**Surface chemical analysis — Auger  
electron spectroscopy — Derivation  
of chemical information**

*Analyse chimique des surfaces — Spectroscopie des électrons  
Auger — Dédution de l'information chimique*

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## Contents

Page

Foreword.....	iv
Introduction .....	v
1 Scope .....	1
2 Normative references .....	1
3 Terms and definitions.....	1
4 Abbreviated terms .....	1
5 Types of chemical and solid-state effects in Auger-electron spectra.....	1
6 Chemical effects arising from core-level Auger-electron transitions .....	3
6.1 Introduction .....	3
6.2 Chemical shifts of Auger-electron energies .....	3
6.3 Chemical shifts of Auger parameters .....	4
6.4 Chemical-state plots.....	5
6.5 Databases of chemical shifts of Auger-electron energies and Auger parameters .....	6
6.6 Chemical effects on Auger-electron satellite structures .....	7
6.7 Chemical effects on the relative intensities and lineshapes of CCC Auger-electron lines .....	8
6.8 Chemical effects on the inelastic region of CCC Auger-electron spectra .....	8
7 Chemical effects on Auger-electron transitions involving valence electrons .....	9
7.1 Introduction .....	9
7.2 Chemical-state-dependent lineshapes of CCV and CVV Auger-electron spectra .....	9
7.3 Information on local electronic structure from analysis of CCV and CVV Auger-electron lineshapes .....	13
Bibliography .....	14

## Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

In exceptional circumstances, when a technical committee has collected data of a different kind from that which is normally published as an International Standard ("state of the art", for example), it may decide by a simple majority vote of its participating members to publish a Technical Report. A Technical Report is entirely informative in nature and does not have to be reviewed until the data it provides are considered to be no longer valid or useful.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO/TR 18394 was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 5, *Auger electron spectroscopy*.

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## Introduction

This Technical Report provides guidelines for the identification of chemical effects on X-ray or electron-excited Auger-electron spectra and for using these effects in chemical characterization.

Auger-electron spectra contain information on surface/interface elemental composition as well as on the environment local to the atom with the initial core hole<sup>[1]-[5]</sup>. Changes in Auger-electron spectra due to alterations of the atomic environment are called chemical (or solid-state) effects. Recognition of chemical effects is very important in proper quantitative applications of Auger-electron spectroscopy and can be very helpful in identification of surface chemical species and of the chemical state of constituent atoms in surface or interface layers.

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# Surface chemical analysis — Auger electron spectroscopy — Derivation of chemical information

## 1 Scope

This Technical Report provides guidelines for identifying chemical effects in X-ray or electron-excited Auger-electron spectra and for using these effects in chemical characterization.

## 2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 18115:2001, *Surface chemical analysis — Vocabulary*

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## 3 Terms and definitions (standards.iteh.ai)

For the purposes of this document, the terms and definitions given in ISO 18115 apply.

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## 4 Abbreviated terms

CCC	core-core-core (Auger-electron transition)
CCV	core-core-valence (Auger-electron transition)
CK	Coster-Kronig
c-BN	cubic boron nitride
CVV	core-valence-valence (Auger-electron transition)
h-BN	hexagonal boron nitride
REELS	Reflection Electron Energy-Loss Spectroscopy

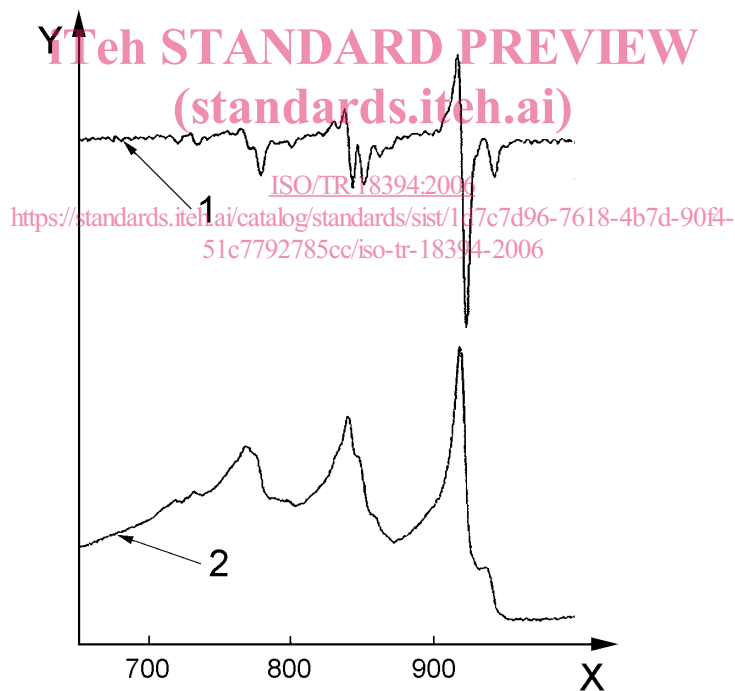
## 5 Types of chemical and solid-state effects in Auger-electron spectra

Many types of chemical or solid-state effects can be observed in Auger-electron spectra [1]-[5]. Changes in the atomic environment of an atom ionized in its inner shell can result in a shift of the kinetic energy of the emitted Auger electron. In the case of X-ray-excited Auger-electron spectra, energy shifts of Auger parameters (i.e. kinetic-energy differences between Auger-electron peaks and the photoelectron peaks corresponding to the core levels involved in the Auger-electron process) can be detected as well. Furthermore, the lineshape, the relative intensity and the satellite structure (induced by the intrinsic excitation processes) of the Auger-electron lines can be considerably influenced by chemical effects, as can the structure of the energy-loss region (induced by extrinsic, electron-scattering processes) accompanying the intrinsic peaks. Strong chemical effects on the Auger-electron spectral shapes offer ways of identification of chemical species using the “fingerprint” approach.

In the case of electron-excited Auger-electron spectra, the Auger peaks are generally weak features superimposed on an intense background caused to a large extent by the primary electrons scattered inelastically within the solid sample. As a consequence, the differential Auger-electron spectrum is often recorded (or calculated from the measured spectrum) rather than the direct energy spectrum, facilitating the observation and identification of the Auger-electron peaks and the measurement of the respective Auger transition energies. Differentiation can, however, enhance the visibility of random fluctuations in recorded intensities, as shown in Figure 1. If chemical-state information is needed from a direct energy spectrum, then the relative energy resolution of the electron spectrometer should be better than 0,15 % (e.g. 0,05 % or 0,02 %). A poorer energy resolution causes a significant broadening of the Auger-electron peaks and prevents observation of small changes of spectral lineshapes or peak energies as chemical-state effects in the spectra. A great advantage of electron-excited Auger-electron spectroscopy over X-ray excitation with laboratory X-ray source, however, is the possibility of using high lateral resolution and obtaining chemical-state maps of surface nanostructures.

NOTE 1 Auger-electron spectra can be reported with the energy scale referenced either to the Fermi level or to the vacuum level. Kinetic energies with the latter reference are typically 4,5 eV less than those referenced to the Fermi level, but the difference in energies for these two references can vary from 4,0 eV to 5,0 eV since the position of the vacuum level depends on the condition of the spectrometer and may, in practice, vary with respect to the Fermi level. When energy shifts are determined from spectra recorded on different instruments, use of different energy references should be taken into account.

NOTE 2 While the visibility of noise features in a differential spectrum can be reduced by use of a larger number of channels in the calculation of the derivative, there may also be distortion of the resulting differential spectrum and loss of fine details associated with chemical-state effects.



**Key**

- X kinetic energy, eV
- Y intensity
- 1 differential spectrum
- 2 direct spectrum

NOTE This figure has been reproduced from Figure 2.8 of Watts, J.F. and Wolstenholme, J. *An Introduction to Surface Analysis by XPS and AES*, with the kind permission of the publishers, John Wiley and Sons Ltd. (Copyright 2003).

**Figure 1 — Comparison of direct and differentiated Auger-electron spectra for copper (Cu LMM peaks)**



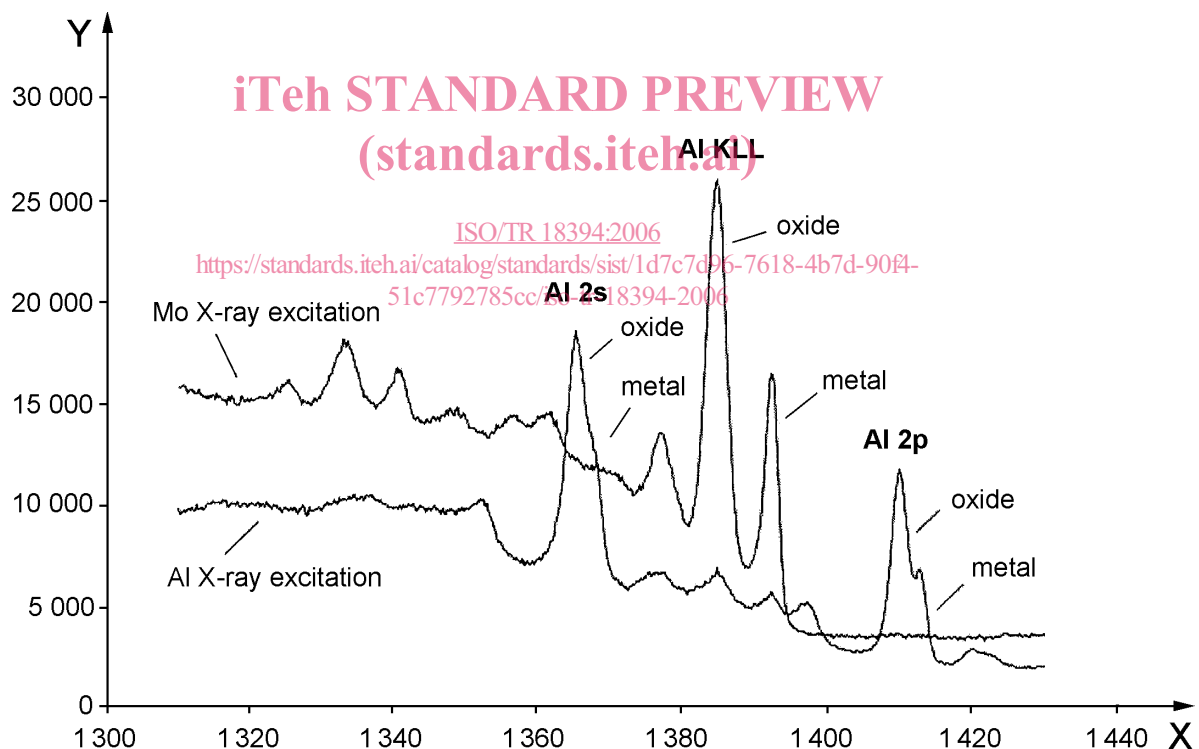
## 6 Chemical effects arising from core-level Auger-electron transitions

### 6.1 Introduction

Core-level (or core-core-core, CCC) Auger-electron transitions occur when all of the levels involved in the Auger transition belong to the atomic core for the atom of interest.

### 6.2 Chemical shifts of Auger-electron energies

The main effect of any change in the solid-state environment on Auger-electron spectra for Auger transitions involving core levels is a shift of the Auger energies. This shift results from a change in the core atomic potential due to the changed environment and from a contribution due to the response of the local electronic structure to the appearance of core holes. Auger chemical shifts are generally larger than the binding-energy shifts of the atomic levels involved in the Auger-electron process because the two-hole final state of the process is more strongly influenced by relaxation effects. This phenomenon is illustrated by the example of aluminium and its oxide in Figure 2 [6]. Large chemical shifts in the energy positions of the Auger-electron lines provide possibilities for chemical-state identification even in the case of electron-excited Auger-electron spectroscopy with, in this case, moderate energy resolution. In X-ray-excited Auger-electron spectra, the peak-to-background intensity ratios are usually larger than those in electron-excited spectra, facilitating accurate determination of peak energies. Information on Auger chemical shifts of particular elements can be obtained from handbooks [7]-[9] and online-accessible databases [10] [11].

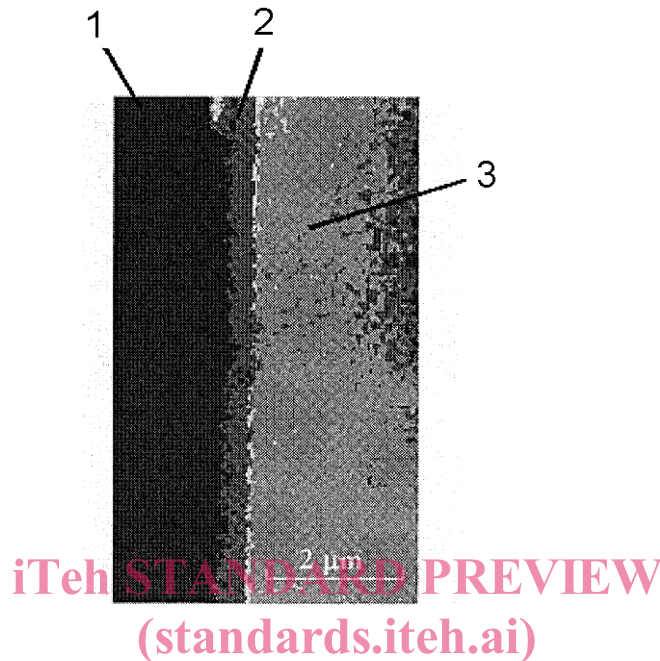


#### Key

- X kinetic energy, eV
- Y intensity, counts/s

**Figure 2 — Photoelectron and Auger-electron spectra of an aluminium foil covered by a thin overlayer of aluminium oxide [6]: Excitation with Al and Mo X-rays**

With the advantage of high-energy-resolution analysers, small chemical shifts of Auger-electron lines due to different type of dopants in semiconductors become discernible (for example, the kinetic-energy difference between Si KLL peaks from *n*-type and *p*-type silicon is 0,6 eV [1]), allowing chemical-state mapping in spite of the extremely low concentration (far below the detection limits of Auger electron spectroscopy) of the dopants. Figure 3 shows an Si KLL Auger-electron map derived from a cross section of a *p*-type silicon sample doped with phosphorus by implantation to obtain *n*-type Si at the sample surface [1].



**Key**

- 1 vacuum
- 2 *n*-type Si (implanted with P)
- 3 *p*-type Si wafer

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NOTE 1 A cross section of the sample is shown, and the Auger-electron spectra were excited with an electron beam.

NOTE 2 This figure has been reproduced from Figure 5.30 of Watts, J.F. and Wolstenholme, J. *An Introduction to Surface Analysis by XPS and AES*, with the kind permission of the publishers, John Wiley and Sons Ltd. (Copyright 2003).

**Figure 3 — Silicon KLL Auger-electron map of a *p*-type silicon sample implanted with phosphorus to produce *n*-type Si at its surface**

**6.3 Chemical shifts of Auger parameters**

Auger parameters, obtained from X-ray-excited Auger-electron spectra, can also be strongly influenced by the environment of the atom emitting photoelectrons and Auger electrons [2], [12]-[14]. The Auger parameter,  $\alpha$ , is given by:

$$\alpha = KE(jkl) - KE(i) \tag{1}$$

where

- $KE(jkl)$  is the kinetic energy of an Auger transition involving core levels *j*, *k* and *l* of an atom;
- $KE(i)$  is the kinetic energy of a photoelectron from core level *i* (which may be the same as the core level *j*).

In order to avoid negative values of the Auger parameter <sup>[12] [14]</sup>, the modified Auger parameter,  $\alpha'$ , is used in most practical cases. The modified Auger parameter is given by:

$$\alpha' = \alpha + E_p = KE(jkl) + BE(i) \quad (2)$$

where

$E_p$  is the exciting photon energy;

$BE(i)$  is the binding energy of an electron in the core level  $i$ .

It is also preferable to use  $\alpha'$  rather than  $\alpha$  because the value of  $\alpha'$  is independent of  $E_p$ .

The Auger parameters can be measured even in the case of static charging, since any charging shift is cancelled as energy separations of peaks are determined. No energy-referencing problems occur <sup>[12] [13]</sup> in the case of measuring Auger parameters; i.e. data obtained using the vacuum level as reference can be compared directly to data obtained using the Fermi level as reference. Auger parameters can therefore be very useful in the characterization of insulators and semiconductors, where the energy position of the Fermi level of the sample is not well defined. A change in the atomic environment of a core-ionized atom can result in a chemical shift of the corresponding Auger parameter. Auger-parameter shifts depend on differences in the valence charge in the initial ground state and in the final state (intra-atomic contribution), as well as on differences in the contribution to the relaxation process of all other atoms in the system (extra-atomic contribution) <sup>[14]</sup>.

When the intra-atomic contribution is dominant, a local screening mechanism of the core hole takes place, while in the case when the extra-atomic contribution is dominant, the screening mechanism is assumed to be non-local. In the latter case, simple electrostatic models can be used for estimating the electronic polarization energy <sup>[5] [14]-[16]</sup>. The model of Moretti <sup>[14]</sup> describes the final-state polarization process in which the sum of the electric fields (at the ligands) is generated by the central positive charge and by induced dipoles on the ligands in the first coordination shell. This model can be applied to estimate the extra-atomic polarization energy and the Auger-parameter shifts. Weightman *et al.* <sup>[17] [18]</sup> developed a different model, the "extended potential model", for estimating the Auger-parameter chemical shift; potential parameters were derived from atomic calculations and the angular-momentum character of the electrons was taken into account. This model gives a good approximation in the case of large charge transfer in the final state (conductors), where the electrostatic model is not applicable, and describes well the local screening mechanism. In the case of binary alloys, the magnitude of the transferred charge can be accurately derived <sup>[3]</sup>.

## 6.4 Chemical-state plots

For chemical-state identification and Auger-parameter analysis, the presentation of Auger parameters in the form of a two-dimensional plot, as proposed by Wagner, proved to be very useful <sup>[13]</sup>. The Auger-electron kinetic energy is indicated on the ordinate of the plot and the corresponding photoelectron binding energy is on the abscissa but oriented in the negative direction, as shown in Figure 4; constant Auger-parameter values are represented on the plot by a straight line with a slope of  $-1$  (note that the abscissa axis in Figure 4 is increasing to the left). In the case of a negligible change in the intra-atomic relaxation energy (due to the varying atomic environment), the change in the extra-atomic-relaxation (final-state-effect) energy dominates, and components with higher extra-atomic relaxation energy lie in the upper part of the chemical-state (or Wagner) plot. On the other hand, when the initial-state effects (proportional to the sum of terms related to the ground-state valence charge and the Madelung potential) dominate, the slope becomes  $-3$  on the chemical-state plot; i.e., chemical states with similar initial-state effects lie on straight lines with a slope of  $-3$ . This result illustrates that chemical-state plots can be analysed to provide information on the nature of the changes in the environment of the core-ionized atom <sup>[15]</sup>. Figure 4 shows a chemical-state plot for tin compounds <sup>[19]</sup>. As can be seen, the chemical-state plot can help to distinguish between chemical states not separable on the basis of core-level binding energy shifts or Auger-electron-energy shifts alone.