
**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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Foreword

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT), see the following URL: [Foreword — Supplementary information](#).

The committee responsible for this document is ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 7, *Electron spectroscopies*.

This second edition cancels and replaces the first edition (ISO/TR 18394:2006), which has been technically revised.

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^{[1][2][3][4][5]}. 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 documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 18115 (all parts), *Surface chemical analysis — Vocabulary*

3 Terms and definitions

For the purposes of this document the terms and definitions given in ISO 18115 (all parts) apply.

4 Abbreviated terms (standards.iteh.ai)

CCC	core-core-core (Auger-electron transition) <small>ISO/TR 18394:2016 https://standards.iteh.ai/catalog/standards/sist/363adcba-2daa-4649-9649-607584501184/iso-tr-18394-2016</small>
CCV	core-core-valence (Auger-electron transition)
CK	Coster-Kronig
c-BN	cubic boron nitride
CVV	core-valence-valence (Auger-electron transition)
DEAR-APECS	Dichroic Effect in Angle Resolved Auger-Photoelectron Coincidence Spectroscopy
h-BN	hexagonal boron nitride
IAE	Interatomic Auger Emission
ICD	Interatomic Coulomb Decay
PAES	Positron-Annihilation-induced Auger Electron Spectroscopy
REELS	Reflection Electron Energy-Loss Spectroscopy

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

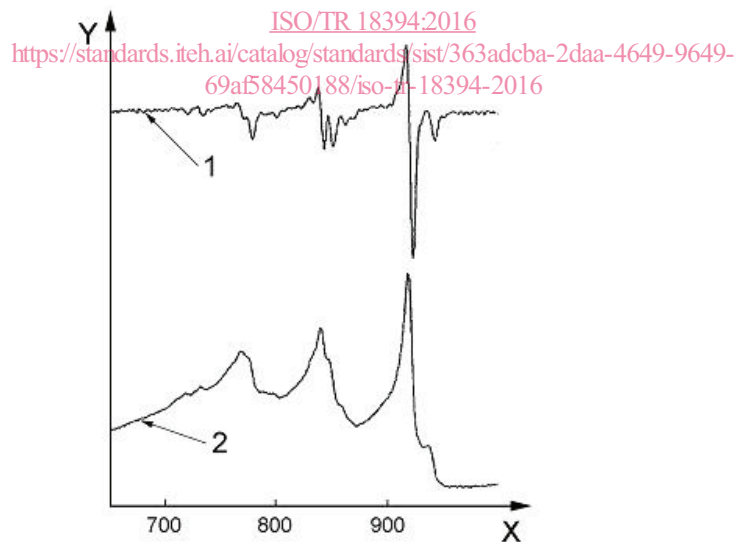
Many types of chemical or solid-state effects can be observed in Auger-electron spectra^{[1][2][3][4][5]}. Changes in the atomic environment of an atom ionized in its inner shell can result in a shift of the kinetic energy of the emitted Auger electron. In the case of X-ray-excited Auger-electron spectra, 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 line shape, 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 line shapes 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 is reproduced from Figure 2.8 of Reference [1].

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

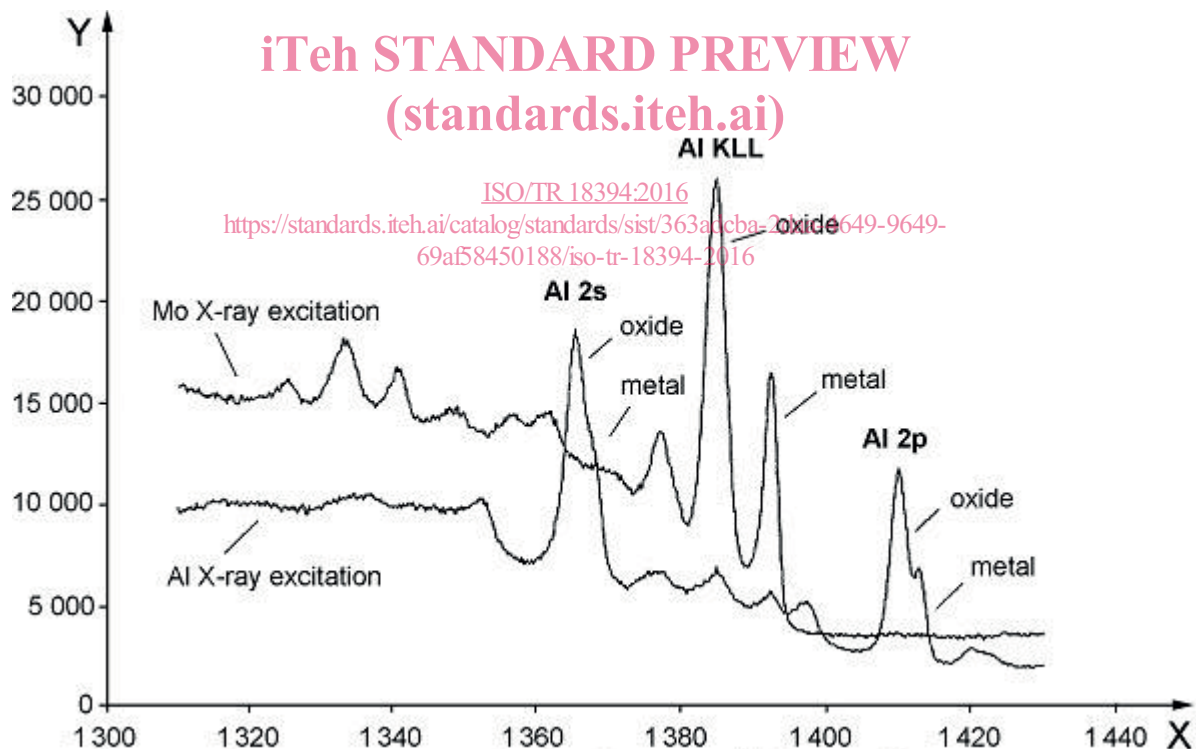
6 Chemical effects arising from core-level Auger-electron transitions

6.1 General

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. Recommended Auger electron energies are available for 42 elemental solids[7]. Information on Auger chemical shifts of particular elements can be obtained from handbooks[8][9][10][11] and online-accessible databases[12][13].

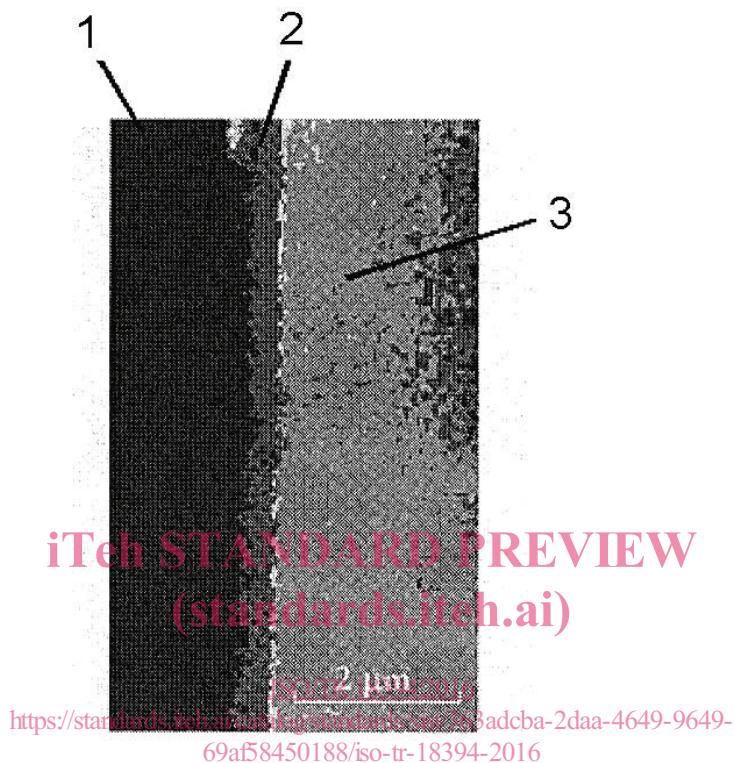


Key

- 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: 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 a 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

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 Reference [1].

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][14][15][16][17][18]. The Auger parameter, α , is given by Formula (1):

$$\alpha = KE(jkl) - KE(i) \quad (1)$$

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[14][15][16], the modified Auger parameter, α' , is used in most practical cases. The modified Auger parameter is given by Formula (2):

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

where

E_p is the exciting photon energy;

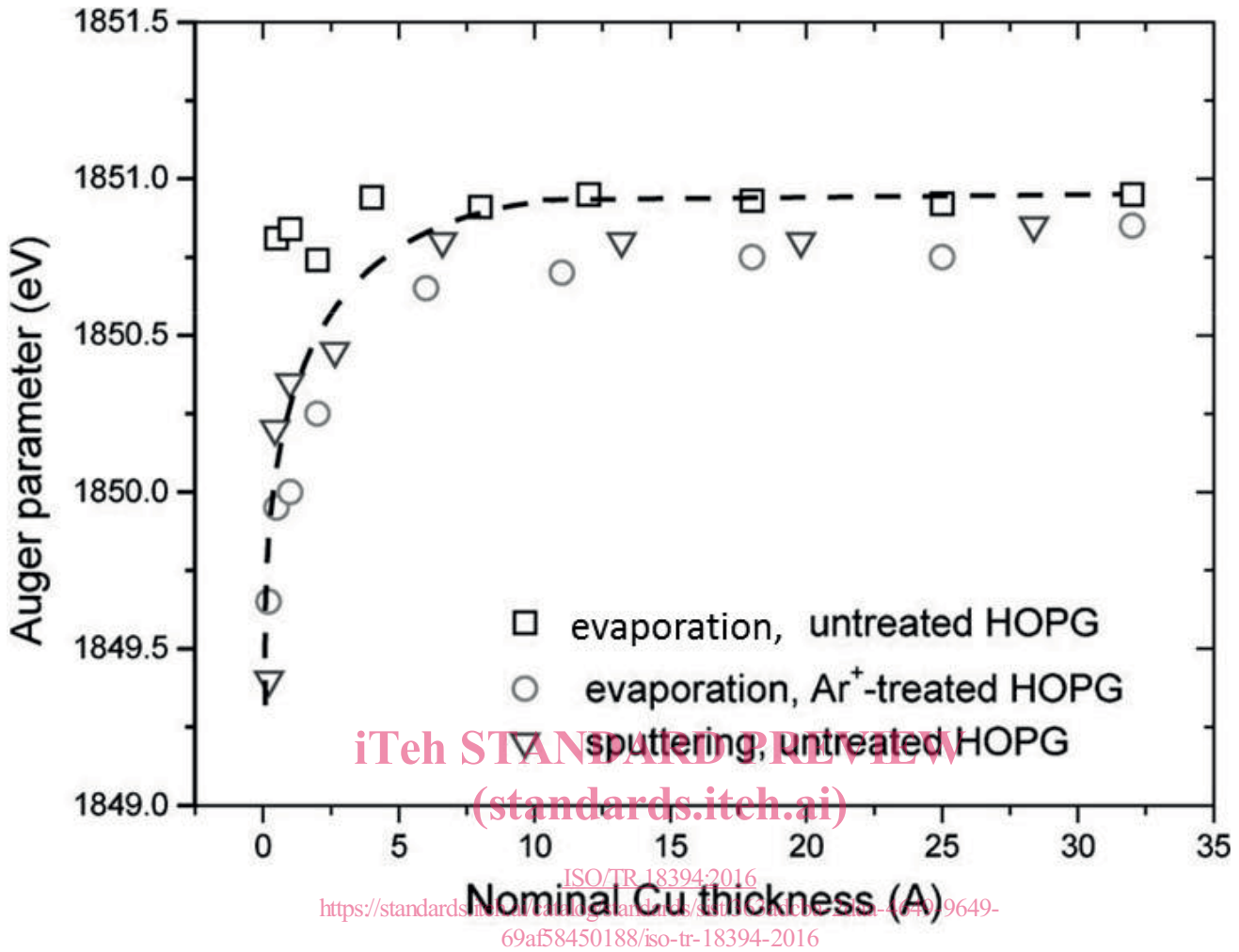
$BE(i)$ is the binding energy of an electron in the core level i .

It is also preferable to use α' rather than α because the value of α' 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[14][15] 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)[16].

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[5][16][17][18][19][20]. The model of Moretti[16] 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. Calculation of Auger parameter shifts using the electrostatic model of Moretti is facilitated by the possibility of applying the freely available Tinker molecular modelling and Molden computer graphic software packages[18]. Weightman, et al.[21][22] 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[3]. A review on first principles calculations of Auger kinetic energy and Auger parameter shifts in metallic bulk solids from the density functional theory are discussed in Reference[23].

In the case of nanoparticles, the Auger parameter can depend on the size of the particles. Figure 4 shows the dependence of the Auger parameter of Cu nanoclusters [deposited by evaporation onto highly oriented pyrolytic graphite (HOPG)] on the nominal thickness of the Cu layer[24]. It was found that the Cu Auger parameter depends linearly on $1/d$, where d is the average diameter of the Cu clusters[24].



NOTE See Figure 2 of Reference[24].

Figure 4 — Dependence of the Cu Auger parameter on the nominal thickness of the Cu layer consisting of Cu clusters deposited by evaporation onto HOPG surface

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[15]. 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 5; 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 5 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[19]. Figure 5 shows a chemical-state plot for tin compounds[25]. 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.