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

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Foreword

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

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]-[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.

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*

3 Terms and definitions

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

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

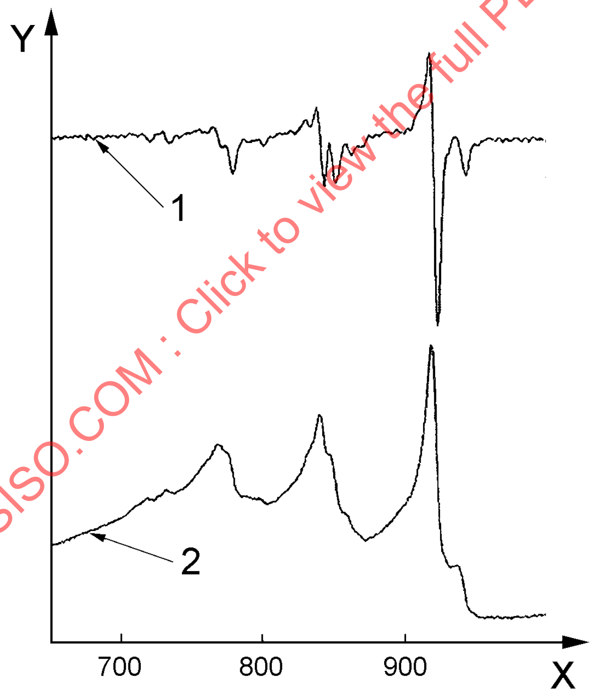
5 Types of chemical and solid-state effects in Auger-electron spectra

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

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

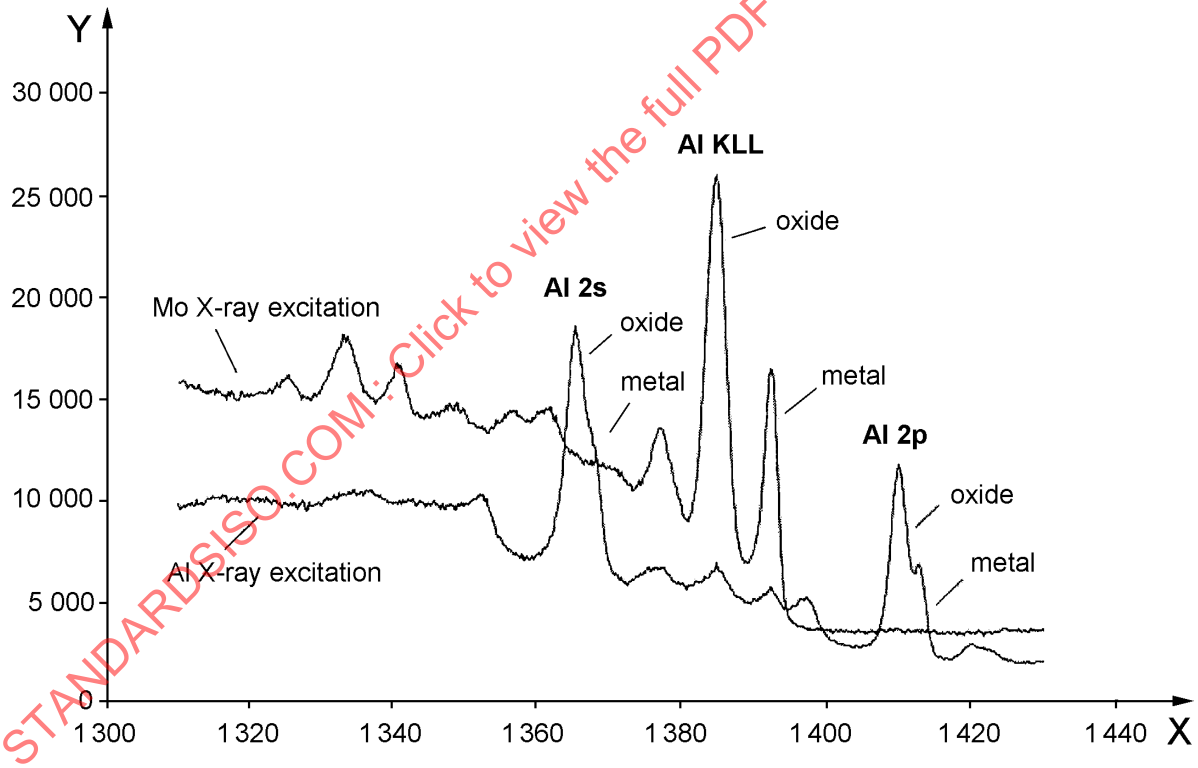
6 Chemical effects arising from core-level Auger-electron transitions

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].



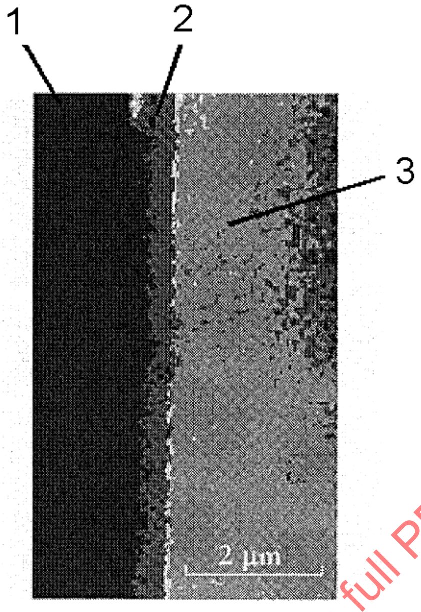
Key

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

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, α, 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 [12] [14], the modified Auger parameter, α', is used in most practical cases. The modified Auger parameter is given by:

$$\alpha' = \alpha + E_\mathrm{p} = KE(jkl) + BE(i) \tag{2}$$

where

E_p is the exciting photon energy;

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

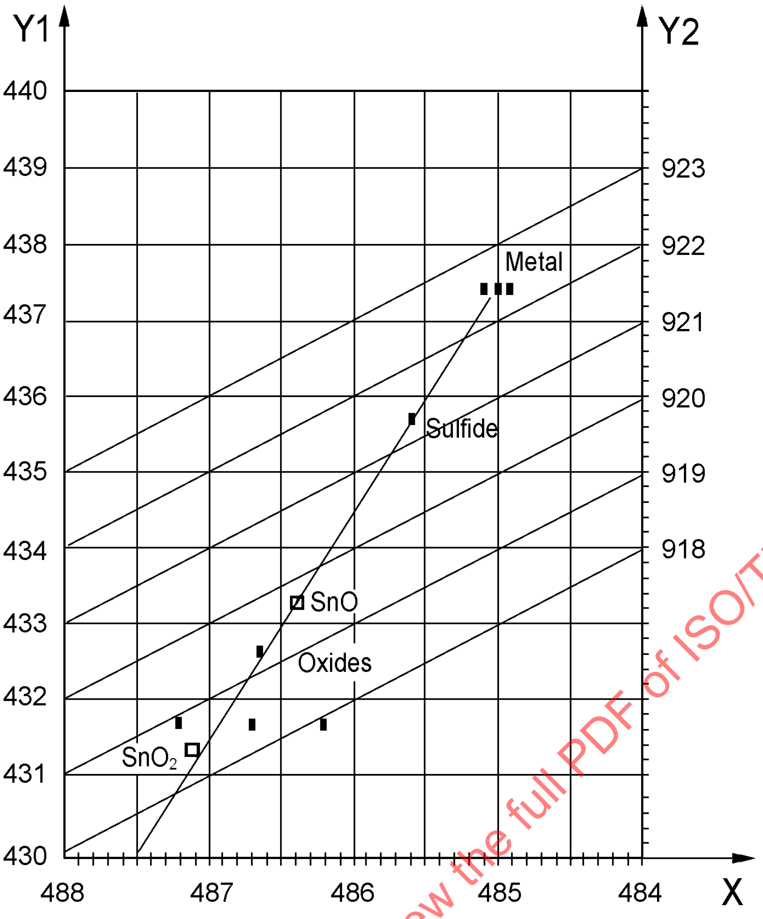
It is also preferable to use α' rather than α because the value of α' is independent of E_p.

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 [12] [13] 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) [14].

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] [14]-[16]. The model of Moretti [14] 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.* [17] [18] 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].

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 [13]. 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 [15]. Figure 4 shows a chemical-state plot for tin compounds [19]. 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.



Key

X Sn $3d_{5/2}$ binding energy, eV

Y_1 Sn MNN Auger kinetic energy, eV

Y_2 Auger parameter + photon energy

NOTE Reprinted with kind permission from Kövér, L., Moretti, G., Kovács, Zs., Sanjinés, R., Cserny, I., Margaritondo, G., Pálinkás, J. and Adachi, H. *Journal of Vacuum Science and Technology A*,1995, **13**, 1382 (Copyright 1995), AVS The Science and Technology Society.

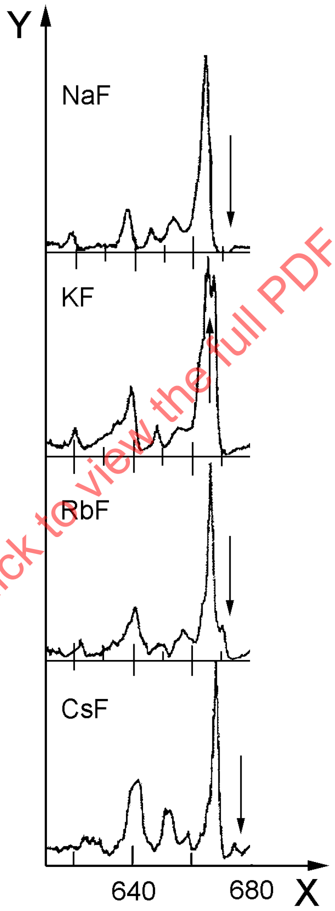
Figure 4 — Chemical-state plot for tin compounds

6.5 Databases of chemical shifts of Auger-electron energies and Auger parameters

The first comprehensive set of critically collected data on Auger parameters, Auger-electron kinetic energies and photoelectron binding energies for several elements was published by Wagner and Joshi [13]. A Handbook contains a collection of experimental photoelectron binding-energy and Auger-electron kinetic-energy data for a large number of compounds [7] and includes several chemical-state plots. The latest version of the US National Institute of Science and Technology XPS Database [10] provides on-line access to over 22 000 records of photoelectron and Auger-electron data involving intense transitions for most elements and many compounds. This database supplies Auger parameters, has the option of displaying chemical-state plots, and is very useful for identification of chemical state as well as in studies of the dependence of polarization energy on chemical state.

6.6 Chemical effects on Auger-electron satellite structures

Auger-electron peaks can be accompanied by satellite lines due to intrinsic excitations. These excitations are often of atomic origin. As a consequence of the creation of the core hole, electrons can be excited from occupied levels to unoccupied states (shake-up) or to the continuum (shake-off); the Auger-electron process then takes place in an excited or multiply ionized atom. Note that not only the shake-up but the shake-off process results in appearance of satellites in Auger-electron spectra, in contrast to photoelectron lines where the shake-off process induces a continuous energy distribution contribution to the spectrum. The excited electron can be either a spectator or a participator in relation to the Auger transition. In this latter case, the energy of the Auger satellite can be even higher than that of the main line. Figure 5 shows an extraordinarily intense satellite occurring in the F KLL spectrum of polycrystalline KF; this satellite is interpreted as a resonance between the ground state and the core-ionized state [20]. Coupling of unpaired spins in the ionized core level and in the outer shell leads to multiplet splitting of Auger lines; these splittings can be affected by changes in the atomic environment as well.



Key

X kinetic energy, eV

Y intensity

NOTE Reprinted from Uda, M., Yamamoto, T., and Takenaga, T. Resonant Orbital Rearrangement During F 1s Ionizaton or Decay Process, *Advances in Quantum Chemistry*, 1997, **29**, pp. 389-419 (Copyright 1997), with kind permission from Elsevier.

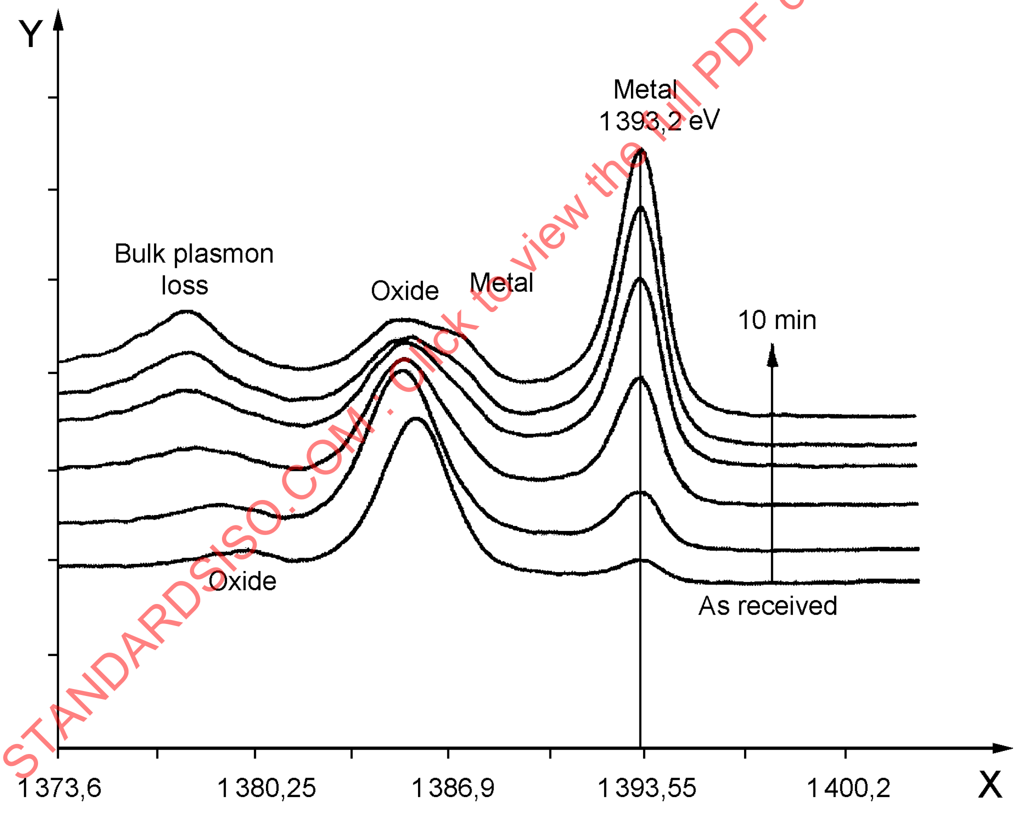
Figure 5 — Satellite structure (designated by arrows) in fluorine KLL Auger-electron spectra of fluorides

6.7 Chemical effects on the relative intensities and lineshapes of CCC Auger-electron lines

The relative intensities of CCC Auger-electron transitions may change as a result of different Auger-transition probabilites in different atomic environments [21] [22]. Very fast Coster-Kronig (CK) processes taking place prior to a particular Auger transition can convert the initial core hole into a vacancy in a core level with a smaller binding energy, leading to a considerable change in the relative intensities of Auger transitions involving levels that participated in the CK process [23]. The probability of these CK processes can strongly depend on the chemical environment [24]. In the case of some metals, CCC Auger lineshapes can be strongly asymmetric due to electron-hole pair excitation in the conduction band [25]. For adsorbates, a considerable broadening of the Auger-electron line can occur as a consequence of phonon excitation by the appearance of the core hole [26].

6.8 Chemical effects on the inelastic region of CCC Auger-electron spectra

Strong variations in the energy-loss structure of Auger-electron spectra can be observed following changes of chemical state, e.g. in the case of some free-electron metals and their compounds. Figure 6 shows the difference between the KLL Auger spectra of metallic Al and that of Al_2O_3 [27]. Reflection Electron Energy Loss Spectroscopy (REELS) can be used to confirm and separate chemical-state-dependent energy-loss structures in Auger-electron spectra. On the other hand, the interpretation of REELS spectra of multi-component systems can be confirmed by the surface chemical composition, obtained from quantitative Auger analysis [28].



Key

X kinetic energy, eV

Y intensity

NOTE This figure has been reproduced from Figure 5 of Allgeyer, D.F. and Pratz, E.H. *Surface and Interface Analysis*, **18**,1992, pp. 465-474, with the kind permission of the publishers, John Wiley and Sons Ltd. (Copyright 1992).

Figure 6 — Aluminium KLL Auger-electron spectra obtained by photo-excitation with Zr X-rays from an oxidized sample (lower curve) and after various times of ion sputtering to remove the oxide (upper curves)

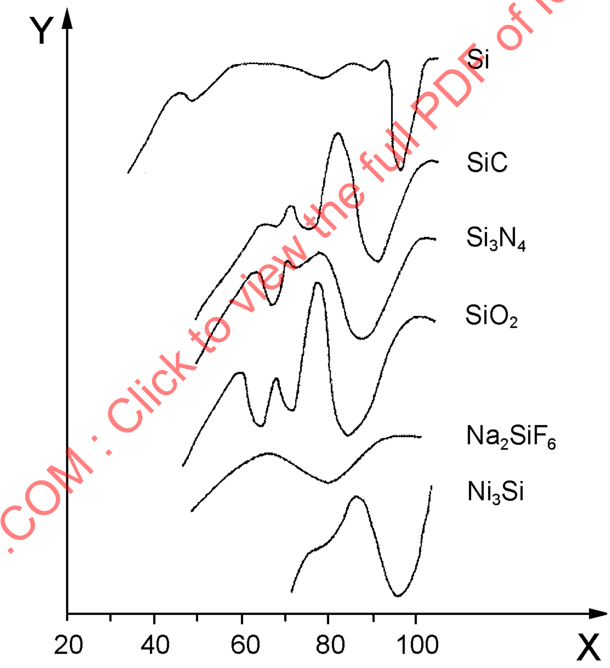
7 Chemical effects on Auger-electron transitions involving valence electrons

7.1 Introduction

In the case of Auger transitions involving valence electrons, the Auger-electron lineshapes are expected to change due to changes in chemical state. The detection of these lineshape changes may require high (better than 0,5 %) relative energy resolution, although the changes are observable at moderate energy resolution in many cases.

7.2 Chemical-state-dependent lineshapes of CCV and CVV Auger-electron spectra

The lineshapes of core-core-valence (CCV) and core-valence-valence (CVV) Auger-electron spectra can depend strongly on the environment (i.e. the chemical state) of the atoms emitting the Auger electrons. This effect can be utilized for fingerprinting, i.e. for identification of chemical state. Early measurements of carbon CVV Auger-electron spectra showed obvious differences in lineshapes for graphite, diamond, metal carbides and carbon monoxide adsorbed on a metal surface [29] [30]. Figure 7 shows electron-excited SiL_{23}VV Auger-electron spectra of solid silicon and of various silicon compounds that show considerable differences in lineshapes [31] [32]. Figure 8 shows Pd $M_{45}N_{45}N_{45}$ Auger-electron spectra for different Cu-Pd and Ag-Pd alloys [33].



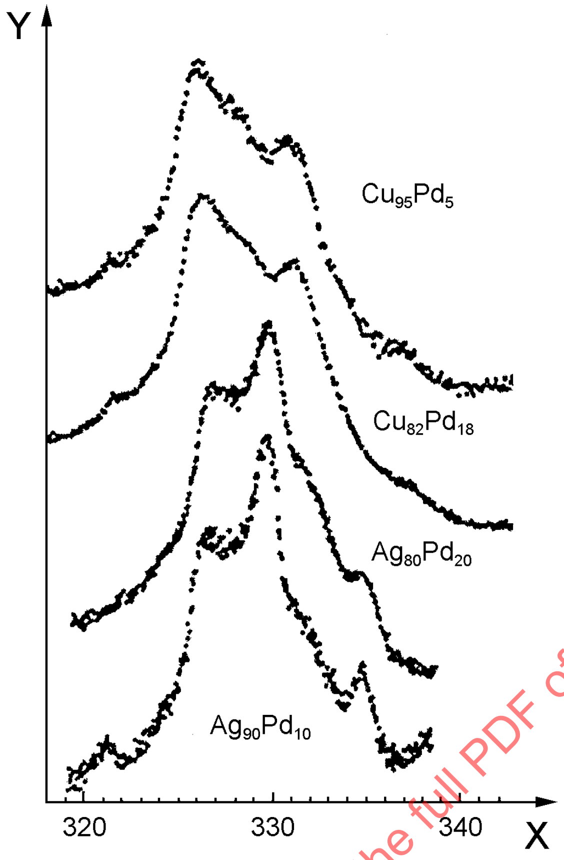
Key

X kinetic energy, eV

Y intensity

NOTE Reprinted from Streubel, P., Fellenberg, R. and Reif, A. Interpretation of Auger Energy Shifts of Silicon in Solid Silicon Compounds, *Journal of Electron Spectroscopy and Related Phenomena*, **34**, 1984, pp. 261-274 (Copyright 1984), with kind permission from Elsevier.

Figure 7 — Silicon LVV Auger-electron spectra in the differential mode for solid silicon and various silicon compounds



Key

X kinetic energy, eV

Y intensity

NOTE 1 Auger spectra were obtained with excitation by Mg X-rays.

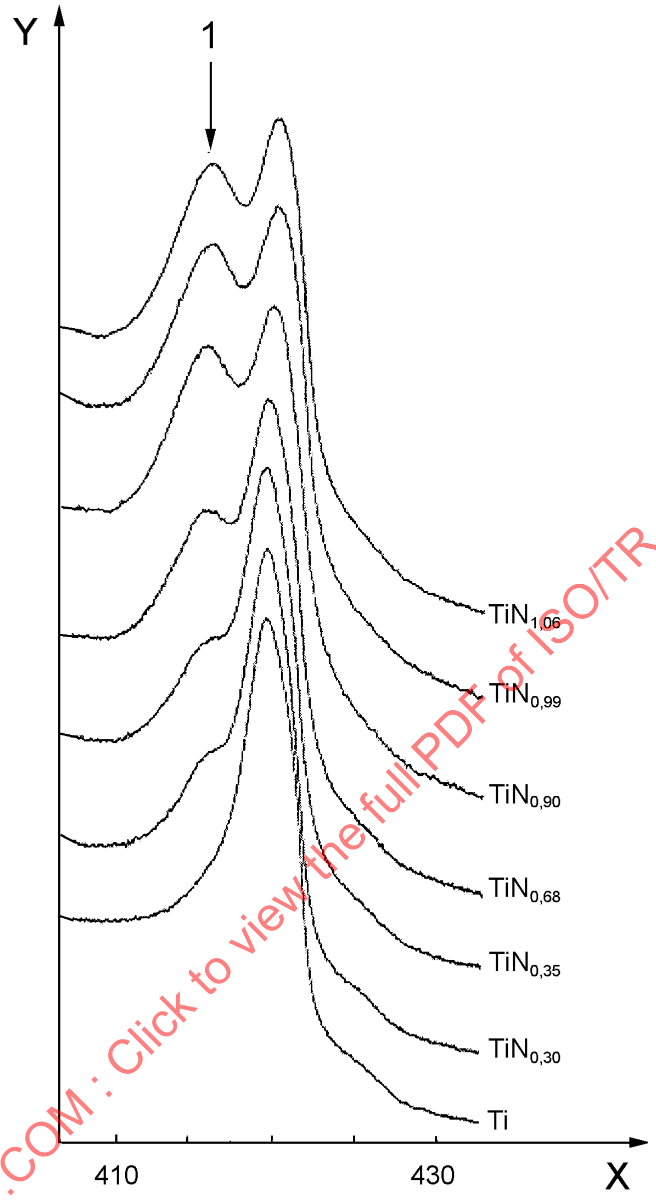
NOTE 2 Reprinted from Weightman, P., Andrews, P.T. and Winter, H. Band Structure Effects on the Pd $M_{45}N_{45}N_{45}$ Auger Spectra of Cu_x Pd_{1-x} and Ag_x Pd_{1-x} Alloys, *Journal of Physics C: Solid State Physics*, **16**, 1983, pp. L81-87 (Copyright 1983), with kind permission from IOP Publishing Ltd.

Figure 8 — Palladium $M_{45}N_{45}N_{45}$ Auger-electron spectra for the indicated Cu-Pd and Ag-Pd alloys

The stronger effect of the environment on the CVV peak compared with the CCV or CCC peaks is shown clearly in the spectra of the metals and their oxides in the series Ti to Zn [34].

These spectra show how the environmental effect depends on the valence-level occupancy; this effect is a maximum in the middle of the Ti-Zn series.

Direct-mode, high-energy-resolution, electron-excited Ti $L_3M_{23}M_{45}$ Auger-electron spectra for TiN samples with relative N concentrations varying from 0 to 1,06 are shown in Figure 9 [35]. The secondary peak on the low-kinetic-energy side of the main peak appears to be due to hybridization of the N 2p and Ti 3d states. The height of this peak relative to that of the main peak shows a linear dependence on the N/Ti concentration ratio; this relationship provides a simple method for determining the latter [35].



Key

X kinetic energy, eV

Y intensity

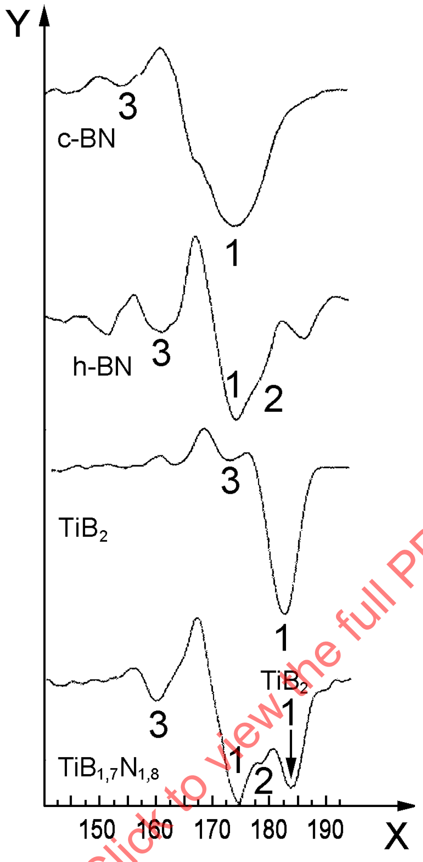
1 hybrid peak

NOTE 1 Auger spectra were obtained with electron excitation and an analyser of high energy resolution.

NOTE 2 This figure has been reproduced from Figure 2 of Haupt, J., Baker, M.A., Stroosnijder, M.F. and Gissler, W. Auger Electron Spectroscopy Studies on TiN_x, *Surface and Interface Analysis*, 1994, **22**, pp. 167-170, with the kind permission of the publishers, John Wiley and Sons Ltd. (Copyright 1994).

Figure 9 — Titanium $L_3M_{23}M_{45}$ Auger-electron spectra of TiN samples of varying nitrogen concentrations

Boron KLL Auger-electron spectra of $TiB_{1,7}N_{1,8}$, TiB_2, cubic-BN (c-BN), and hexagonal-BN (h-BN) obtained in the differential mode are shown in Figure 10 [36]. The agreement of the energies of the main peak (labelled by 1) in the spectra of $TiB_{1,7}N_{1,8}$ and of h-BN, as well as the similarity in the positions of the minor peaks in these spectra (labelled by 2 and 3) indicate that the BN in the $TiB_{1,7}N_{1,8}$ sample is present in the *sp*^{2} hybridized hexagonal form [36].



Key

X kinetic energy, eV

Y intensity

1 main peak

2 minor peak

3 minor peak

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Figure 10 — Boron KLL Auger-electron spectra of $TiB_{1,7}N_{1,8}$, TiB_2, h-BN, and c-BN obtained in the differential mode

If a measured Auger-electron spectrum consists of components arising from different chemical species and the component spectra have different lineshapes, factor analysis can be helpful in distinguishing the relevant spectral components. Least-squares fitting of the entire spectrum with varying contributions of component spectra is also helpful in interpreting the whole spectrum. These methods were successfully applied to quantitative studies of the oxidation of ternary alloys [37] [38]. A comprehensive review of cases where chemical effects on Auger lineshapes were predicted or used for chemical-state identification can be found in Reference [39].

7.3 Information on local electronic structure from analysis of CCV and CVV Auger-electron lineshapes

Lineshapes of CCV and CVV Auger-electron transitions can be analysed to give information on the local electronic structure of the emitting atom (i.e. on the local density of electronic states and on the magnitude of correlation effects) [3] [4] [40]-[43]. For the case of CCV Auger spectra of metals that have no contribution of *d* electrons in their conduction bands and for which the character of the initial state is very different from that of the final state, the '*final state rule*' has been established for describing the spectral lineshape [3]. According to this rule, the *lineshape* is determined by the *partial (s,p) local density of states in the final state*, and the *line intensities* are determined by the *local electronic configuration in the initial state.* For simple metals, this approach yields generally good agreement with experimental CCV and CVV lineshapes [40]. The *final state rule* neglects electronic correlations between the two holes in the final state. In the case of *d* transition metals, however, the two final-state holes are in the *d* band and their interaction is usually strong, especially when the band is completely filled and the Coulombic repulsion between the holes is large compared to the bandwidth. In such cases, sharp, *quasi-atomic* lineshapes are observed in CVV Auger-electron spectra [41]-[43]. The ratio of the Coulombic repulsion energy and the bandwidth can be varied by alloying, thus varying the strength of the quasi-atomic component relative to that expected from the self-convolution of the valence-band density of states [3].