Designation: E984 − 12

Standard Guide for Identifying Chemical Effects and Matrix Effects in Auger Electron Spectroscopy[1]

This standard is issued under the fixed designation E984; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This guide outlines the types of chemical effects and matrix effects which are observed in Auger electron spectroscopy.

1.2 Guidelines are given for the reporting of chemical and matrix effects in Auger spectra.

1.3 Guidelines are given for utilizing Auger chemical effects for identification or characterization.

1.4 This guide is applicable to both electron excited and X-ray excited Auger electron spectroscopy.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E673 Terminology Relating to Surface Analysis (Withdrawn 2012)[3]

E827 Practice for Identifying Elements by the Peaks in Auger Electron Spectroscopy

E983 Guide for Minimizing Unwanted Electron Beam Effects in Auger Electron Spectroscopy

E996 Practice for Reporting Data in Auger Electron Spectroscopy and X-ray Photoelectron Spectroscopy

2.2 *Other Documents:*

ISO 18118:2004 Surface Chemical Analysis—Auger Electron Spectroscopy and X-ray Photoelectron Spectroscopy—Guide to the Use of Experimentally Determined Relative Sensitivity Factors for the Quantitative Analysis of Homogenous Materials

3. Terminology

3.1 Terms used in Auger electron spectroscopy are defined in Terminology E673.

4. Significance and Use

4.1 Auger electron spectroscopy is often capable of yielding information concerning the chemical and physical environment of atoms in the near-surface region of a solid as well as giving elemental and quantitative information. This information is manifested as changes in the observed Auger electron spectrum for a particular element in the specimen under study compared to the Auger spectrum produced by the same element when it is in some reference form. The differences in the two spectra are said to be due to a chemical effect or a matrix effect. Despite sometimes making elemental identification and quantitative measurements more difficult, these effects in the Auger spectrum are considered valuable tools for characterizing the environment of the near-surface atoms in a solid.

5. Defining Auger Chemical Effects and Matrix Effects

5.1 In general, Auger chemical and matrix effects may result in (*a*) a shift in the energy of an Auger peak, (*b*) a change in the shape of an Auger electron energy distribution, (*c*) a change in the shape of the electron energy loss distribution associated with an Auger peak, or (*d*) a change in the Auger signal strengths of an Auger transition. The above changes may be due to the bonding or chemical environment of the element (chemical effect) or to the distribution of the element or compound within the specimen (matrix effect).

5.2 The Auger chemical shift is one of the most commonly observed chemical effects. A comparison can be made to the more familiar chemical shifts in XPS (X-ray photoelectron spectroscopy) photoelectron lines, where energy shifts are caused by changes in the ionic charge on an atom, the lattice potential at that atomic site, and the final-state relaxation energy contributed by adjacent atoms (**1 and 2**).[4] Frequently an

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[1] This guide is under the jurisdiction of ASTM Committee E42 on Surface Analysis and is the direct responsibility of Subcommittee E42.03 on Auger Electron Spectroscopy and X-Ray Photoelectron Spectroscopy.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The last approved version of this historical standard is referenced on www.astm.org.

[4] The boldface numbers in parentheses refer to the references at the end of this standard.

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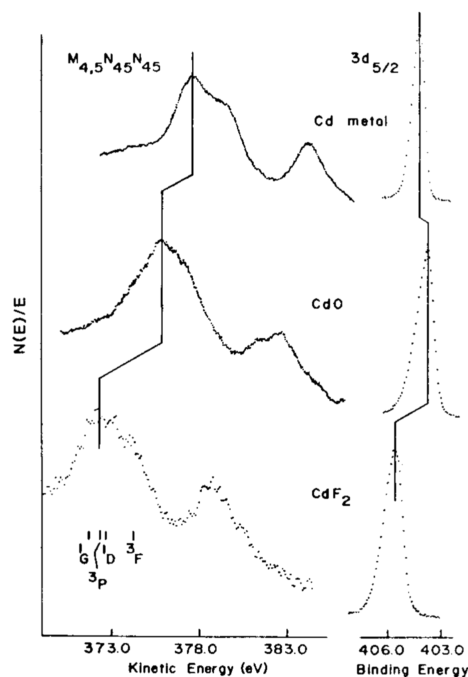


FIG. 1 Comparison of X-Ray Excited Cd MNN Auger and 3d Photoelectron Energy Shifts for Cd Metal, CdO, and CdF_2 (Ref. 16)

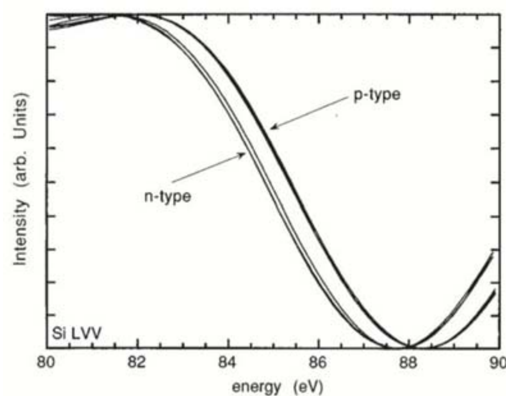


FIG. 2 Silicon LVV Auger Spectra for Seven Samples of Differing Dopant Concentrations and Types (Ref. 4)

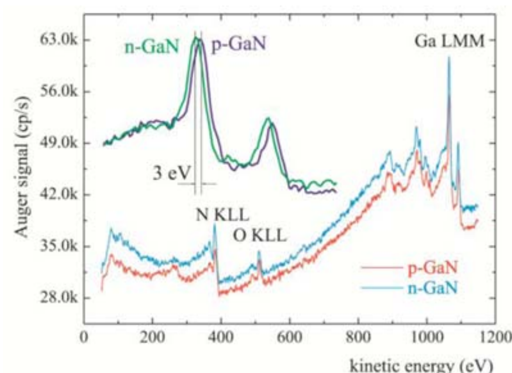


FIG. 3 Auger Spectra for p- and n- Type GaN Heteroepitaxial, the Inset Shows the Ga LMM Lines (Ref. 5)

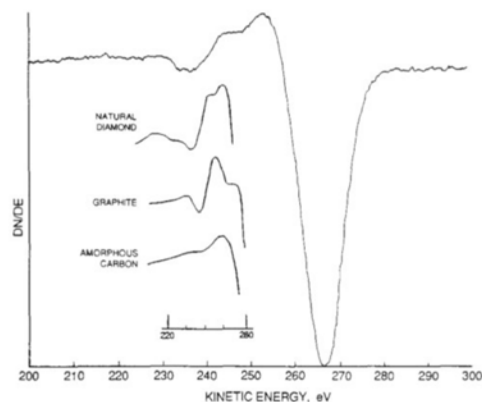


FIG. 4 Carbon KLL Auger Spectra for Diamond, Graphite, and Amorphous Carbon (Refs. 17 and 18)

Auger chemical shift is larger than an XPS chemical shift (see Fig. 1) because the Auger process involves a two-hole final state for the atom which is more strongly influenced by extra-atomic relaxation. Coverage by gas adsorbates on metal surfaces may also cause shifts in the metal Auger peak energies (**3**). Band bending across junctions between p- and n-type materials shift the energy levels of each material relative to the Fermi level resulting in an apparent shift in the Auger line energies. This effect has been observed for p-n junctions of silicon (see Fig. 2) (**4**) and those of heteroepitaxial layers such as GaN/AlGaN (see Fig. 3) (**5**).

5.2.1 Related to chemical shifts is the (modified) Auger parameter, defined as the sum of the photoelectron binding energy and the Auger electron kinetic energy (**6**). Because the Auger parameter is the difference between two line energies of the same element of the same specimen, it is independent of any electrical charging of the specimen and spectrometer energy reference level, making it easier to identify chemical states of elements in insulating specimens. Naturally, since both photoelectron lines and Auger lines must be measured, the Auger parameter can only be used with X-ray excited spectra.

5.3 The second category of chemical information from Auger spectroscopy is the Auger lineshapes observed for transitions involving valence electron orbitals. Shown in Fig. 4 are variations in the lineshapes for electron-excited carbon KLL for different phases of carbon, in Fig. 5 are lineshapes for carbon KLL for different chemical environments of carbon, and in Fig. 6 are lineshapes for aluminum LVV for different levels of oxidation. While it is possible to relate the prominent peaks in the Auger spectrum to transitions from particular bands in the density of states (for solids) or to particular molecular orbitals (for molecules) (**7**), this is not an easy task. The large number of possible two-hole final states, taken together with shake-up and shake-off transitions and uncertainty on all their final energies and intensities make the job of constructing a valence orbital density map from the Auger spectrum next to impossible for all but the simplest systems. Further, some spectra exhibit a quasiatomic character (**8**). Accordingly, most studies use the "fingerprint" approach when attempting to identify unknown species based on their Auger

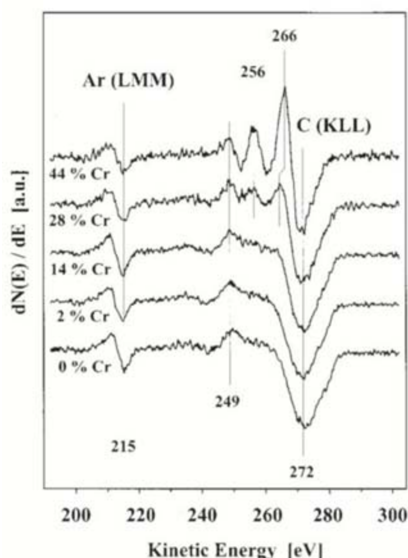
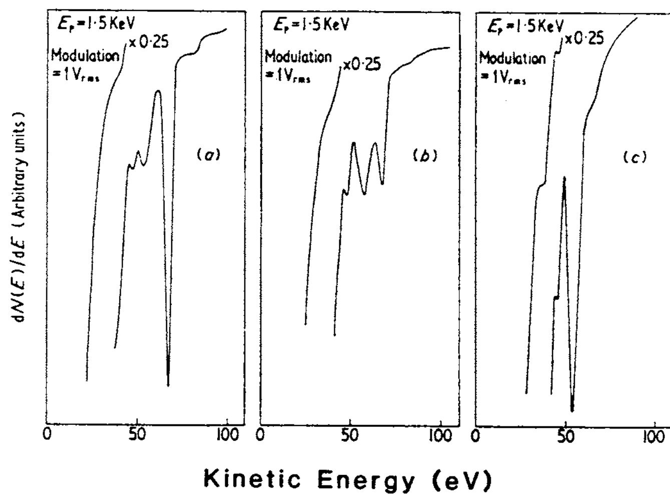


FIG. 5 A comparison of the Carbon KLL Auger Lineshape with increasing chromium content in a gradient layer of α-C/Si(100) showing the evolution of the C KLL lineshape from one typical of graphite (0 % Cr) to one typical of a metal carbide (44 % Cr) (Ref. 19)



(*a*) Almost no Oxidation (*b*) Partial Oxidation (*c*) After Oxidation has Reached a Saturation Stage

FIG. 6 Changes in the Aluminum LVV Auger spectrum as Oxygen is Absorbed on the Surface (Ref. 20)

lineshape. Of course reference spectra are necessary in this approach for a positive identification. "Surface Science Spectra" is an international journal and database devoted to archiving spectra from surfaces and interfaces (**9**).

5.4 Other effects besides energy shifts and valence lineshapes may be classified as chemical effects in Auger spectroscopy. For instance, many body effects in metals, such as plasmons, may make the lineshapes of Auger transitions of atoms in the metallic state very different from the Auger lineshapes for other chemical states, even for transitions involving only core-type electrons, Al and Mg (**10**). In single crystals, diffraction effects will produce different lineshapes (**11**). Relative intensities of several Auger transitions may change, either from attenuation of overlayers (**12**), or from different chemical states resulting in different Auger transition probabilities (**13 and 14**). Phonon broadening and inelastic electron energy loss effects will result in different linewidths and backgrounds for gases, adsorbates, and condensed phases (**15**).

5.5 For both X-ray and electron excited Auger spectra, quantitative corrections for matrix effects are discussed in detail in ISO 18118:2004.

6. Guidelines for Reporting Auger Chemical and Matrix Effects

6.1 In general, the guidelines outlined in Practice E996 should be used. This practice covers reporting of the spectrometer, specimen preparation, excitation source, analyzer and detector modes, and data processing. Also, if measures were taken to control damage or charging of the specimen, report those conditions in a manner consistent with Guide E983.

6.1.1 Practice E827 should be used to confirm the elemental identification. The elemental information should be consistent with the presumed chemical state identification.

6.1.2 When reporting chemical and matrix effects in an Auger spectrum, the main feature of interest is the Auger peak energy (reported in eV). This is the energy of the largest negative excursion in the dN/dE spectrum or the most intense peak in the N(E) spectrum. (Of course, these two peak positions' measurements will have different energy values.) The energy location of the major Auger peak should be in agreement with the reference value, consistent with the experimental parameters and calibrations as discussed in Practice E996.

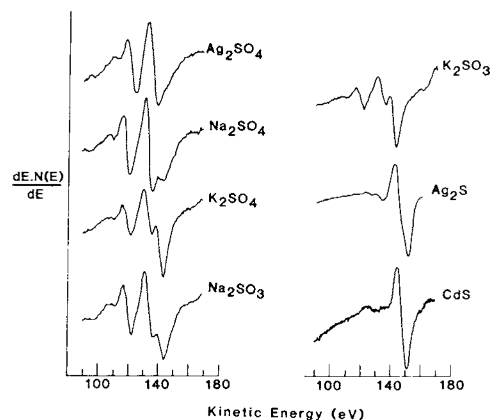


FIG. 7 Sulfur LVV Auger Spectra for Ag_2SO_4, Na_2SO_4, K_2SO_4, Na_2SO_3, K_2SO_3, Ag_2S, CdS (Ref. 21)

6.1.3 The reference level for the energy scale of the electron energy analyzer and the method for calibrating the energy scale should be specified. The relative peak energy shifts between the chemical states of interest and that element in its elemental state (or some other standard state) should also be reported.

TABLE 1 Sulfur in Sulfur Compounds

NOTE 1—Data Compiled From Auger Spectra (Ref. **19**).

Compound	Electron Excited LVV[A,B]	New Peak[A]	ΔE[A,C]	X-ray Excited LVV[A,D]	Auger Parameter Plus Photon Energy[A,D]
K_2SO_4	138.7	123.9	11.7	...	...
Ag_2SO_4	141.7	127.4	8.7	...	...
Na_2SO_4	138.3	123.0	12.1	...	...
Na_2SO_3	139.1	124.8	11.3	...	...
K_2SO_3	139.4	124.5	11.0	...	...
Ag_2S	150.4	...	...	149.3	516.9

[A] Energy in eV.
[B] Zero point of derivative spectra.
[C] Ag_2S used for reference.
[D] Al Kα X rays.

6.1.4 Other spectral features which may be useful include the number, relative energy positions, and relative signal strengths of the secondary peaks. The reporting of these values should also be in agreement with the reference value and consistent with the experimental parameters and calibrations discussed in Practice E996.

6.2 When spectra are presented for publication, the energy range should be wide enough that the shape of the background on either side of the Auger line is apparent. Shown in Fig. 7 are Auger spectra for several sulfur-containing compounds, and in Table 1 information from these spectra.

7. Keywords

7.1 Auger electron spectroscopy; chemical effect; matrix effect; spectroscopy

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