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Surface chemical analysis — Auger electron spectroscopy — Reporting of methods used for charge control and charge correction

Analyse chimique des surfaces — Spectroscopie des électrons Auger — Indication des méthodes mises en œuvre pour le contrôle et la correction de la charge

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Foreword

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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.

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.

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Introduction

Auger electron spectroscopy (AES) is widely used for characterization of surfaces of materials. Elements in the sample (with the exception of hydrogen and helium) are identified from comparisons of Auger transition energies, determined from measured Auger spectra, with tabulations of these energies for the various elements. Although Auger electrons are observed during X-ray irradiation of specimens (X-ray photoelectron spectroscopy), AES, as used in this document, is associated with electron irradiation of a specimen. Because the incident electron beam can be focused to sizes approximating 10 nm, AES is an important tool for characterization of small surface features and of nanostructured materials. Information on the elements present, and sometimes the chemical state of the detected elements, can frequently be obtained from examination of the line shape and energies of the peaks (see ISO/TR 18394[43]). Reliable determination of elements present requires appropriate calibration of the energy scale (as described in ISO 17973 and ISO 17974).

The surface potential of an insulating specimen may change during an AES measurement due to the build-up of surface and near-surface electrical charge, and this charge can shift the energy of Auger electrons, thus complicating elemental (and chemical state) identification, especially when a negative surface potential moves the Auger spectrum above the energy interval selected by the electron analyser. The build-up of surface potential can also move the location of the electron beam, effectively shifting the region on the specimen or even off the specimen that is being analysed. Similar changes occur for metals during electron irradiation if they are not connected to ground. This would occur, for example, if small metal particles are incorporated in an insulating matrix. Depending on the secondary-electron yield, the surface potential may shift positively or negatively. In some circumstances, these two shifts (energy and position) create an unstable feedback system, rendering the collection of AES spectra nearly impossible. In addition to changes in the Auger-electron peak energy and intensity, the specimen surface composition might be altered (specimen damage) directly by the incident electron beam or due to electric-field-induced diffusion when a field is set up in the surface region of the specimen. A variety of methods and approaches have been developed to control and minimize charging effects in AES. The application of a particular method can be highly dependent on the details of the instrument being used, the size and shape of the specimen being examined, the specimen morphology and composition, and the information to be collected. Although the build-up of surface charge can complicate analysis, in some circumstances it can also be used creatively as a tool to gain information about the specimen.

The amount of induced charge near the surface, its distribution across the specimen surface, and its dependence on experimental conditions are determined by many factors, including those associated with the specimen and the characteristics of the spectrometer. Charge build-up is a well-studied[1] three-dimensional phenomenon that occurs along the specimen surface and into the material. Charge build-up may also occur at phase boundaries or interface regions within the depth of a specimen that is irradiated by electrons. Some specimens undergo time-dependent changes in charge build-up due to charge trapping, chemical changes or component diffusion or volatilization induced by heating or by incident or secondary electrons. Such specimens may never achieve steady-state potentials.

There is, at present, no universally applicable method or set of methods for charge control or for charge correction in AES[2],[3]. This International Standard specifies the information that has to be provided to document the method of charge control during data acquisition and/or the method of charge correction during data analysis of insulating specimens. Information is given in Annex A on common methods for charge control that can be useful for many applications. The particular charge-control method that may be chosen in practice depends on the type of specimen (e.g. powder, thin film or thick specimen), the nature of the instrumentation, the size of the specimen and the extent to which the specimen surface might be modified by a particular procedure. To assist an analyst, a summary table lists the common charge-control methods in approximate order of simplicity of application.

This International Standard has two main areas of application. First, it identifies information on methods of charge control and/or charge correction to be included in reports of AES measurements (e.g. from an analyst to a customer or in publications) in order to evaluate and reproduce data on insulating materials and to ensure that measurements on similar materials can be meaningfully compared. Second, adherence to the International Standard will enable published AES spectra to be used with confidence by other analysts.

Surface chemical analysis — Auger electron spectroscopy — Reporting of methods used for charge control and charge correction

1 Scope

This International Standard specifies the minimum amount of information required for describing the methods of charge control in measurements of Auger electron transitions from insulating specimens by electron-stimulated Auger electron spectroscopy and to be reported with the analytical results. Information is provided in Annex A on methods that have been found useful for charge control prior to or during AES analysis. This annex also contains a table summarizing the methods or approaches, ordered by simplicity of approach. Some methods will be applicable to most instruments, others require special hardware, others might involve remounting the specimen or changing it. A similar International Standard has been published for X-ray photoelectron spectroscopy (ISO 19318[44]).

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 17973, *Surface chemical analysis — Medium-resolution Auger electron spectrometers — Calibration of energy scales for elemental analysis*

ISO 17974, *Surface chemical analysis — High-resolution Auger electron spectrometers — Calibration of energy scales for elemental and chemical-state analysis*

ISO 18115, *Surface chemical analysis — Vocabulary*

3 Terms and definitions

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

4 Symbols and abbreviated terms

AES   Auger electron spectroscopy

E_p primary-electron energy, in keV

$E_{p(max)}$ energy at which the TSEEY is a maximum

E^0_{p1} energy at which the secondary-electron emission yield rises above unity

E^0_{p2} energy at which the secondary-electron emission yield drops below unity

1

$E^c{}_{p2}$	energy at which the range of the incident electrons is approximately equal to the maximum escape depth of the secondary electrons
FIB	focused ion beam
FWHM	full width at half maximum, in eV
I_p	primary-electron current
I_s	secondary-electron current
j_p	current density of the primary-electron beam on the specimen surface
KE_{corr}	corrected kinetic energy, in eV
KE_{meas}	measured kinetic energy, in eV
KE_{ref}	reference kinetic energy, in eV
N	charging index
R	range of primary electrons
SEM	scanning electron microscopy
t	electron irradiation time
TSEEY	total secondary-electron emission yield
U_s	surface potential
V_e	electron interaction volume
z	specimen thickness
ρ	electrical resistivity of the specimen
σ	total secondary-electron yield
θ	angle of incidence of primary-electron beam on the specimen with respect to the surface normal, in degrees
Δ_{corr}	correction energy, to be added to measured Auger electron energies for charge correction, in eV

5 Apparatus

5.1 Charge-control technique

One or more of the charge-control techniques described in Clause A.3 may be employed in most AES spectrometers. The AES instrument shall be operated in accordance with the manufacturer's or other documented procedures.

5.2 Special apparatus

Some of the techniques outlined in Clause A.3 require special apparatus, such as a low-energy ion source or a source for evaporative deposition of gold. Some of the referenced items may be the subject of patent rights for specific vendors. Mention of them here is for convenience and does not represent an endorsement by ISO or a member body.

5.3   Specimen mounting and preparation

Certain specimen-mounting procedures, such as mounting the specimen under a fine metal mesh[3],[4], can enhance electrical contact of the specimen with the specimen holder or reduce the amount of surface charge build-up. This and other methods of specimen mounting to reduce static charge are described in detail in ISO 18116[5] and ISO 18117[42] (and in ASTM E1078[4] and ASTM E1829[6].

5.4   Instrument calibration

The kinetic-energy scale of the Auger electron spectrometer shall be calibrated using ISO 17973 or ISO 17974 or another documented method before using this International Standard.

6   Reporting of information related to charge control

6.1   Methods of charge control

Many of the methods commonly used to control the surface potential and to minimize surface charging are described in Clause A.3. Information on reasons for charge control, choice of a charge-control method, and critical specimen and experimental conditions, as described in 6.2, 6.3 and 6.4, shall be reported (or referenced) for individual specimens or collections of similar specimens.

6.2   Reasons for needing charge control and choice of method

The reasons for needing charge control and for choosing a particular method shall be reported.

EXAMPLE 1   The specimen was an insulating film deposited on a conducting substrate. By using an electron primary-beam energy above 10 keV, no specimen charging was observed.

EXAMPLE 2   Experience with similar specimens indicated that charging was likely. To minimize charging, the specimens were mounted under a conducting aperture and beam energies below 3 keV were used. The current was adjusted until the AES spectra obtained were reproducible and stable.

EXAMPLE 3   Spectra recorded initially without any charge control showed peak shifting and broadening. Placing a grounded fine-mesh grid above the specimen minimized these problems. Repeated analyses showed that changes in specimen composition due to charge build-up were below 10 % if the total electron dose was below 1 000 C/m^2.

If the components used for charge control are not standard for the AES instrument, information on the manufacturer or on the relevant design characteristics shall be provided or referenced.

NOTE   A specimen does not need to be a good conductor for routine AES analysis to be accomplished without charging problems. Although it is important to be aware of potential charging issues, experimental verification that they are present is useful before great effort is spent minimizing possible difficulties.

6.3   Specimen information

6.3.1   Specimen form

The form of the specimen shall be reported. The physical nature, source, preparation method and structure of a specimen can influence its charging behaviour[1],[2],[3].

EXAMPLE 1   Powder.

EXAMPLE 2   Thin film spin-cast on silicon.

EXAMPLE 3   Macroscopic mineral specimen.

6.3.2 Specimen dimensions

The size, shape and surface roughness of a specimen can have a significant effect on the extent of specimen charging. The shape of the specimen shall be reported, together with approximate values of the dimensions of the specimen or of any relevant specimen features (e.g. particle diameters, surface roughness).

6.3.3 Specimen-mounting methods

Specimen mounting and contact with the specimen holder can significantly impact charging[1]. The method by which a specimen is mounted, including information about special methods used to increase conductivity or isolate a specimen from ground, shall be reported.

EXAMPLE 1   Powder specimen pressed into foil, which was attached to the specimen holder by conducting tape.

EXAMPLE 2   1 ml of solution containing nanoparticles was deposited on a silicon substrate and dried prior to analysis.

EXAMPLE 3   Specimen held to holder using conductive adhesive tape (with manufacturer and type of tape specified).

EXAMPLE 4   Corroded specimen held on specimen holder by metal screw.

EXAMPLE 5   Mineral specimen and conducting aperture mounted using metal screw.

EXAMPLE 6   Specimen mounted with the primary-electron beam at glancing incidence on the specimen surface.

6.3.4 Specimen treatment prior to or during analysis

Any specimen treatment prior to or during analysis, including any physical or chemical treatment that could affect charging of the specimen during AES measurements, shall be reported.

NOTE   Such treatment of the specimen can modify the surface composition as well as the electrical conductivity, and hence charging, of the surface region.

6.4 Values of experimental parameters

Values of parameters used for AES measurements and charge control, including beam parameters (energy, nominal incident current, beam size, raster area on the specimen, angle of incidence on the specimen), irradiation time of the specimen during set-up and AES measurements, and operating parameters of ancillary components such as a low-energy ion gun shall be recorded (or referenced).

EXAMPLE   A focused electron beam with energy of 10 keV and 1 nA current at 45° incidence to the specimen normal, rastered over an area of 200 nm by 200 nm, was used for the analysis.

6.5 Information on the effectiveness of methods of charge control

The adequacy of the charge-control method(s) used for the type of analysis being conducted shall be established. Auger line peak positions (or peak widths) with and without a method of charge control provide one way of determining the adequacy of the charge-control method. In some cases, the ability to determine that the AES lines are within 5 eV of the expected value and that the relative peak amplitudes are stable might be satisfactory.

EXAMPLE 1   The AES peak positions were within 5 eV of the nominal values and the peak shapes were both similar to reference data and stable on repeated scans.

EXAMPLE 2   Repeated measurements in new areas demonstrated consistent agreement regarding peak shape and relative intensity.

It is recommended that specimens be examined for the presence or absence of specimen damage and that the results be recorded.

7 Reporting of method(s) used for charge correction and the value of that correction

7.1 Methods of charge correction

In many cases, the methods used to control charge eliminate the need for further correction of the Auger peak energies. If a method of charge correction is applied to AES data, the following critical specimen and experimental parameters shall be reported.

7.2 Approach

Any method for correcting the measured kinetic energy of the Auger peaks for charging effects shall be specified in sufficient detail so that the method can be reproduced and its effectiveness judged.

7.3 Value of correction energy

Information shall be given on the magnitude of the correction energy Δ_{corr} for each spectrum and how this correction energy was determined. The corrected kinetic energies and the values of the reference energies shall be reported.

The correction energy Δ_{corr} is determined by taking the difference between the measured kinetic energy of a reference line KE_{meas} and the accepted or reference value for this kinetic energy KE_{ref}, using the following relation:

$$\Delta_{corr} = KE_{ref} - KE_{meas} \tag{1}$$

The corrected kinetic energy for another Auger peak in the same spectrum KE_{corr} can then be found from the sum of the measured kinetic energy for that peak KE_{meas} and the correction energy:

$$KE_{corr} = KE_{meas} + \Delta_{corr} \tag{2}$$

NOTE   Equations (1) and (2) apply only when charge compensation has adequately removed differential charging effects.

Annex A
(informative)

Description of methods of charge control for Auger electron spectroscopy

A.1 Introduction

In this annex, methods used to minimize or control changes in surface potential during electron-stimulated Auger electron spectroscopy are briefly described. The methods and approaches are dependent on the types of instrumentation available and the types of specimen being examined. To assist analysts in dealing with charging in AES, Table A.1 lists approaches in the approximate order that they might be attempted. In any laboratory, the precise order will depend on the facilities available and experience in the particular application. Short descriptions and references to the approaches in Table A.1 are provided in Clause A.3. Specific issues that might arise for non-uniform specimens and during sputter profiling, and some approaches for dealing with them, are discussed in Clause A.4. A short background to general physical considerations of charge build-up during AES analysis is provided in Clause A.5, which outlines a conceptual framework for the issues that arise for different types of specimen. It must be noted that, although specimen charging can be a complication to analysis, it can be used to obtain information about the properties of a specimen or regions of a specimen.

A major strength of AES is the high spatial resolution (in three dimensions) available for chemical analysis. However, along with the generation of Auger electron peaks, the electron beam used for AES can alter the electrical potential of the specimen by introducing charge at the surface and in the near-surface region of insulating materials and might initiate several processes that can change or damage the specimen. The amount and distribution of surface and near-surface charge for a specific experimental system (instrument and specimen) are determined by many factors, including the electron-beam energy, current density and angle of incidence of the beam on the specimen, specimen composition, specimen homogeneity, surface contamination, magnitude of bulk and surface conductivities, surface topography, vacuum environment and availability of neutralizing low-energy electrons or ions. Charge build-up occurs along the specimen surface and into the material[1]. The presence of particles on, or of different phases in, the specimen surface may result in an uneven distribution of charge across the surface, a phenomenon known as differential charging. Charge build-up can also occur at phase boundaries or interface regions within the specimen. Many insulating specimens undergo time-dependent changes in the amount of charging because of charge build-up within the material or because of chemical and physical changes induced by primary or secondary electrons (including electron-stimulated desorption[2],[3], electron-induced sputtering[7] and electron-induced adsorption) or specimen heating.

Many different factors, including the specimen resistivity, specimen thickness and mounting approach used, contribute to changes in the surface potential. However, it is useful to know, as pointed out by Hofmann[3], that a specimen does not need to be a particularly good conductor to enable collection of AES data without observable charging. As one threshold, when using an electron current of approximately 1 µA, an effective resistance of ~1 MΩ from the specimen surface to ground is not likely to produce observable charging. Using the examples defined by Hofmann, charging might appear in AES for specimens with resistivity values between 10^{-3} Ω·m and 10^{+3} Ω·m (or 10^5 µΩ·cm and 10^{11} µΩ·cm). As used in Table A.1, a specimen is considered to be an insulator for AES analysis when it has a resistivity of ~5 Ω·m or higher. High-quality insulators have resistivity values of $> 10^5$ Ω·m [the resistivity of SiO_2 is approximately 10^{14} Ω·m in contrast to the resistivity of Cu of about 10^{-8} Ω·m], but the actual resistivity values of importance for AES depend on specimen, instrumental and operational details.

There is no single method to overcome all charging problems during AES analysis[2],[3], and in some circumstances charging difficulties might be impossible to avoid. Due to the development of new tools and the need to characterize nanostructured materials, several new approaches for dealing with charging during AES started appearing in the literature in the late 1990s and early 2000s. These include specimen preparation methods and increased use of low-energy ions to assist charge compensation. Whereas major advances in

dealing with charging for XPS appeared in the early 1990s, "less progress has been made in analysis of such specimens with AES, which remains a challenging task in many cases."[2]

Although AES analysis introduces some additional challenges, some or even many of the strategies for dealing with charging in scanning electron microscopy (SEM) apply to AES[8],[9]. For a given specimen and primary-beam energy, the mechanisms of charging are generally the same in AES and in SEM (although positive charging can occur in SEM due to a positively biased collector of the secondary electrons whereas there is generally a field-free region around an uncharged specimen in AES).

A.2 Hierarchical table of methods for reducing charging

Many of the approaches used to minimize charging during AES analysis are listed in Table A.1. The table is structured in a hierarchical manner based roughly on simplicity of application. The first group of methods are those usually within the control of an analyst that can be used for specimens already loaded in a spectrometer if charging is observed. The second group of methods requires the presence of specific capabilities that are not available for all spectrometers. However, if they are available they can be used with specimens already loaded in a spectrometer. The third set of methods concerns how the specimen is mounted (or might be remounted). These methods can be used during the initial mounting of specimens for which charging is a possible concern or for remounting specimens with which charging was observed during analysis. The final group involves either the initial specimen design or some type of special specimen preparation or processing. By experience with the available equipment, an analyst will be able to re-order the list for local applications.

Short descriptions of the methods listed in the table and relevant references are provided in Clause A.3. Special issues or approaches that apply to fibres, particles or other highly non-uniform materials and to AES sputter depth profiling of insulators are discussed in Clause A.4. Use of these methods does not necessarily require an understanding of the physical basis of the approach, and analysts often try different methods in an attempt to find an approach which works. In some circumstances, it is helpful to understand the nature of the specimens, the processes involved in charging and the objective of the charge-minimization approach. Therefore, simplified overviews of some aspects of charging processes and related objectives of the charge minimization approach are described in Clause A.5.

Table A.1 — Grouped hierarchical summary of methods for minimizing charging in AES
[The methods are listed in rough order of simplicity of application, with those that might be most easily used by an analyst listed first. The first group involves parameters that are within the control of an analyst for most instruments. The second group uses capabilities available on some, but not all, instruments. The third group involves specimen mounting (or remounting), while the fourth group includes special specimen-preparation methods.]

Method	General approach or objective	Types of specimen	Subclause number(s)	References
a) Generally applicable methods				
Tilt specimen relative to electron beam	Enhancing secondary-electron emission Matching electron penetration to escape distance	Bulk insulators and highly insulating films	A.5.3 A.3.5	1, 3, 10, 11, 13, 26
Lower electron-beam energy	Enhancing secondary-electron emission Matching electron penetration to escape distance	Bulk insulators and highly insulating films	A.5.3 A.3.5	1, 3, 9-11, 13
Increase electron-beam energy	Minimizing specimen resistivity (creating conduction pathway through film)	Thin films on a conducting substrate through which a higher-energy electron beam can penetrate	A.3.3.3	3, 19

Table A.1 (*continued*)

Method	General approach or objective	Types of specimen	Subclause number(s)	References
Minimize total electron dose	Minimizing charge build-up and maintaining specimen integrity	Dielectrics for which time-dependent surface-potential changes (and sometimes potential-dependent composition changes) have been observed	A.3.4.2	10, 21, 22
Lower beam current or current density	Minimizing current through specimen Lowering U_s	High-resistance specimens	A.3.4.1	3, 12, 18
b) Use of special capabilities				
Low-energy ion source	Minimizing current by charge compensation and creating more uniform surface potential	Bulk materials and mixed conducting and non-conducting phases	A.3.4.3	3, 14, 21
Secondary-electron source	Minimizing current by establishing positive potential, establishing self-compensation condition	Bulk insulators	A.3.4.3	3, 22, 33
Heat specimen	Decreasing specimen resistivity Detrapping trapped charge	Bulk specimens and films that are stable upon heating and have lower resistivities at moderate temperatures	A.3.2	3, 12
Add gases to vacuum system	Minimizing surface damage and increasing charge transport	Oxides (and possibly other dielectrics)	A.3.4.3	23
c) Specimen mounting or remounting				
Mount on conducting metal or other conducting tape	Minimizing specimen resistivity (creating short pathway to ground)	Fine particles and powders	A.4.2	2, 5
Cover with conducting mask or grid	Minimizing specimen resistivity (creating short pathway to ground) Increasing capacitance	Bulk insulators and highly insulating films	A.3.3.4	2, 3, 5, 17
d) Special specimen treatments				
Clean specimens	Enhancing secondary-electron emission Removing contaminants which often change secondary-electron yield, sometimes lowering charging	Bulk insulators and insulating films	A.3.5 A.5.3	26, 27
Prepare thinned specimens	Minimizing specimen resistivity (decreasing effective specimen thickness) Increasing capacitance	Bulk specimens thinned by a variety of methods, including ion sputtering	A.3.3.2	8, 12, 13-15, 28
Prepare thinned specimens and use low-atomic-number substrate	Minimizing specimen resistivity and enhancing spatial resolution by minimizing electron backscattering	Specimens that can be thinned by FIB (see A.3.3.2) or another precise method and for which high-resolution information is needed	A.3.3.3	14, 15, 31, 32
Dope or otherwise process specimens	Decreasing specimen resistivity	Specimens that can be either doped during synthesis or processed to increase conductivity	A.3.2	10

A.3 Methods for minimizing charging during AES

A.3.1 Introduction

The essential issue of charging in AES is the build-up of a potential on the surface of the specimen being analysed that influences the primary-electron beam and the emitted Auger electrons. Many methods have been developed (and are still being developed) to control the extent of charge accumulation at the surface during AES analysis. Since specimen resistivity, effective specimen thickness, specimen capacitance and net current to the specimen (the sum of all positive and negative currents) are specimen or instrumental properties that will determine the near-surface charge, many of the approaches use one or more methods to alter these combined specimen and system properties. The discussions of the methods are organized around the properties being altered, as outlined in A.5.2. Note that the approaches in A.3.2 and A.3.3 influence the resistance to ground and the specimen capacitance while the approaches in Clauses A.4 and A.5 involve different approaches for altering the net current to the specimen. Because the charge that leaves the specimen [the total secondary-electron emission yield (TSEEY)] in response to the primary-electron beam is as important as the incident beam, aspects of the TSEEY show up many times. Some ways of altering the TSEEY are discussed in A.3.5, but a more general background is provided in A.5.3.

A.3.2 Decreasing specimen resistivity

Decreasing the specimen resistivity can be a useful approach to minimizing or avoiding specimen charging[3],[9]. Depending on the specimen, this might be accomplished in several different ways, including: adding impurities or dopants to the material, irradiation with ultraviolet light, introducing radiation-induced defects or implanting a dopant, or heating the specimen.

Each of these approaches has been used, but they have significant limitations. Doping a material during film growth can effectively create a conducting material if the doping does not alter other properties. The frequently studied rutile (TiO_2) is often heated in a reducing environment to create oxygen vacancies and increase specimen conductivity to allow experimental examination[10]. The unexpected impacts of this reduction on surface chemistry are becoming increasingly understood[11]. One common complication with specimen heating is surface segregation of material components or impurities.

Although it is common to think of altering overall specimen resistivity to minimize charging, changes in surface resistivity and the detrapping of trapped charges are effective means of controlling the specimen surface potential (even if the bulk resistance is not altered significantly). It should be noted that, in the discussion of TSEEY in A.5.3, a steady-state condition is established when the primary-electron penetration depth is approximately equal to the secondary-electron escape distance[12]. In this zone of holes (created by secondary-electron departure) and electrons, there is a good deal of charge mobility, and it could be argued that this represents a local decrease in resistivity.

A.3.3 Decreasing the insulator thickness (or effective insulator thickness)

A.3.3.1 General

Decreasing the distance (resistance) between an area being analysed on an insulating material mounted on a conducting material connected to the spectrometer can lower the total resistance to ground, which decreases any charging potential [see Equation (A.1)]. Decreasing the thickness of a good insulator grown or mounted on a conducting substrate increases the capacitance, lowering the surface potential [see Equation (A.2)]. In either circumstance, decreasing the insulator thickness (the electrical pathway to ground) can have useful effects. This can be accomplished by preparing thin specimens or otherwise decreasing the effective distance between the surface being probed and ground. It is also useful to remember that surface conduction may provide a good conduction pathway in many circumstances, even when the bulk resistivity is high.

A.3.3.2 Thinned specimens

Specimens may be thinned in a variety of ways, either when they are initially prepared or shortly before analysis. Some of these thinning approaches can be applied to insulating films grown on conducting substrates, while others may be applied to "bulk" insulators and involve creative mounting of the specimen or

thinned sections of a specimen on a conducting substrate. The recent development of focused ion beam (FIB) capabilities[13],[14] and creative methods of argon-ion sputtering for cross-section preparation[15] have introduced new and potentially very powerful methods of thinning materials for AES analysis. Any degree of thinning can help decrease the surface charging but, if the specimens can be thinned to less than the depth of primary-electron penetration, it is generally observed that no significant charging occurs. The FIB approach allows very thin sections of a material to be prepared and placed on a low-atomic-number substrate and treated as a thin film, as described in A.3.3.3. This approach minimizes charging and decreases the AES signal from backscattered electrons[13],[14]. These methods can be particularly useful for examining nanostructured materials where selected regions can be prepared for analysis and some of the background or interference impact of other materials removed or minimized.

It is necessary to consider the impact of any specimen thinning on the information that is desired from the analysis. Specimen damage can include oxide reduction and the creation of an amorphous or damaged layer with significant atomic rearrangement. There are approaches using the FIB by which rapid sputtering is done at high energy and a final polish is done at lower energy to minimize specimen damage.

A.3.3.3 Thin films

Specimens created in thin-film form can be considered as a special case of a thinned specimen but deserve special mention. Analysis of many highly insulating materials can be accomplished with minimal charging if they can be created or grown as very thin films on a conducting substrate. Such specimens are common in the electronics and sensor industries. In these cases, it is often useful to use an electron-beam energy high enough so that the beam penetrates the insulating layer to create a conductive pathway within the electron interaction volume V_e that minimizes charging[3],[16], as shown in Figure A.1.
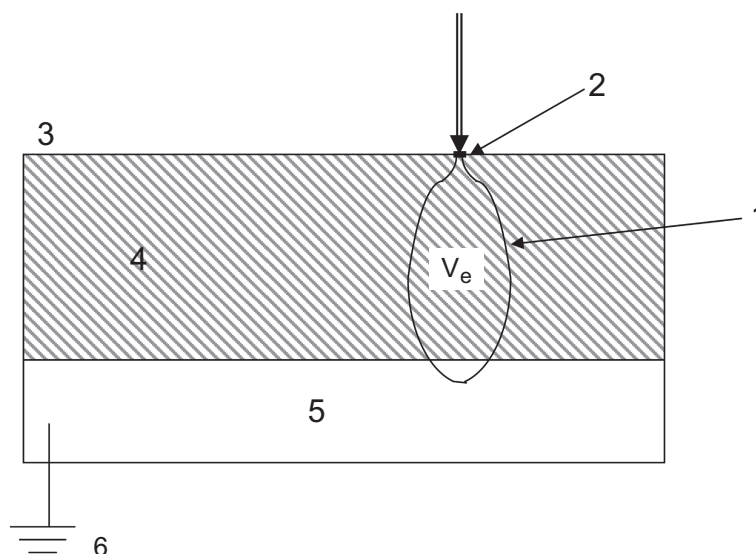
Key

1   electron interaction volume V_e within which there is a conductive pathway for current flow that yields a stable surface potential
2   volume of specimen within which the detected Auger electrons are generated
3   vacuum
4   insulator
5   conductive layer
6   electrical contact to specimen mount

Figure A.1 — Schematic drawing showing the conduction pathway created through an insulating layer by a penetrating electron beam (adapted from Reference [45])

A.3.3.4 Conduction paths — Masks, meshes, coatings and deposits

Another method of providing a pathway to ground is to minimize the distance between the area irradiated by the incident electron beam and a conductor connected to ground[2],[3]. This can be accomplished by placing a mask or grid on the specimen surface around the region to be analysed during specimen mounting. It is also possible to temporarily cover the region to be analysed and coat the remainder of the specimen with a conducting layer. If the outer surface is not the primary region of interest, the whole specimen may be coated and a portion of the coating removed by sputtering. By collecting AES spectra near the region of the conductor, the path (resistance) between the surface being examined and ground is minimized, and surface charging can sometimes be avoided. Although this approach can lower the resistivity of the specimen (similar to decreasing the specimen thickness z), some manipulations are also likely to increase the capacitance of the specimen, thereby also lowering the tendency towards build-up of surface potential.

The advent of FIB or electron-beam-stimulated chemical-vapour deposition is a new way to deposit a metal on the surface of interest[17]. By depositing Pt "wires" on a printed-circuit board, it has been possible to analyse materials in regions isolated from ground using AES without the normal charging difficulties.

A.3.4 Reducing the current density, limiting primary-electron dose and using additional current sources

A.3.4.1 Current density

In some circumstances, it has been found useful to reduce the primary-electron current density on the specimen[3]. This might be accomplished by defocusing or rastering the electron beam. Cazaux[12] notes that the rastered focused beam retains some TSEEY difficulties and is not as effective as a defocused beam in reducing charging. An obvious disadvantage of this approach is that the spatial resolution will be degraded to a value that may be inconsistent with the analysis needs. In addition, Seah and Spencer[18] showed that, for some specimen conditions, some aspects of charging were independent of beam-raster size.

A.3.4.2 Total primary-electron dose

The analysis of total secondary-electron emission yield (TSEEY) in A.5.3 notes conditions for different dose- or time-dependent effects on the surface potential[12]. Seah and Spencer[18] observed the predicted type of total primary-electron dose threshold for subsurface charging that complicates AES analysis. Their data showed that there were at least two different charging mechanisms. One occurred almost immediately and was nearly independent of the primary-beam current density. The second effect depended upon the total dose of primary electrons on the specimen and was, therefore, time dependent. A specimen that first charged positively might eventually charge negatively as the total dose increases (see also Figure A.2). Further recommendations on the total dose are given in A.3.5.

It is also important to note that the amount of electron-induced desorption from a surface (and related specimen damage) is dependent upon the total dose of primary electrons on the specimen. Tables of dose thresholds for 10 % change in signal have been published by Pantano and co-workers[19],[20].

A.3.4.3 Use of additional current sources (ions, electrons or photons)

The net current to the specimen can be altered by providing some additional current. The use of low-energy ion beams to neutralize or at least stabilize the surface potential is one of the new and seemingly powerful advances that are taking place for charge compensation during AES analysis. It is possible to balance the electron current (and in theory reduce the net current) to the surface by introducing a positive current of low-energy ions. This approach was discussed by Hofmann[3] in 1992, but has only recently been routinely available on commercial AES instruments[14],[21]. Low-energy ions (that produce minimal sputtering) have been shown to be very effective at minimizing surface charging associated with conducting regions in a non-conductive matrix, as commonly found during analysis of integrated circuits. This method sometimes has a persistent effect in that the stability lasts after the ions are turned off[14]. Many aspects of low-energy ion-beam "neutralization" are not well understood and methods may improve as users gain experience. While a low-energy ion beam will reduce the net specimen current and stabilize a positive surface potential on the specimen, thereby allowing stable long-term AES analyses, the ions will not appreciably reduce the

subsurface charge induced by the primary electrons. Nonetheless, this approach has proven to be a useful method for AES analyses of insulators.

Low-energy electrons might be useful for producing a surface potential closer to zero and, in some circumstances, have been found effective[3],[22]. The energies of the electrons used appear to vary from a few eV to as much as 400 eV[23]. Such low-energy electrons could compensate the charge on a positively charged surface and produce additional secondary electrons on a negatively charged surface[3],[18].

Ion sputtering and irradiation by ultraviolet light can increase the number of charge carriers within a specimen and near the specimen surface. Any mobile charge can help neutralize charge build-up on a specimen, but this may have additional consequences for AES analysis and the collection of the desired information.

It is also worth noting that, for some oxides, the presence of oxygen at low pressures (or the use of ozone) minimizes electron-beam-induced reduction of the oxide, decreases the build-up of carbon from the ambient gas, and minimizes the accumulation of surface charge[24]. Other gases may similarly decrease charge build-up (as commonly observed in environmental secondary-electron microscopes)[25],[26], but such effects have not been adequately studied or reported for AES.

A.3.5 Optimizing the total secondary-electron emission yield

Charge build-up on the surface depends both on the electron current arriving at the specimen and the total current leaving the specimen (secondary electrons, including Auger and backscattered electrons). The total secondary-electron yield from a specimen is, therefore, a complex but highly important property of the specimen, discussed in more detail in Clause A.5. The schematic data shown in Figures A.2, A.3 and A.4 and the discussion in A.5.3 show that the total secondary-electron yield σ depends on the primary-electron energy, the primary-beam angle of incidence θ on the surface, the presence of surface contamination, and the total electron dose. Both beam energy and incidence angle have traditionally been varied to facilitate AES analyses of bulk insulators. See Reference [23] for a discussion of the role of angle of incidence on TSEEY. Based on the model and analysis presented in A.5.3, beam energies and incidence angles that produce $\sigma > 1$ result in a positive surface potential which should allow relatively stable analysis conditions. The experimental results of Seah and Spencer[18] demonstrate that this model is reasonably valid for a range of clean and well-characterized insulators (at least for low electron doses). In addition to measuring the short-term surface potentials for various conditions, Seah and Spencer also examined the longer-term stability and frequently observed a high-dose effect. They were able to summarize the data collected for each material in a relatively simple diagram that presents useful combinations of primary-beam energy and θ for the specific materials they examined. The low- and high-dose stability diagram for silicon nitride is shown in Figure A.2 and serves as an example of the considerations relevant for AES analyses of insulating materials.

Data collected by Seah and Spencer[18] include shifts in AES line positions (to give the low-dose curve in Figure A.2) and the beam energies for which charge accumulation could be observed in secondary-electron microscopy (SEM) images (high-dose curve in Figure A.2). The authors describe Figure A.2 as a low-dose and high-dose stability diagram. The figure describes some of the behaviours predicted by the TSEEY model (see A.5.3). For higher beam energies, charging is observed. The energies for which charging is not present increase as θ increases. For relatively rapid data collection (that should be typical of many analysis conditions), Figure A.2 indicates that silicon nitride will not show significant charging for beam voltages below 5,2 kV. As the total electron dose increases, however, charging will occur. At energies of around 2 keV, no charging effect is observed regardless of dose. The critical energy E and incidence angle for which low-dose charging could be observed can be defined by a curve with the form $E_p^{0,6} \cos\theta = N$. The higher the value of N, the higher the energy for which the material will be stable for AES analysis. Seah and Spencer's data suggest that the form of the equation represents general behaviour of insulating materials but that the particular value of N will depend on the instrument and the specimen holder in addition to the specimen material and any surface treatments (see 6.3.4 and A.5.3).

The high-dose region occurs when significant subsurface charge is accumulated in the bulk specimen (see Figure A.4 and related discussion). The subsurface charge eventually reaches an amount sufficient to change the TSEEY, the surface charge and thus the surface potential. The measurements summarized in Figure A.2 demonstrate the relationships between beam energy and incidence angle for stable AES analyses. These measurements also show that charging is a highly complex phenomenon that is not simply explained by a single TSEEY curve for a material. The secondary-electron yield will vary depending upon the composition of

the specimen, the experimental configuration and the presence of any surface contamination. It is noted that carbon has a relatively low secondary-electron yield. Materials highly contaminated by a carbonaceous layer might be particularly difficult to analyse because it is difficult to obtain a stable surface charge using beam energy and incidence angle as the primary variables.
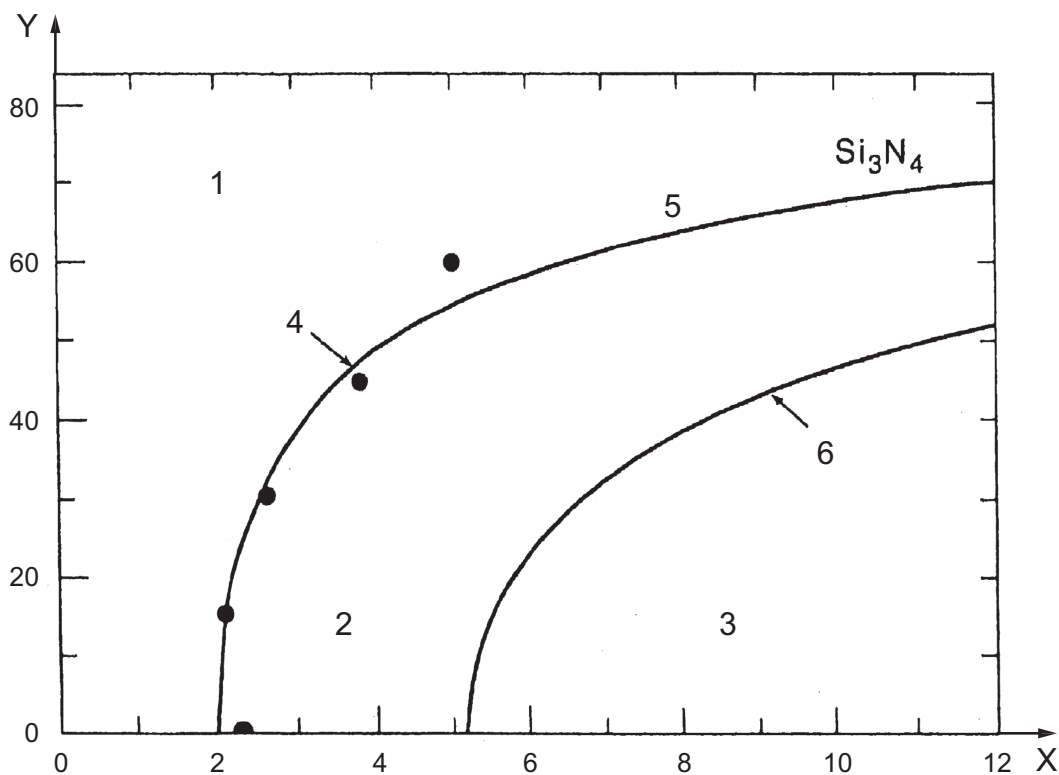
Key

X   electron-beam energy (keV)
Y   angle of incidence, θ (degrees)

1   low-charging zone
2   zone of depth-dependent charging
3   high-charging zone
4   SEM charging data after a large dose
5   line above which charging occurs at a large electron dose
6   line above which shifts occur in the nitrogen Auger peak after a small electron dose

Figure A.2 — Low- and high-dose stability diagram for Si$_3$N$_4$ showing the regions of low charging and high charging for different combinations of primary-beam energy and angle of incidence θ
(the region between the two will show charging given sufficient electron dose) (from Reference [18])

It should be remembered that alterations of the beam voltage change the relative elemental sensitivity factors and thus impact quantitative analyses by AES.

Since the surface composition will impact the secondary-electron yield, the presence of surface contaminants can sometimes have a significant impact on the specimen surface potential[3],[27]. For example, carbon has been shown to decrease the electron yield and enhance negative surface charge build-up[3],[28],[29]. Geller has shown that removal of surface carbon (using CO_2) on MgO significantly enhanced charge dissipation. However, specimen cleaning is not a universal solution as, in some circumstances, specimen cleaning by short durations of ion sputtering has been observed to increase charge build-up.

A.4 Considerations for highly non-uniform specimens, fibres and particles and the use of sputter depth profiling

A.4.1 Introduction

This clause briefly discusses special issues or approaches that could apply to highly rough surfaces, fibres, nanoparticle composites and other non-uniform specimens and the AES analysis during sputter depth profiles of insulating materials.

A.4.2 Dealing with rough surfaces, particles, fibres and other non-uniform specimens

Much of the analysis above applied to specimens that have uniform composition, and in some cases the specimens were assumed to be specimens of thick insulating material. These are often not the specimens of interest for Auger analysis. In general, the use of a focused beam will set up conditions under which the surface potential on an insulator will vary laterally along the surface. The potential has been described by Cazaux[12]. Guo et al.[24] have found that AES peaks sometimes split into two parts that can be attributed to Auger electrons emitted from the centre of the primary beam and those originating from secondary electrons from the edge of the irradiated zone.

The analysis of finely structured materials is often a high priority for AES analysis. This is a challenging problem for which there are few general solutions. Situations when local charging prevents the electron beam from being used to analyse the region of greatest interest are particularly difficult. Although versions of the approaches described above can be applied, the multiple-flux approaches and ion-beam-thinned specimens are among the newer methods being used for analysis of these types of specimen. Although there are no general solutions, many different approaches have been found useful for specific specimens.

Specimens containing small insulating particles or fibres, as well as insulating specimens with rough surfaces, often exhibit differential charging during AES analyses. Clearly, it is much more difficult to control the local primary-beam incidence angle for such specimens. However, if the particles or fibres have sufficiently small diameters and can be mounted in a single layer on a conducting substrate, they can be treated as a thin film (see A.3.3.3), and minimal charging will be observed. It is often useful to press powders, particles and fibres into a soft conducting metal such as indium[2] or onto double sticky conducting tape. For rough surfaces, Park recommends focusing the primary-electron beam on the top of the most prominent protrusion[31].

Some of the newly developing technologies seem particularly useful for examining small features in specimens containing both conducting and non-conducting regions. Specimens with fine features, including those buried below the surface, can sometimes be identified and analysed using an FIB and argon-ion cross-section specimen preparation, in combination with thinning or other charge-compensation approaches[11],[13],[32]. Because of damage and sputter effects, the use of sputter-based thinning methods must be applied with caution. When the thin-film specimens are mounted on a low electron-scattering support such as carbon, the effects of backscattered electrons on lateral resolution in AES are minimized[13],[33],[34]. The use of low-energy positive ions also appears quite effective in allowing analysis of conducting regions in a non-conducting matrix. Improved lateral resolution is obtained for both imaging and point AES analyses[14],[21].

A.4.3 Sputter depth profiling

The use of AES in combination with ion milling to obtain sputter depth profiles of the near-surface region of many types of material, including poorly conducting materials, has been one of the major uses of the technique. One early application of the depth profiling of insulating materials was for weathered or corroded glasses[35],[36]. Researchers routinely used the range of methods described above to minimize charging when profiling bulk or thick films of insulating materials. During sputter profiling of glasses, specimens were commonly tilted away from the normal of the electron beam and low-energy electrons were added to stabilize the specimen surface potential and AES signals[35]. It might seem that the application of a positive-ion beam during sputtering in addition to the negative electrons could help stabilize the surface. However, Borchardt et al.[32] note that ion sputtering can perturb the surface and near-surface charge build-up that would normally occur during AES analysis of an insulator (described above), and the overall effect on surface potential and compositional stability is difficult to assess.

It is important to remember that many studies have been made on the perturbing effects of both electron beams[19],[20] and ion beams[37] on the nature of glass and mineral surfaces, including alterations of near-surface composition and chemistry. In spite of possible charging and damage complications, researchers routinely collect informative profiles of glasses and other insulators, including studies that measure, using depth profiling, the extent to which the electron beam induces elemental migration[16],[37].

Although the combination of AES and sputtering of insulators is relatively common and often very informative, it is frequently not routine. Consequently, several additional approaches have been used to enhance the reliability, and sometimes the speed, of collecting composition information as a function of depth into the material. In some cases, ion sputtering has been used to open a tapered or angled surface, exposing a cross-section of the surface region that has then been examined by AES analysis of the exposed surface. One research group found that this approach was advantageous over the traditional sputter profile method[38]. The extraction of thin specimens using FIB technology will also facilitate obtaining cross-section depth profiles[14] and represents a new approach to getting depth information by AES.

Although getting profiles of "bulk" insulating materials can be challenging, obtaining sputter profiles of thin insulating films on conducting substrates (including corrosion layers) is common and sometimes benefits from the increased beam-energy approach described in A.3.3.3[16]. Covering an insulator surface with a metal coating before sputtering could be considered a special case of the aperture or mask approach described in A.3.3.4[39], and has proven useful in some circumstances.

When high spatial resolution is required, charge build-up in the specimen can cause the beam position to shift. Some type of image registration or position adjustment might be needed.

A.5 General considerations concerning charge build-up during AES

A.5.1 Introduction

This clause briefly examines some aspects of the physical basis of different charging processes and the approaches that are sometimes used to address them. Simplified versions of equations that describe specific elements are used to identify the basis of the charge-minimization approaches and provide an outline for the discussion.

The central issue of charging during AES analysis is the build-up of charge near the surface of the specimen, which alters the electrical potential. This potential can alter the energy of Auger electrons, can sometimes change the location at which the analysis beam strikes the specimen and can induce damage in the near surface region of the specimen. Any process that causes the accumulation of charge near the surface can cause these effects. There is very little charge build-up on highly conducting specimens or on specimens with low resistivity if they are properly grounded. In many cases, even specimens with low conductivity do not charge significantly for AES, and for these cases the specimen may be thought of as a simple resistor. The appropriate model for a highly insulating specimen is that of a capacitor, possibly a leaky capacitor. Some of the factors contributing to specimen charging, including specimen resistivity, specimen capacitance, the total secondary-electron yield and time-dependent phenomena, are outlined in the following subclauses. The discussion is not intended to be comprehensive, but to provide a conceptual framework for approaches to dealing with charging in AES.

A.5.2 Resistivity, capacitance and surface potential

The charge build-up on insulators due to incident electron beams has been examined for many years. Depending on the circumstances and specimen type, different phenomena may contribute to the charge build-up. The first issue considered is often the specimen resistivity. What level of specimen resistance will cause a charging problem? Using the assumption that 1 V of charge shift is not an issue for AES analysis, Hofmann[3] showed that many resistive materials are sufficiently conducting to allow typical AES analyses with little charging.

Considering a specimen as a leaky capacitor, Hofmann estimated, using a version of Ohm's law, that conditions when charging might exceed 1 V. The surface potential U_s of a resistive specimen on a conducting substrate was approximated as follows:

$$U_s \approx \rho z j_p (1 - \sigma) \tag{A.1}$$

where

    ρ is the electrical resistivity of the specimen;

    z is the specimen thickness;

    j_p is the incident (i.e. primary) electron current density;

    σ is the total secondary-electron emission yield (TSEEY).

The total secondary-electron yield is defined as the ratio of the total number of electrons emitted from a specimen (i.e. secondary electrons as well as Auger electrons and backscattered electrons) to the total number of electrons incident at a given energy and angle of incidence. If the incident (i.e. primary) beam current is I_p and the secondary-electron current is I_s, $\sigma = I_s/I_p$. Using Equation (A.1) and an assumed specimen thickness of 1 mm, Hofmann[3] showed that many relatively highly resistive materials are sufficiently conducting for typical AES analyses. However, the conductivity needed is highly sensitive to the beam-current density, specimen size and specimen geometry, and the conductivity requirements for highly focused electron beams can differ by a factor of up to 10^6 when compared to a large-area analysis (which would be possible for a uniform material[3]). As one specific example, a potential of 1 V or less will occur for a 10 nA beam defocused into an area of 1 μm^2 for any 1-mm-thick specimen with a resistivity of 0,1 $\Omega \cdot m$ or less. Typical values of resistivity are given in Table A.2[40]. These conditions change for thicker (or thinner) specimens and depend on the beam current and beam area.

Although Equation (A.1) provides information about when specimen resistivity can make a specimen susceptible to charging, it offers only a highly simplified view of a complex problem. The equation does not, for example, accurately predict the surface potentials of highly insulating materials, for which an issue of particular importance is the nature and variability (including changes due to surface charging) of the TSEEY which is briefly discussed in A.5.3.

Table A.2 — Typical values of the volume resistivity of selected classes of material

Class of material	Resistivity $\Omega \cdot m$
Metals	10^{-8} to 10^{-6}
Ceramics	10^6 to 10^{14}
Polymers	10^6 to 10^{19}
Glasses	10^9 to 10^{12}
Diamond	10^{10} to 10^{11}

For specimens that accumulate charge upon beam irradiation, it is necessary to think of the specimen as a capacitor of capacitance C. In this case, the surface potential is related to the charge Q per surface area S (Q/S), the specimen thickness and the dielectric constant ε[8],[30]:

$$U_s \approx Q/C \cong Qz/\varepsilon S \tag{A.2}$$

The net charge on the specimen Q will be due to the balance between the incoming electrons and the outgoing electrons. This balance may be positive or negative. Thus, assuming no leakage (or infinite

resistivity), the change in charge accumulated on the specimen $\partial Q/\partial t$ will be related to the TSEEY through the following relationship:

$$\partial Q/\partial t = I_p(1 - \sigma) \tag{A.3}$$

When ∂t is chosen to be t, the irradiation time, $j_p t$ is the fluence (or dose) of the radiation, but the total secondary-electron emission σ changes during irradiation, and Equation (A.3) is only valid for short-pulse excitation. The reason is that σ changes as a function of time during the specimen irradiation and approaches a steady-state value of unity.

Consideration of the specimen as a capacitor during AES, XPS and SEM analysis has been discussed in detail by Cazaux for both uniform large-beam irradiation and for focused-beam conditions[9],[12],[30]. Although some of the material in these articles is summarized in the following subclauses, the actual articles should be consulted for greater detail.

Even a very cursory examination of Equations (A.1), (A.2) and (A.3) provides some important general information. For example, decreasing the thickness z of a specimen lowers the surface potential in both Equation (A.1) and Equation (A.2). The time dependence introduced in Equation (A.3) indicates that some behaviours will be time-dependent. Finally, the TSEEY (σ) plays a very important role in charging. Although TSEEY properties can be complex and time-dependent, Cazaux and other workers have established a solid understanding of many of these behaviours. Some of the particularly relevant characteristics of TSEEY are discussed in A.5.3.

A.5.3 Total secondary-electron yield and surface potential

The total secondary-electron yield of a specimen is a complex but important property of the specimen, playing a major role in the charge build-up. For a highly insulating material, the sign and extent of the potential in Equation (A.1) or Equation (A.2) depends on the magnitude and the change of σ during irradiation. If σ was permanently equal to 1, I_s would be equal to I_p and the surface potential would be zero. When σ is initially > 1 (more electrons leaving the surface than arriving), the surface potential will be positive. However, σ will decrease toward unity as a function of time because the growing positive potential will eventually keep secondary electrons from escaping from the surface or attract them back to the specimen. When σ is initially < 1 (more electrons arriving than departing), U_s is negative and the incident electrons are slowed down before reaching the specimen and low-energy electrons are repelled. In this case, σ will increase, as a function of time, towards unity, when a stable surface potential (sometimes very large) will be established. Note that there is a self-stabilization that can occur[12],[18],[32],[41]. A positive surface potential of a few volts is sufficient to re-attract low-energy secondary electrons back to the surface and to minimize the total secondary-electron yield at unity. Conversely, a negative surface potential pushes away secondary electrons and might grow to be very large. It increases with time and, for highly insulating materials, can approach values associated with the accelerating voltage of the primary electrons. If total charge neutrality cannot be obtained, this analysis suggests that, because of self-stabilization (or self-compensation), positively charged surfaces will be more stable than negatively charged surfaces. (A deeper understanding of self-stabilization in relation to the time-dependent build-up of charge is described below based on Reference [12].)

Although the description above is simple and intuitive, there are several physical considerations that apply to TSEEY curves, and a more in-depth understanding of the physical aspects of TSEEY and time dependence can help an analyst deal with some types of charging issue. As discussed above, TSEEY for a specimen varies with beam energy, the angle of the incident electron beam and total beam exposure (time). Figure A.3 shows a schematic plot of σ characteristic of a metal as a function of electron-beam energy for four angles of incidence θ (measured with respect to the surface normal), and Figure A.4 shows the nature of the time dependence.

At low energies, σ increases from zero to a maximum value typically greater than one. As the electron energy increases beyond the value for the maximum, σ decreases and often drops below unity at high energies.

For discussion of some important physical aspects of TSEEY, it is useful to identify some energy regions and physical parameters[12]:

E_p is the energy of the primary, or incident, electron beam;

$E_{p(max)}$ is the energy at which the TSEEY is a maximum;

E^0_{p1} is the energy at which secondary-electron emission rises above 1;

E^0_{p2} is the energy at which the secondary-electron emission drops below 1;

E^c_{p2} is the energy at which the range R of the incident electrons is approximately equal to the maximum escape depth of the secondary electrons [typically, E^c_{p2} is higher than $E_{p(max)}$ and below E^0_{p2}].

The example in Figure A.3 shows that the maximum value of σ usually increases as θ increases from zero to larger values, and particularly for glancing angles of incidence. If, as discussed above, a positive surface potential is desired if neutrality is not possible for one angle of incidence, there can be advantages to increasing θ and adjusting the beam energy.

Key
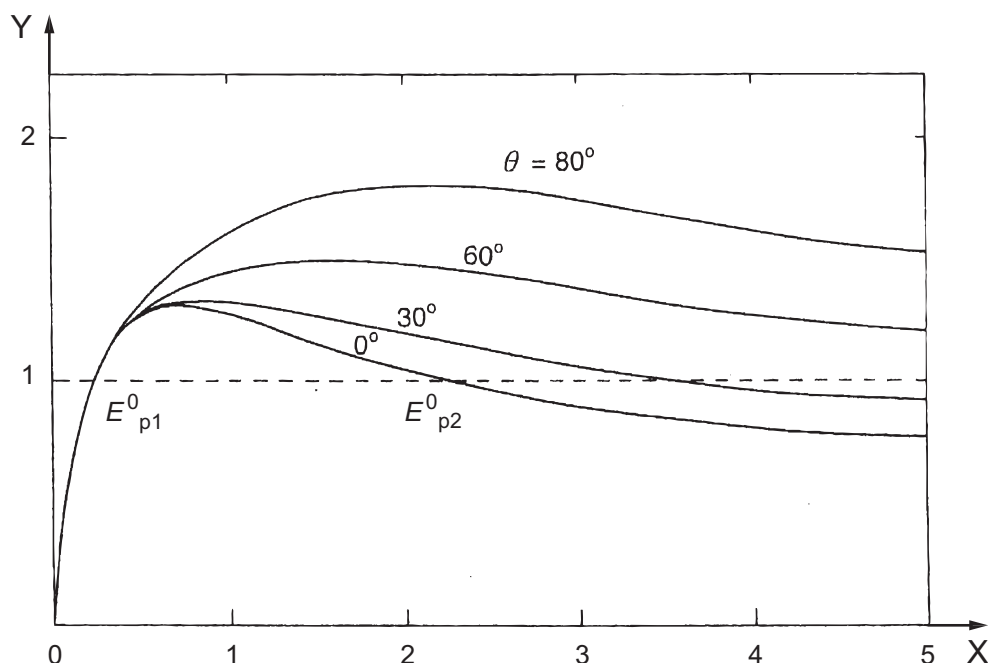
X   incident electron beam energy, E_p (keV)
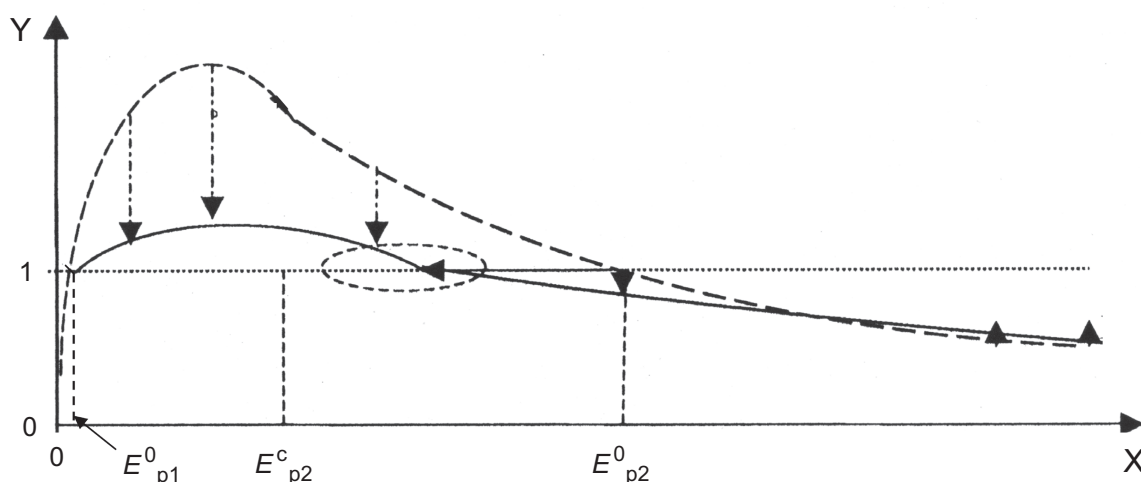Y   total secondary-electron yield, σ

Figure A.3 — Schematic plot of the total secondary-electron yield σ as a function of the energy of the primary-electron beam E_p in keV for four angles of incidence θ with respect to the surface normal (from Reference [18])

Measurements of the surface potentials of some materials during electron-beam irradiation have produced a variety of results. For example, Hofmann[3] and many others have found that surface potentials in many circumstances are negative, while theoretical analysis[1], the examples given above and the careful measurements of Seah and Spencer[18] and of Oechsner[41] show positive potentials for a variety of insulators. These apparent contradictions can be resolved by realizing that the magnitude and time dependence of the TSEEY from an insulator (and therefore the observed surface potential) is not fully determined by the bulk chemical composition but will vary depending on the crystalline state of the sample (i.e. whether it is amorphous, polycrystalline or a single crystal), the sample temperature, the surface structure, previous surface treatments (e.g. whether the sample has been cleaved or is a polished crystal[12]), the total electron dose and the presence of surface contamination.

A systematic effort to understand and model TSEEY curves has been described by Cazaux[12],[30], and this approach can be used to explain a wide variety of phenomena reported by different researchers. The time dependence of the TSEEY curve for an insulator is shown schematically in Figure A.4. The dashed TSEEY curve represents what occurs on a surface without the build-up of surface charge. The solid line provides some indication of how the secondary-electron yield changes with time as charge accumulates near the surface. Understanding the charging processes requires paying special attention to the relationship of E_p relative to E^0_{p2} and E^c_{p2} and the knowledge that charging is a three-dimensional phenomenon that occurs in the near-surface region of the specimen and not simply at the surface.

As summarized by Cazaux[12] and shown pictorially in Figure A.4, different charge distributions form as a function of time depending upon the energy of the primary beam E_p in relation to these energies and the total incident electron flux. If $E^0_{p1} < E_p < E^c_{p2}$, the surface will charge positively to a depth approximately equal to the penetration range of the incident electrons because more negative charges leave the surface than arrive. As the charge builds up, the number of secondary electrons will decrease since low-energy electrons cannot escape. If $E^c_{p2} < E_p < E^0_{p2}$, the surface will initially charge positively because of the secondary-electron loss, but primary electrons travelling deeper than the secondary-electron escape depth will also cause a negative-charge build-up below the surface. This charge will increase with time, setting up a near-surface dipole layer and possibly leading to a net negative charge over time. As charge builds up, the effective TSEEY will change with time and the effective E^0_{p2} will shift toward E^c_{p2} as indicated by the inflection point in the solid-line curve in Figure A.4 (highlighted by the elliptical dashed line). When $E_p \approx E^c_{p2}$, the near equality of the penetration range of primary electrons and the escape depth of secondary electrons permits the rapid recombination of electrons and positive charges (left by secondary-electron emission) in the same layer, and a steady-state condition can be established. Here, $qU_s \approx E_p - E^c_{p2}$ (where q, the surface charge, and U_s are negative). In these conditions, the sign of the surface charge will vary with time, starting positive and eventually changing to negative. If $E^0_{p2} < E_p$, the surface and near-surface region will be negatively charged, although the charge build-up will slowly increase the secondary-electron yield toward $\sigma \approx 1$.

Key

X   incident electron beam energy, E_p

Y   total secondary-electron yield, σ

Figure A.4 — The expected changes in the secondary-electron yield from an insulator as a function of the nominal E_p for a total current dose
(The dashed line is the initial TSEEY curve and the solid line is the curve as it evolved after a dose of electrons. There is a much more rapid decrease in the electron yield when $E^0_{p1} < E_p < E^0_{p2}$ than the increase when $E_p > E^0_{p2}$. There is also a decrease in the energy for $\sigma = 1$ towards E^c_{p2}.)
(From Reference [12])

One impact of the understanding of Figure A.4 is that a stable condition can be achieved when E_p is less than but nearly equal to E^c_{p2}. This condition corresponds to the situation when the range of the primary beam into the specimen is roughly equal to the depth from which electrons can escape. The condition is angle-dependent as the penetration range decreases where the electrons are incident on the specimen at glancing

angles, effectively moving E^c_{p2} to higher energies. As noted below, surface contamination on the specimen, the vacuum conditions and the presence of impurities or dopants in the specimen can alter secondary-electron yields and specimen resistivity. In particular, Hofmann[3] reported negative charging over all the primary-energy range $50\,\text{eV} < E_p < 10\,\text{keV}$ for carbon-contaminated oxide surfaces. Therefore, for most specimens, the presence or absence of charging, along with approaches to minimize it, should be determined during the analysis for the experimental conditions actually used.

A.5.4 Charge transport and accumulation below the surface, time-dependent charge accumulation and specimen damage

Since primary electrons with an energy of 25 keV can penetrate the specimen up to a micrometre below the surface, there will be both charge movement through the material below the surface and, for good insulators, charge accumulation. The charge accumulation below the surface and the surface potential it induces will have an impact on AES measurements. The relationship between surface potential and incident flux can be estimated using the capacitance equations [Equations (A.2) and (A.3)]. These effects have been noted above, discussed theoretically by Cazaux[1],[12],[30] and demonstrated by Seah and Spencer[18]. There are effectively three different physical causes of time-dependent behaviour. First, the build-up and alteration of surface potential can occur almost instantly[12][18]. Second, the build-up of subsurface charge changes the surface potential, which in turn changes the TSEEY at generally longer times as a function of the sign of U_s. Because of these two time scales for charging effects, it can be important to minimize total exposure to the electron beam. Finally, specimen damage can occur or diffusion may be induced in the specimen due to the build-up of the electric field. The extent of subsurface charge build-up is increased (for bulk specimens) as beam voltage increases.

Charge transport into the specimen may cause difficulty for analysis of a "thick" insulating material, but provides a tool for analysis of thin specimens. When an electron beam penetrates an insulating thin specimen (or thin film), it effectively creates a conducting path through the specimen that serves to minimize overall specimen charging. As discussed in A.3.3.3, one method of minimizing charging (and the time-dependent build-up of subsurface charge in particular) for thin insulating specimens on a conducting substrate can be to ensure that the electron beam penetrates the insulating layer (i.e. by ensuring that the beam energy is high enough for the electron range to be larger than the thickness of the insulating layer).

As noted above, there are other effects of electron irradiation and charge build-up in the specimen in addition to changes in specimen potential. These include the production of surface and near-surface defects and charge (or field) induced diffusion of components of the material being examined (see A.3.4.2). Ambient gases in the vacuum chamber can alter the rate and extent of beam damage and influence the extent of charge build-up (see A.3.4.3).

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