

SEMI F72-0214 (Reapproved 0221)

TEST METHOD FOR AUGER ELECTRON SPECTROSCOPY (AES)

EVALUATION OF OXIDE LAYER OF WETTED SURFACES OF PASSIVATED 316L STAINLESS STEEL COMPONENTS

This Standard was technically approved by the Gases Global Technical Committee. This edition was approved for publication by the global Audits and Reviews Subcommittee on January 8, 2021. Available at www.semiviews.org and www.semi.org in February 2021; originally published November 2002; previously published February 2014.

NOTICE: This Document was reapproved with minor editorial changes.

1 Purpose

1.1 The purpose of this Document is to define a test method to characterize the surface composition of passivated 316L stainless steel components being considered for installation into a high-purity gas distribution system. This Test Method is intended to be applied to the wetted surfaces of stainless steel tubing, fittings, valves, and other components as a measure of the effectiveness of passivation.

1.2 This Document defines a method of testing the wetted surfaces of stainless steel tubing, fittings, valves, and other components to determine the surface and near-surface composition as a measure of the effectiveness of passivation processes.

1.3 The objective of this Test Method is to describe a general set of instrument parameters and conditions that will achieve reproducible measurements within the chromium-enriched passive oxide layer.

2 Scope

2.1 This Document describes a test method to characterize the composition and thickness of the chromium-enriched oxide layer of stainless steel surfaces and to detect surface contamination in tubing, fittings, valves, and other components. The procedure involves detection and measurement of the surface elemental composition by Auger electron spectroscopy (AES). This procedure also describes the test method for a depth compositional profile of Cr, Fe, Ni, O, and C from the as-received surface, through the oxide layers, and extending into the base metal. This measurement provides oxide thickness and chromium enrichment information throughout the passivated region.

NOTICE: SEMI Standards and Safety Guidelines do not purport to address all safety issues associated with their use. It is the responsibility of the users of the Documents to establish appropriate safety and health practices, and determine the applicability of regulatory or other limitations prior to use.

3 Limitations

3.1 This Test Method is intended to be used by AES analysts familiar with the instrumentation and technique. The AES instrument must be calibrated and maintained to pertinent manufacturer's specifications. The method is not intended to preclude the use of any particular brand or model of surface analysis equipment. While most of the test methodology has been developed using specific instrumentation, this method can be adapted to most Auger surface analytical instrumentation.

3.2 Quantification of the elemental compositions is performed with handbook values of the relative elemental sensitivity factors. These sensitivity factors do not allow for differences due to the chemical environment of the elements, and are thus not accurate in this instance in which the chemical environment changes from the passive oxide layer to the metal alloy. In addition, quantification is affected by the choice of instruments and instrument parameters. For these reasons the results of this Test Method may not be reproducible between different instruments and operators. Use of the results of this Test Method should be restricted to process development and comparison to an historical database of AES data from the same source.

3.3 The effects of the depth of analysis of the technique and surface contamination affect the results of this Test Method. These are discussed in the attached Appendix 1.

3.4 Surface roughness, non-planarity of the surface, orientation of the surface relative to the ion sputtering beam, and differential sputtering rates for the different chemical species also cause measurement uncertainties in this Test Method. This is discussed in Appendix 2.

3.5 The results of this Test Method have not been demonstrated to affect performance of stainless steel components in high purity gas distribution systems for semiconductor manufacturing.

4 Referenced Standards and Documents

4.1 SEMI Standards and Safety Guidelines

SEMI F19 — Specification for the Surface Condition of the Wetted Surfaces of Stainless Steel Components

SEMI F60 — Test Method for ESCA Evaluation of Surface Composition of Wetted Surfaces of Passivated 316L Stainless Steel Components

4.2 ASTM Standards¹

ASTM E673 — Standard Terminology Relating to Surface Analysis

ASTM E1078 — Standard Guide for Specimen Handling in Auger Electron Spectroscopy and X-ray Photoelectron Spectroscopy

ASTM E1127 — Standard Guide for Depth Profiling in Auger Electron Spectroscopy

NOTICE: Unless otherwise indicated, all documents cited shall be the latest published versions.

5 Terminology

5.1 Terminology is per ASTM E673 unless otherwise specified.

5.2 Abbreviations and Acronyms

5.2.1 *AES* — Auger electron spectroscopy

5.2.2 *TOA* — take-off angle

5.3 Definitions

5.3.1 *carbon thickness* — the thickness of carbon on the initial surface, determined from the depth composition profile as the sputter etch depth at which the carbon concentration decreases to ½ its maximum value. (See Figure 1.)

5.3.2 *chromium enriched layer thickness* — the depth within the passive oxide layer for which the chromium atomic concentration is greater than the iron atomic concentration, determined from the depth composition profile as the depth from the initial surface to the point where the chromium atomic concentration equals the iron atomic concentration, if an iron enriched layer is not present. If an iron enriched layer is present, then its thickness must be subtracted from the above value to calculate the chromium enriched layer thickness. (See Figure 1.)

5.3.3 *Cr/Fe ratio at 10 Angstroms* — the ratio of the chromium atomic concentration to the iron atomic concentration at 10 angstroms (1 nm) from the initial surface, determined from the depth composition profile.

5.3.4 *depth composition profile* — the atomic concentration of the elements present as a function of depth determined by surface analysis in conjunction with the removal of successive atomic layers by ion sputter etching. (Identified as *depth profile analysis* in SEMI F60.)

5.3.5 *iron enriched oxide layer thickness* — the depth from the initial surface for which the iron atomic concentration is greater than the chromium atomic concentration of the passive oxide layer, determined from the depth composition profile. Sometimes also called a *detached Iron Oxide layer*. (See Figure 1.)

5.3.6 *KLL Auger peaks* — standard terminology for the identification of Auger peaks, derived from the identification of the atomic electron shells participating in the production of the Auger electron. (See Appendix 1.)

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5.3.7 *maximum Cr/Fe ratio* — the maximum of the Cr/Fe ratio, determined by inspection and calculation from the depth composition profile. (See Figure 1.)

5.3.8 *oxide thickness* — the thickness of the passive oxide layer on the surface, determined from the depth composition profile as the sputter etch depth at which the oxide concentration decreases to ½ its maximum value. (See Figure 1.)

5.3.9 *passivation* — the chemical treatment of a stainless steel surface with a mild oxidant for the purpose of enhancing the corrosion resistant surface film.

5.3.10 *passive oxide layer* — the chromium enriched oxide adherent surface film resulting from the passivation process that gives stainless steel its enhanced corrosion resistance.

5.3.11 *sampling volume* — the volume in the sample from which Auger electrons are detected. The electron beam spot size or the scan area, and the acceptance angle of the electron analyzer determine the lateral dimensions. A length of three times the Auger electron mean free path is considered the maximum depth sensitivity. Sampling volume is dependent on the sample material and TOA.

5.3.12 *sensitivity factor* — the factor relating the height of an element's Auger peak to its relative atomic concentration. The sensitivity factors do not take into account the chemical environment of the elements, which does cause variations in peak heights. Therefore they are not accurate in this instance in which the chemical environment changes from the passive oxide layer to the metal alloy. Also, the sensitivity factors may vary between different Auger analysis instruments and choice of operating parameter. For these reasons the determination of atomic concentrations from Auger data is approximate.

5.3.13 *sputter etching* — removal of successive atomic layers from the surface by bombardment with ions.

5.3.14 *take-off angle (TOA)* — the angle that the Auger electron collection lens forms with the sample plane.

5.3.15 *wetted surface* — surfaces of the components that are in contact with the contained gases and/or liquids used in the semiconductor manufacturing processes.

5.4 *Symbols*

5.4.1 *Cr/Fe* — ratio of the chromium atomic concentration to Iron atomic concentration in the passive oxide layer.

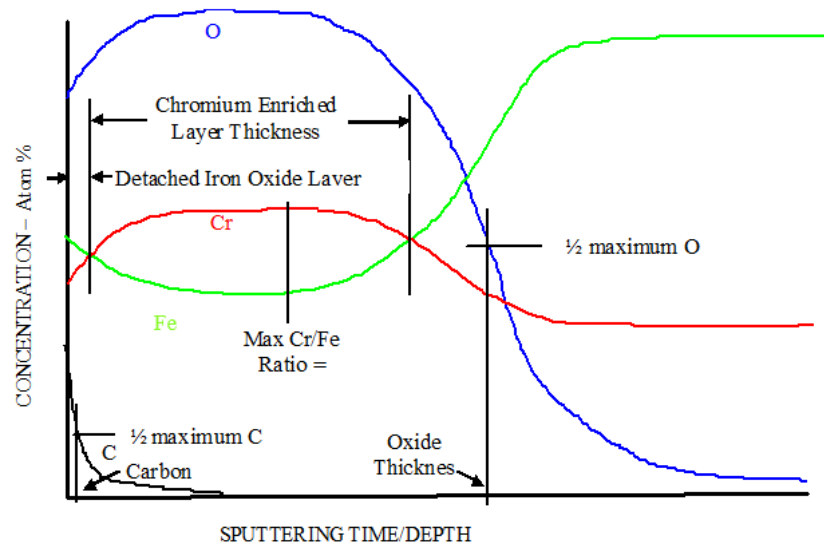


Diagram of Depth Profile Analysis of Stainless Steel Illustrating Definitions

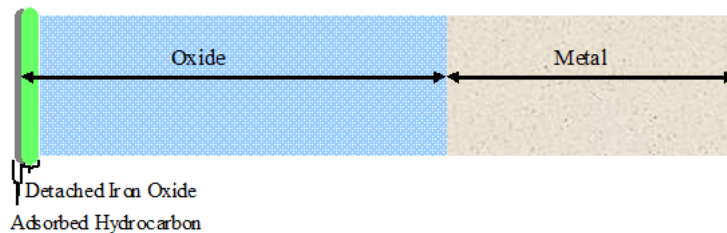


Illustration of Surface Layers on Stainless Steel Corresponding to the Depth Profile

Figure 1
Diagram of Depth Composition Profile of Stainless Steel

6 Summary of Method

6.1 Data Acquisition

6.1.1 Acquire initial elemental survey and calculate elemental composition of 'as received' wetted surface.

6.1.2 Acquire a depth composition profile by ion etching to determine the relative abundance of C, O, Cr, Fe and Ni. Additional elements may be included as desired (i.e., molybdenum, silicon and nitrogen). The thickness of the passive oxide layer and carbon is also determined from the depth composition profile.

6.2 Reporting — Data is provided consisting of:

6.2.1 An initial survey spectrum extending from approximately 0 to 2000 eV.

6.2.2 A depth composition profile plot including C, O, Cr, Fe and Ni as a function of sputtering depth.

6.2.3 A table of the as-received surface elemental composition calculated from the initial survey spectrum.

6.2.4 A table of the oxide thickness, the carbon thickness, the chromium enriched layer thickness, the maximum of the Cr/Fe ratio, the Cr/Fe ratio at 10 angstroms, and the presence and thickness of the iron enriched oxide layer calculated from the depth composition profile.

7 Possible Interferences

7.1 *Cr and O* — Carefully select windows for oxygen and chromium to minimize interference. Monitor individual windows after profile is complete to evaluate effects. Some instruments may have enhanced ability to compensate for overlaps.

8 Apparatus

8.1 *Instrumentation* — Any AES instrument equipped with an ion gun for sputter etching may be used, whether it etches and measures simultaneously or in alternating fashion. An instrument that analyzes and etches in alternating fashion should be evaluated to assure that no significant oxygen level redeposits onto the sample surface between etching intervals. The electron analyzer may be of either the hemispherical or cylindrical mirror analyzer (CMA) type. The electron energy analyzer shall be of high enough energy resolution to permit adequate separation of the chromium KLL and oxygen KLL Auger peaks.

8.2 Instruments with geometries significantly different from one another may provide analysis from different sampling volumes. The incident electron beam energy, the angle of the incident electron beam to the sample plane, and the TOA must be recorded.

9 Reagents and Materials

9.1 *Instrument Calibration Materials* — Refer to instrument manufacturer recommendations or ASTM E1127 for standard materials.

10 Safety Precautions

10.1 This Test Method does not purport to address the safety considerations associated with use of high voltage, vacuum, and electron producing equipment. The method assumes an AES analyst with adequate skill level as well as knowledge of instrumentation and associated safety precautions.

11 Test Specimens

11.1 Specimens are to be sectioned to appropriate size for the particular AES instrument using a clean, dry hacksaw or dry low speed bandsaw. Any sample preparation shall avoid introducing contamination onto the surface to be measured. Clean noncontaminating gloves and tweezers should be used to handle samples, avoiding contact with the area of interest. In addition, preparation must avoid excessive heating of the sample (i.e., the surface temperature shall not exceed 50°C) to avoid oxide growth or change in surface composition.

11.2 Sample preparation should preferably be done by the component manufacturer. Following sectioning the sample(s) are to be cleaned and packaged per the manufacturer's standard final cleaning and packaging procedures.

11.3 If sample preparation is done by other than the manufacturer, the sample(s) may be cleaned in DI water and dried promptly. If the sample(s) are not to be analyzed immediately they should be packaged by wrapping in clean metal foil or sealing in cleanroom quality nylon bags.

11.4 If sample preparation is done by other than the manufacturer this shall be stated in the report narrative and the analytical results are not to be interpreted as indicative of the manufacturer's quality of cleaning and packaging procedures. A note to this effect shall be included in all tables of reported results of the composition of the surface.

11.5 After preparation, samples should be analyzed promptly, with allowance for shipping times and queuing time at the analyst.

12 Preparation of Apparatus

12.1 Instruments shall be routinely tested in accordance with manufacturer recommendations to assure proper performance. The instrument vacuum shall be 1.0×10^{-7} Torr or better during the analysis.

13 Calibration and Standardization

13.1 Instrument calibration for sputter etch rates and sensitivity factors shall be performed in accordance with instrument manufacturer recommendations or other established method.

14 Procedure

14.1 The sample is to be mounted in accordance with manufacturer's recommendations and in a manner consistent with ultra-high vacuum surface analytical procedures. Some of these practices are detailed in ASTM E1078. The area to be analyzed should be mounted parallel to the sample holder surface so that the TOA is known.

14.2 Place the sample in the AES introduction chamber for pump down. Transfer to the analytical chamber at the manufacturer's recommended base pressure.

14.3 Align the sample with respect to the electron beam and analyzer so that optimum count rate from the desired analytical location is obtained. The surface area to be analyzed should be free of sample preparation debris, visible particles and large defect features, if possible.

14.4 A large beam size or scan area should be used to attempt measurement of a representative surface. Elemental survey data (approximately 0 to 2000 eV) are to be measured from the sample surface to determine the elements present and their approximate surface abundances. A signal-to-noise ratio of 2 is usually adequate to ensure detection of elements present at one atomic percent or greater levels. A typical survey spectrum is shown in Figure 2.

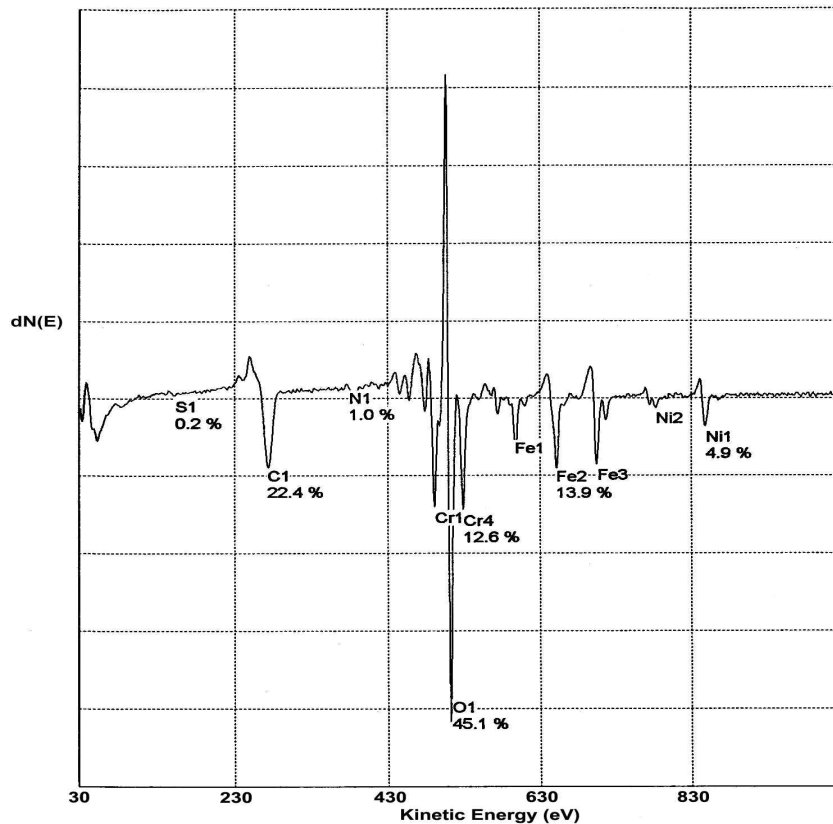


Figure 2
Auger Spectrum of 316L Stainless Steel Surface

14.5 Acquire a depth composition profile to determine the relative abundances of Cr, Fe, Ni, O, and C. The profile may be acquired in a simultaneous or an alternating etch/data acquisition mode. Measurement of each element shall be made at a frequency of at least one data point every 5 angstroms within the first 50 angstroms and one data point every 10 angstroms from 50 angstroms to the profile end. An appropriate scan acquisition time is one that optimizes spectral resolution and signal/noise, and that has at least ten data points in each spectral window. The depth composition profile should be continued into the depth of the sample until the Fe, Cr and Ni levels are approximately constant.