



# Standard Test Method for Trace Metallic Impurities in Electronic Grade Aluminum- Copper, Aluminum-Silicon, and Aluminum-Copper-Silicon Alloys by High-Mass-Resolution Glow Discharge Mass Spectrometer<sup>1</sup>

This standard is issued under the fixed designation F 1845; 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 reappraisal. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

## 1. Scope

1.1 This test method determines the concentrations of trace metallic impurities in high purity (99.99 wt. % pure, or purer, with respect to metallic trace impurities) aluminum-copper, aluminum-silicon and aluminum-copper-silicon alloys with major alloy constituents as follows:

|          |                          |
|----------|--------------------------|
| aluminum | Greater than 95.0 %      |
| copper   | Less or equal than 5.0 % |
| silicon  | Less or equal than 5.0 % |

1.2 This test method pertains to analysis by magnetic-sector glow discharge mass spectrometer (GDMS).

1.3 This test method does not include all the information needed to complete GDMS analyses. Sophisticated computer-controlled laboratory equipment, skillfully used by an experienced operator, is required to achieve the required sensitivity. This test method does cover the particular factors (for example, specimen preparation, setting of relative sensitivity factors, determination of detection limits, etc.) known by the responsible technical committee to effect the reliability of high purity aluminum analyses.

1.4 *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:

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials<sup>2</sup>

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals<sup>3</sup>

E 673 Terminology Relating to Surface Analysis<sup>4</sup>

E 876 Practice for Use of Statistics in the Evaluation of Spectrometric Data<sup>4</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee F-1 on Electronics and is the direct responsibility of Subcommittee F01.17 on Sputtered Thin Films.

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<sup>2</sup> Annual Book of ASTM Standards, Vol 03.05.

<sup>3</sup> Annual Book of ASTM Standards, Vol 15.05.

<sup>4</sup> Annual Book of ASTM Standards, Vol 03.06.

F 1593 Test Method for Trace Metallic Impurities in Electronic Grade Aluminum by High-Mass-Resolution Glow Discharge Mass Spectrometer<sup>5</sup>

F 1594 Specification for Pure Aluminum (Unalloyed) Source Material for Vacuum Coating Applications<sup>5</sup>

## 3. Terminology

3.1 Terminology in this test method is consistent with Terminology E 135. Required terminology specific to this test method, not covered in Terminology E 135, is indicated in 3.2.

### 3.2 Definitions:

3.2.1 *campaign*—a test procedure to determine the accuracy of the instrument, which was normally performed at the beginning of the day or after the instrument modification, or both.

3.2.2 *reference sample*—material accepted as suitable for use as a calibration/sensitivity reference standard by all parties concerned with the analyses.

3.2.3 *specimen*—a suitably sized piece cut from a reference or test sample, prepared for installation in the GDMS ion source, and analyzed.

3.2.4 *test sample*—material (aluminum alloy) to be analyzed for trace metallic impurities by this GDMS method.

3.2.4.1 *Discussion*—Generally the test sample is extracted from a larger batch (lot, casting) of product and is intended to be representative of the batch.

## 4. Summary of Test Method

4.1 A specimen is mounted in a plasma discharge cell. Atoms subsequently sputtered from the specimen surface are ionized, and then focused as an ion beam through a double-focusing magnetic-sector mass separation apparatus. The mass spectrum (the ion current) is collected as magnetic field or acceleration voltage, (or both) is scanned.

4.2 The ion current of an isotope at mass  $M_i$  is the total measured current, less contributions from all other interfering sources. Portions of the measured current may originate from the ion detector alone (detector noise). Portions may be due to incompletely mass resolved ions of an isotope or molecule with

<sup>5</sup> Annual Book of ASTM Standards, Vol 10.04.

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mass close to, but not identical with,  $M_i$ . In all such instances the interfering contributions must be estimated and subtracted from the measured signal.

4.2.1 If the source of interfering contributions to the measured ion current at  $M_i$  cannot be determined unambiguously, the measured current less the interfering contributions from identified sources constitutes an upper bound of the detection limit for the current due to the isotope.

4.3 The composition of the test specimen is calculated from the mass spectrum by applying a relative sensitivity factor (RSF(X/M)) for each contaminant element, X, compared to the matrix element, M. RSF's are determined in a separate analysis of a reference material performed under the same analytical conditions, source configuration, and operating protocol as for the test specimen.

4.4 The relative concentrations of elements X and Y are calculated from the relative isotopic ion currents  $I(X_i)$  and  $I(Y_j)$  in the mass spectrum, adjusted for the appropriate isotopic abundance factors ( $A(X_i)$ ,  $A(Y_j)$ ) and RSF's.  $I(X_i)$  and  $I(Y_j)$  refer to the measured ion current from isotopes  $X_i$  and  $Y_j$ , respectively, of atomic species X and Y as follows:

$$(X)/(Y) = RSF(X/M)/RSF(Y/M) \times A(Y_j)/A(X_i) \times I(X_i)/I(Y_j) \quad (1)$$

where (X)/(Y) is the concentration ratio of atomic species X to species Y. If species Y is taken to be the aluminum matrix ( $RSF(M/M) = 1.0$ ), (X) is (with only very small error for pure metal matrices) the absolute impurity concentration of X.

## 5. Significance and Use

5.1 This test method is intended for application in the semiconductor industry for evaluating the purity of materials (for example, sputtering targets, evaporation sources) used in thin film metallization processes. This test method may be useful in additional applications, not envisioned by the responsible technical committee, as agreed upon between the parties concerned.

5.2 This test method is intended for use by GDMS analysts in various laboratories for unifying the protocol and parameters for determining trace impurities in aluminum-copper, aluminum-silicon, and aluminum-copper-silicon alloys. The objective is to improve laboratory-to-laboratory agreement of analysis data. This test method is also directed to the users of GDMS analyses as an aid to understanding the determination method, and the significance and reliability of reported GDMS data.

5.3 For most metallic species the detection limit for routine analysis is on the order of 0.01 wt. ppm. With special precautions, detection limits to sub-ppb levels are possible.

5.4 This test method may be used as a referee method for producers and users of electronic-grade aluminum-copper, aluminum-silicon and aluminum-copper-silicon materials.

## 6. Apparatus

6.1 *Glow Discharge Mass Spectrometer*, with mass resolution greater than 3500, and associated equipment and supplies.

6.2 *Machining Apparatus*, capable of preparing specimens and reference samples in the desired geometry and with smooth surfaces.

6.3 *Electro-Polishing Apparatus*, capable of removing the contaminants from the surfaces of specimens.

## 7. Reagents and Materials

7.1 *Reagents*—Reagent and high purity grade reagents as required (MeHO, HNO<sub>3</sub> and HCl....)

7.2 *Demineralized Water*.

7.3 *Tantalum Reference Sample*.

7.4 *Aluminum Reference Sample*.

7.4.1 To the extent available, aluminum reference materials shall be used to produce the GDMS relative sensitivity factors for the various elements being determined (see Table 1).

7.4.1.1 As necessary, non-aluminum reference materials may be used to produce the GDMS relative sensitivity factors for the various elements being determined.

7.4.2 Reference materials should be homogeneous (see 11.1) and free of cracks or porosity.

7.4.3 At least two reference materials are required to establish the relative sensitivity factors, including a 99.9999 % pure aluminum metal to establish the background contribution in analyses.

7.4.4 The concentration of each analyte for relative sensitivity factor determination should be at a factor of 100 greater than the detection limit determined using a 99.9999 % pure aluminum specimen, but less than 100 ppmw.

7.4.5 To meet expected analysis precision, it is necessary that specimens of reference and test material present the same size and configuration (shape and exposed length) in the glow discharge ion source, with a tolerance of 0.2 mm in diameter and 0.5 mm in the distance of sample to cell ion exit slit.

## 8. Preparation of Reference Standards and Test Specimens

8.1 The surface of the parent material must not be included in the specimen.

8.2 The machined surface of the specimen must be cleaned by electropolishing or etching immediately prior to mounting the specimen and inserting it into the glow discharge ion source.

8.2.1 In order to obtain a representative bulk composition in a reasonable analytical time, surface cleaning must remove all contaminants without altering the composition of the specimen surface.

8.2.2 To minimize the possibility of contamination, clean

**TABLE 1 Suite of Impurity Elements to Be Analyzed<sup>A</sup>**

NOTE 1—Establish RSFs for the following suite of elements:

|           |         |           |           |           |         |            |          |         |        |         |
|-----------|---------|-----------|-----------|-----------|---------|------------|----------|---------|--------|---------|
| silver    | arsenic | gold      | boron     | beryllium | calcium | cerium     | chromium | cesium  | copper | iron    |
| potassium | lithium | magnesium | manganese | sodium    | nickel  | phosphorus | antimony | silicon | tin    | thorium |
| titanium  | uranium | vanadium  | zinc      | zirconium |         |            |          |         |        |         |

<sup>A</sup>Additional species may be determined and reported, as agreed upon between all parties concerned with the analyses.

each specimen separately immediately prior to mounting in the glow discharge ion source.

8.2.3 Prepare and use electropolishing or etching solutions in a clean container insoluble in the contained solution.

8.2.3.1 *Electropolishing*—perform electropolishing in a suitable electropolishing solution (2:1 MeOH:HNO<sub>3</sub> was found applicable). Apply 5 to 15 V (dc) across the cell, with the specimen as anode. Electropolish to expose smooth, clean metal over the entire polished surface.

8.2.3.2 *Etching*—perform etching by immersing the specimen in suitable acid mixture solution (4:1:1 H<sub>2</sub>O:HF:HNO<sub>3</sub> was found applicable). Etch the specimen until smooth, clean metal is exposed over the entire surface.

8.3 Immediately after cleaning, wash the specimen with several rinses of high purity methanol, or other high purity reagent able to remove water from the specimen surface, and dry the specimen in the laboratory environment.

8.4 Immediately mount and insert the specimen into the glow discharge ion source, minimizing exposure of the cleaned, rinsed and dried specimen surface to the laboratory environment.

8.4.1 As necessary, use a noncontacting gage when mounting specimens in the analysis cell specimen holder to ensure the proper sample configuration in the glow discharge cell (see 7.4.5).

8.5 Sputter etch the specimen surface in the glow discharge plasma for a period of time before data acquisition to ensure the cleanness of the surface (see 12.3). Pre-analysis sputtering conditions are limited by the need to maintain sample integrity. Pre-analysis sputtering at twice the power used for analysis should be adequate for sputter etch cleaning.

## 9. Preparation of the GDMS Apparatus

9.1 Reference to Test Method F 1593, Section 9.

## 10. Instrument Quality Control

10.1 Reference to Test Method F 1593, Section 10.

## 11. Standardization

11.1 The GDMS instrument should be standardized using NIST traceable reference materials, preferably aluminum to the extent such reference samples are available.

11.1.1 RSF values should, in the best case, be determined from the ion beam ratio measurements of four randomly selected specimens from each standard required, with four independent measurements of each pin.

11.1.2 RSF values must be determined for the suite of impurity elements for which specimens are to be analyzed (see Table 1) using selected isotopes for measurement and RSF calculation (see Table 2).

## 12. Analysis Procedure

12.1 Establish a suitable data acquisition protocol (DAP) appropriate for the GDMS instrument used for the analysis.

12.1.1 The protocol must include, but is not limited to, the measurement of elements tabulated in Table 1 and isotopes tabulated in Table 2 for respective matrix. Annex A1 lists significant spectral interferences in this testing.

12.1.2 Instrumental parameters selected for isotope measurements must be appropriate for the analysis

TABLE 2 Isotope Selection<sup>A</sup>

NOTE 1—Use the following isotopes for establishing RSF values and for performing analyses on test specimens.

|            | Aluminum-Copper | Aluminum-Silicon | Aluminum-Copper-Silicon |
|------------|-----------------|------------------|-------------------------|
| Silver     | 109             | 109              | 109                     |
| Arsenic    | 75              | 75               | 75                      |
| Gold       | 197             | 197              | 197                     |
| Boron      | 11              | 11               | 11                      |
| Beryllium  | 9               | 9                | 9                       |
| Calcium    | 44              | 44               | 44                      |
| Cerium     | 140             | 140              | 140                     |
| Chromium   | 52              | 52               | 52                      |
| Cesium     | 133             | 133              | 133                     |
| Copper     | 65              | 65               | 65                      |
| Iron       | 56              | 56               | 56                      |
| Potassium  | 39              | 39               | 39                      |
| Lithium    | 7               | 7                | 7                       |
| Magnesium  | 24              | 24               | 24                      |
| Manganese  | 55              | 55               | 55                      |
| Sodium     | 23              | 23               | 23                      |
| Nickel     | 58              | 60               | 60                      |
| Phosphorus | 31              | 31               | 31                      |
| Antimony   | 208             | 208              | 208                     |
| Silicon    | 28              | 28               | 28                      |
| Tin        | 124             | 119              | 124                     |
| Thorium    | 232             | 232              | 232                     |
| Titanium   | 48              | 48               | 48                      |
| Uranium    | 238             | 238              | 238                     |
| Vanadium   | 51              | 51               | 51                      |
| Zinc       | 66              | 66               | 66                      |
| Zirconium  | 94              | 90               | 94                      |

<sup>A</sup>This selection of isotopes minimizes significant interferences. Additional species may be determined and reported, as agreed upon between all parties concerned with the analyses.

requirements: (a) ion current integration times to achieve desired precision and detection limits; (b) mass ranges about the analyte mass peak over which measurements are acquired to clarify mass interferences.

12.2 Insert the prepared specimen into the GDMS ion source, allow the specimen to cool to source temperature, and initiate the glow discharge at pre-analysis sputtering conditions.

12.3 After at least 5 min of pre-analysis sputtering, adjust the glow discharge ion source sputtering conditions to the conditions required for analysis, ensuring that the gas pressure required to do so is within normal range.

12.4 Analyze the specimen using the DAP protocol and accept as final the concentration values determined only as detection limits.

12.5 Generate a MDAP protocol including only the elements determined to be present in the sample (from results of 12.4).

12.6 Measure the sample at least two additional times (with at least 10-min intervals between the measurements) using the MDAP protocol until the criteria of 12.6.1 is met.

12.6.1 If the concentration differences between the last two measurements are less than 5, 10 or 20 %, depending on concentration (Table 3), the measurements are confirmed and the last two measurements are averaged.

12.7 The confirmed values from 12.6 and the detection limits determined from 12.4 are reported together as the result of the analysis.

**TABLE 3 Required Relative Standard Deviation (RSD) for RSF Determinations, Pre-sputtering Period, and Plasma Stability Tests**

| Analyte Content Range       | Required RSD, % |
|-----------------------------|-----------------|
| Major (> 100 ppm)           | 5               |
| Minor (100 ppm > × > 1 ppm) | 10              |
| Trace (1 ppm > × > 100 ppb) | 20              |

### 13. Detection Limit Determination

13.1 Reference to Test Method F 1593, Section 13.

### 14. GDMS Analysis for Thorium, Uranium and Similar Elements

14.1 Because of the sensitivities of thorium, uranium, and other Group 3 and Group 4 elements to instrument changes and analytical conditions, the operator is advised to take extra caution in determining those analytes.

14.2 Thorium, uranium, and other elements with significantly lower specification limits should be determined separately according to instrument performance, for example, increased ion counting times to lower the detection limits.

### 15. Report

15.1 Provide concentration data for the suite of elements

listed in Table 1, unless the element is present as an alloying element. Additional elements may be listed as agreed upon between all parties concerned with the analysis.

15.2 Element concentration shall be reported, typically, in units of parts per million by weight.

15.3 Numerical results shall be presented using all certain digits plus the first uncertain digit, consistent with the precision of the determination.

15.4 Non-detected elements shall be reported at the detection limit.

15.5 Unmeasured elements shall be designated with an asterisk (\*) or other notation.

### 16. Precision and Bias

16.1 As stated in Test Method F 1593.

### 17. Keywords

17.1 aluminum; aluminum-copper alloys; aluminum-copper-silicon alloys; aluminum-silicon alloys; electronics; glow discharge mass spectrometer (GDMS); purity analysis; sputtering target; trace metallic impurities

## ANNEX

### (Mandatory Information)

#### A1. MASS SPECTRUM INTERFERENCES

A1.1 Ions of the following atoms and molecular combinations of aluminum, argon plasma gas isotopes, plasma impurities (carbon, nitrogen, oxygen, fluorine, chlorine) and tantalum source components can significantly interfere with the determination of the ion current of the selected isotopes at low element concentrations.

$^{38}\text{Ar}^{++}$  interferes with  $^{19}\text{F}^{+}$   
 $^{12}\text{C}^{16}\text{O}^{+}$  interferes with  $^{28}\text{Si}^{+}$   
 $(^{16}\text{O}_2)^{+}$  interferes with  $^{32}\text{S}^{+}$   
 $^{38}\text{Ar}^1\text{H}^{+}$  interferes with  $^{39}\text{K}^{+}$   
 $^{40}\text{Ar}^{+}$  scattered ions interfere with  $^{39}\text{K}^{+}$

$^{12}\text{C}^{16}\text{O}_2^{+}$  interferes with  $^{44}\text{Ca}^{+}$   
 $^{40}\text{Ar}^{12}\text{C}^{+}$  interferes with  $^{52}\text{Cr}^{+}$   
 $^{40}\text{Ar}^{16}\text{O}^{+}$  interferes with  $^{56}\text{Fe}^{+}$   
 $^{36}\text{Ar}^{27}\text{Al}^{+}$  interferes with  $^{63}\text{Cu}^{+}$   
 $^{40}\text{Ar}^{35}\text{Cl}^{+}$  interferes with  $^{75}\text{As}^{+}$   
 $^{40}\text{Ar}^{36}\text{Ar}^1\text{H}^{+}$  interferes with  $^{77}\text{Se}^{+}$   
 $^{40}\text{Ar}^{38}\text{Ar}^1\text{H}^{+}$  interferes with  $^{79}\text{Br}^{+}$   
 $(^{40}\text{Ar}_2)^{+}$  scattered ions interfere with  $^{79}\text{Br}^{+}$   
 $^{40}\text{Ar}^{36}\text{Ar}^{27}\text{Al}^{+}$  interferes with  $^{103}\text{Rh}^{+}$   
 $^{40}\text{Ar}^{36}\text{Ar}^{38}\text{Ar}^{+}$  interferes with  $^{114}\text{Cd}^{+}$   
 $^{181}\text{Ta}^{16}\text{O}^{+}$  interferes with  $^{197}\text{Au}^{+}$

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