



Standard Test Method for Measuring Surface Metal Contamination of Polycrystalline Silicon by Acid Extraction-Atomic Absorption Spectroscopy¹

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1. Scope

1.1 This test method covers the quantitative determination of surface trace metal contamination on the surface of polycrystalline silicon using an acid to extract the metals from the surface. The metals content of the acid is then analyzed by graphite furnace atomic-absorption spectroscopy.

1.2 This test method can be used for various rod, chunk, granule and chip sizes, for polycrystalline or single crystal silicon, to determine surface metal contaminants. Since the area of irregularly-shaped chunks, chips, or granules is difficult to measure accurately, values are based on sample weight. Using a sample weight of 300 g allows detection limits at the 0.1 ppbw (parts per billion weight) level.

1.3 The strength, composition, temperature, and exposure time of the acid determine the depth of surface etching and the efficiency of the extraction of the contaminants from the surface. Less than 1 % of the sample weight is removed in this test method.

1.4 This test method is useful for determining the alkali elements, alkali earth, and first series transition elements, such as sodium, potassium, calcium, iron, chromium, nickel, copper, zinc, as well as other elements such as aluminum. The recovery of these elements from the silicon surface is measured as greater than 90 %, using control standards intentionally added to the polysilicon surface.

1.5 This test method suggests a particular sample size, acid composition, etch cycle, testing environment, and instrument protocol. Variations in these parameters may be used, but may effect the recovery efficiency or retention of metals during processing. In practice, this test method is used for sample weights of 25 to 5000 g. For referee purposes, this test method specifies a sample weight of 300 g. This test method includes guidelines to alert the analyst to the interferences and resultant variations in this test method, and includes standard methods for quantifying and reporting these variations.

1.6 This test method specifies the use of graphite furnace atomic-absorption spectroscopy to analyze trace metals content of the acid extract. Other instruments of equivalent sensitivity,

such as inductively-coupled plasma/mass spectrometry, may be used.

1.7 The detection limit and method variation depend on the efficiency of the acid extraction procedure, sample size, the method interferences, the absorption spectrum of each element, and the instrumental sensitivity, background, and blank value.

1.8 This test method uses hot acid to etch away the surface of the silicon. The etchant is potentially harmful and must be handled in an acid exhaust fume hood, with utmost care at all times. Hydrofluoric acid solutions are particularly hazardous and should not be used by anyone who is not familiar with the specific preventive measures and first aid treatments given in the appropriate Material Safety Data Sheet.

1.9 *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.* Specific precautionary statements are given in Section 9.

2. Referenced Documents

2.1 ASTM Standards:

D 5127 Guide for Electronic Grade Water²
E 122 Practice for Choice of Sample Size to Estimate a Measure of Quality of a Lot or Process³

2.2 SEMI Standards:

C 7 Specification for Reagents⁴

2.3 Federal Standard:

209E Airborne Particulate Cleanliness Classes in Cleanrooms and Clean Zones⁵

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

3.1.1 *acid blank*—a sample of acid used to establish the background spectrum and trace metal contamination of the extraction acid used in the procedure.

3.1.2 *carousel protocol*—the order and function of

² Annual Book of ASTM Standards, Vol 11.01.

³ Annual Book of ASTM Standards, Vol 14.02.

⁴ Available from Semiconductor Equipment and Materials International, 805 E. Middlefield Road, Mountain View, CA 94043.

⁵ Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

¹ This test method is under the jurisdiction of ASTM Committee F-1 on Electronics and is the direct responsibility of Subcommittee F01.06 on Silicon Materials and Process Control.

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samples, standards, and blanks loaded into the sampling tray of the atomic absorption spectrograph (AAS).

3.1.3 *digestion*—holding the polysilicon chunks in the acid mixture at temperature until the surface metal contaminants are dissolved into solution.

3.1.4 *digested blank*—samples of acid, with no analytes added, taken through the digestion process and analyzed to provide a monitor of the analytical process that includes acid purity, digestion bottles cleanliness, and environment purity.

3.1.5 *digested control standard*—samples prepared to known concentrations of the analytes to provide calibration checks on the instrument and the digestion procedure.

3.1.6 *GFAAS*—graphite furnace atomic absorption spectrophotometer.

3.1.7 *PTFE, polytetrafluoroethylene*—an HF-resistant material for sample bottles, lids, and tongs.

3.1.8 *standard samples*—samples prepared to known concentrations of the analytes, typically 5 ppbw and 10 ppbw, to provide a calibration standard and set absorption values for the GFAAS instrument.

4. Summary of Test Method

4.1 A standard weight and volume of chunk sample is chosen in order to provide a consistent basis for the analysis and provide a basis for interlaboratory correlation of analytical values. For referee purposes, a total sample weight of 300 g, taken as six chunks, each approximately 3 by 3 by 3 cm, at 50 g each, is recommended. A minimum of three of the six pieces should have an outside surface. The outside surface, or skin of the polysilicon rod, is thought to be the most susceptible to contamination during the rod removal and chunk processing steps. Choosing a minimum of half of the chunk samples to have an outside surface is assumed to be representative of the lot characteristics.

4.2 The six chunks are loaded into clean PTFE bottles, covered with acid etchant, heated in a fume hood and the surface of the chunks dissolved. The chunks are removed from the etchant, and the etchant heated to dryness on a hotplate.

4.3 The dried etchant residue is dissolved by adding 2 mL of 5 % HNO₃ and 8 mL of H₂O to make a total of 10 mL. This extract is then analyzed by GFAAS for trace metals.

4.4 The sample carousel tray of the GFAAS instrument is loaded with a series of blanks, calibration standards, and monitor standards, along with the acid extract samples. The temperature program for the graphite furnace is optimized for maximum sensitivity and the absorption spectral lines chosen for maximum sensitivity and minimum interferences for each element.

4.5 Data from the GFAAS instrument is collected and the value for each analyte in the lot sample calculated. For each analyte, the two digested blanks are averaged to provide a zero reference. This average value is subtracted from the lot sample value, and the remaining value multiplied by the dilution factor to obtain the reported result. The dilution factor is the final volume of the acid extract, 10 mL, divided by the starting weight of the polysilicon sample, 300 g.

4.6 This acid mixture has a measured recovery efficiency of 95 % or greater for iron, chromium, nickel, sodium, zinc, aluminum, copper, calcium, and potassium, in the chemically-

bound form usually found on the polysilicon surface, after one etch cycle. By measuring the analytes after a second etch cycle, the recovery efficiency of the first cycle is determined. Recovery efficiencies above 90 % are required to verify the accuracy of the analysis. Recovery efficiency was confirmed by neutron activation analyses.⁶ To ensure that no analytes are lost through chemical reaction or evaporation processes, digested control standards are prepared and monitored for each analyses.

4.7 Contamination from the room environment, apparatus, reagents, sampling techniques, and handling techniques is monitored statistically by the absorption values for the digested blanks and digested control standards.

4.8 The detection limit depends on the dilution factor, instrument sensitivity, spectral response of the analyte, acid recovery efficiency, blank value, and method interferences. Instrument and method variations are given in Section 15.

5. Significance and Use

5.1 This test method can measure the elemental, particularly metal, surface contamination on polysilicon chunks. Values are related to sample weight rather than area due to the irregular size and form of the sample.

5.2 This surface measurement of metal contamination is used for monitoring polysilicon production processes, development of new processes, and materials acceptance purposes.

5.3 This test method is used as a standard for defining detection limits, and quantifying variations and method interferences to allow interlaboratory correlations (Section 11, 15).

6. Interferences

6.1 The common interferences of absorption spectroscopy are present in this test method, including overlap of absorption peaks, nonlinearity of absorption peaks, matrix effects, background noise, interelement interferences, and instrument drift.

6.2 Interferences from contamination due to reagent purity, cleanliness of apparatus, cleanliness of the room, and handling techniques during sampling and processing are critical concerns. This test method describes a series of blanks and controls to monitor and quantify these interferences.

6.3 The recovery efficiency of the acid mixture and extraction process must be measured in order to monitor any interference from this source. Metal contaminants chemically bound to the surface by various treatments or in the bulk of the polysilicon may not be recovered by this acid mixture. Recovery efficiency can be confirmed by neutron activation analyses, or by another test method.

6.4 This test method specifies a sample size of 300 g to be representative of the lot sample. Since surface contamination is not distributed evenly upon a surface, sample size and volume must be chosen to be representative of the lot. If the sample size is too small, the sample may not be representative of the lot, resulting in excessive variation in duplicate samples.

7. Apparatus

7.1 *GFAAS Instrument*, graphite furnace atomic absorption

⁶ Maurits, J. E. A., Dawson, H. J., and Barker, T. H., "The Analysis of Surface Metals in Polycrystalline Silicon," *Abstract No. 401, Extended Abstracts*, Vol 94-2, Fall Meeting of the Electrochemical Society, October 9–14, 1994, Miami Beach, FL.

spectrometer, with sufficient resolving power to perform elemental analysis at the sub-ppb level. A sample tray with selective sampling capability is integral to the instrument. A computerized data system calculates peak absorbance values, provides the instrument calibration curve, and reports sample values.

7.2 *Class 1000 Air Environment*—The area for sample collection, acid extraction, and GFAAS analysis must be enclosed in a clean room with a minimum standard of Class 1000.

7.3 *Clean Room Clothing*—Analysts must be attired in full clean room clothing, including hoods, masks, boots, and gloves. Clean room practices must be observed.

7.4 *Acid Exhaust Fume Hood*—An acid exhaust fume hood, equipped to provide a clean air (Class 1000 minimum) environment, and with hot plates for the acid extraction and extract concentration steps.

7.5 *Sample Bottles and Tongs*—Sample bottles, size 500-mL, lids, and tongs are made of polytetrafluoroethylene (PTFE) or similar polymer material that will not be attacked by hydrofluoric acid and can be cleaned to avoid contamination interferences.

7.6 *Analytical Balance*—Balance capable of weighing 300 g to an accuracy of 0.01 g.

8. Reagents

8.1 *Electronic Grade Acids*, in accordance with SEMI Specification C 7.

8.2 *Deionized Water*, with a purity equal to or greater than that specified for Type E-1 in Guide 1527.

8.3 *Nitric Acid (HNO₃)*, 65 %.

8.4 *Hydrofluoric Acid (HF)*, 48 %.

8.5 *Hydrogen Peroxide (H₂O₂)*, 30 %.

8.6 *Acid Cleaning Mixture*, (1:1:1:25) HNO₃:HF:H₂O₂: H₂O.

8.7 *Acid Etching Mixture*, (1:1:1:50) HNO₃:HF:H₂O₂: H₂O.

9. Hazards

9.1 The acids used in this test method are hazardous. All precautions normally used with these chemicals should be strictly observed. The acid extraction procedure must be done in an acid exhaust fume hood. Obtain and read the Material Safety Data Sheet prior to the use of any chemical.

10. Sampling

10.1 This test method is intended for sampling of polysilicon lots. Typically, one 5-kg bag from a lot is selected for sampling. The 300-g sample is taken from this bag, and the surface metals values analyzed are assumed representative of the lot. Statistical techniques, such as process capability ratios, are used to determine actual sampling plans for manufacturing processes. A choice of sampling plans is found in Practice E 122. For referee purposes, a sampling plan shall be agreed upon before conducting the test. Contamination during the sampling procedure is a critical concern and must be avoided.

11. Calibration

11.1 Prepare calibration and control standards for each analyte, according to instrument manufacturer's instructions,

from commercially-available atomic-absorption elemental calibration standards, at 1000 ppm, traceable to NIST Reference Standards.

11.2 Prepare a series of calibration and control standards for each analyte to determine the instrument calibration curve, monitor recovery efficiency of the acid etchant, and monitor reagent purity and purity of the environment. Purpose of the calibration and control standards is shown in Table 1.

11.2.1 Determine a calibration curve for each element with a blank and a minimum of three elemental standards. Dilute the 1000-ppm elemental standards to 1-ppm standards (0.1 mL/100 mL in acid etch mixture). Prepare calibration standards of 5 ppb, 10 ppb, and 20 ppb by diluting 0.5 mL, 1 mL and 2 mL of the 1-ppm standard to 100 mL with 18-mL acid etch mixture and deionized (DI) water. Prepare the standards to provide a range close to the suspected concentration of the analyte. Determine the four-point calibration curve according to the instructions of the instrument manufacturer. Monitor any changes in the calibration curve by checking the linearity against previous runs.

NOTE 1—These standards were chosen to provide calibration for various samples over a range corresponding to 0.1 to 100 ppbw in the polysilicon sample. The use of a 1-ppb standard will provide a lower method variation for analytes in the sub-ppb range.

11.2.2 Collect the absorption values for the 5 ppb, 10 ppb, and 20 ppb calibration standards in a database, and establish statistical rules to determine any drift or excessive variation in the instrument readings. Repeat the analysis if these values exceed the statistical limit. Make corrections in the procedure or instrument if these values continue out of statistical control.

11.2.3 Prepare two control standards, at 10 ppb, by adding 10 mL of the 10-ppb calibration standards to samples of clean polysilicon chunks. Digest these standards along with the lot samples.

NOTE 2—These standards have a similar matrix to the lot samples. The analysis of these standards provides a quantification of the variation in metals retention efficiency, instrument matrix effects, and variations due to cleanliness of apparatus and contamination during handling and sample processing.

11.2.4 Collect the absorption values for the 10-ppb digested control standards in a database, and establish statistical rules to determine if metals retention and variations due to method interferences are in statistical control. Repeat the analysis if these values exceed the statistical limits. Make corrections in

TABLE 1 Sample Cup Loading Protocol with Function of Calibration and Control Standards

Sample Cup	Function
Acid Blank	To provide a 4-point calibration curve in the range of the analyte and set the 5-ppb instrument absorption value.
5-ppb calibration standard	
10-ppb calibration standard	
20-ppb calibration standard	To monitor the dissolved metals retention of the method and quantify variations in the method.
Two 10-ppb digested control standards	
Two digested blanks, acid etch mixture	To monitor reagent purity and purity of the environment and to provide a zero reference for the lot sample.
Lot samples	To determine concentrations of the analytes.