

SEMI PV49-0613 (Reapproved 1018)

TEST METHOD FOR THE MEASUREMENT OF ELEMENTAL IMPURITY CONCENTRATIONS IN SILICON FEEDSTOCK FOR SILICON SOLAR CELLS BY BULK DIGESTION, INDUCTIVELY COUPLED-PLASMA MASS SPECTROMETRY

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1 Purpose

1.1 This Test Method can be used to monitor the bulk trace level elemental impurities in Silicon Feedstock for Silicon Solar Cells that affect the performance of the silicon solar cell, in particular,

1. the concentration of intentionally added dopants, and unintentionally added dopants, that can affect the target bulk resistivity of the solar cell wafer,
2. the concentration of metals (e.g., iron) and other impurities that can degrade the minority carrier lifetime of the solar cell wafer.

1.2 This Test Method can be used to monitor or qualify photovoltaic (PV) silicon feedstock to be used in either crystalline or multicrystalline silicon wafer production.

1.3 This Test Method can be used for research and development of PV silicon processes and products, such as PV silicon feedstock and crystalline and multicrystalline silicon growth processes.

1.4 This Test Method can facilitate a unifying of protocols and test results among worldwide laboratories used for research and development support, monitoring or qualifying product for purchase or sale or internal use.

2 Scope

2.1 This Test Method covers the quantitative determination of bulk trace dopant and metal contamination of crystalline, and amorphous silicon chunks using an acid mixture to dissolve the silicon matrix and analytes. The metals content of the acid, after drying, is then diluted and analyzed by inductively coupled plasma mass spectrometry (ICP-MS). For most elements the detection limit for routine analysis is on the order of 0.1 to 10,000 µg/kg (0.1 to 10,000 ppbW).

2.1.1 This Test Method does not include all the information needed to complete ICP-MS analyses. Sophisticated computer-controlled laboratory equipment, skillfully used by an experienced operator, is required to achieve the desired sensitivity. This Test Method does cover the particular factors (e.g., specimen preparation, standardization, determination of detection limits) known to affect the reliability of trace element analysis.

2.1.2 This Test Method is useful for determining the alkali elements, alkali earth, and first series transition elements, for example, sodium, potassium, calcium, iron, chromium, nickel, copper, zinc, titanium, molybdenum, boron, as well as other elements such as aluminum. The recovery of these elements from the silicon bulk is measured between 75% to 125%, using Certified Reference Materials (CRMs) intentionally added to the silicon.

2.2 Chunk, granule and chip sizes of or single crystal silicon can be used to determine trace metal contaminants. Since the area of irregularly-shaped chunks, chips, or granules is difficult to measure accurately, values are based on test sample weight. Using a test sample weight of 0.1 to 10 g allows detection limits at the 0.1 ppbW (parts per billion weight) level.

2.3 This Test Method can be used for PV silicon irrespective of all dopant species and concentrations.

2.4 This Test Method is especially designed to be used for bulk analysis of PV silicon with elemental concentrations in the range of ppbW to ppmW.

2.5 The limit of detection is determined by the method blank value limitations, and may vary with instrumentation and preparation technique.

2.6 This Test Method is complementary to:

2.6.1 Resistivity measurements that can determine the bulk resistivity of wafers, ingots or blocks, but cannot accurately determine the dopant concentrations when there are multiple dopant types at levels that can compensate or enhance resistivity in the silicon (SEMI MF397, SEMI MF43, SEMI MF525, SEMI MF673, SEMI MF84, SEMI PV1).

2.6.2 Low temperature Fourier transform infrared spectroscopy (SEMI MF1630) that can determine trace level concentrations of dopants, but which is only effective for dopants in substitutional sites, (i.e., in a Si crystal) and therefore not effective in silicon unless a crystal is grown.

2.6.3 Photoluminescence (SEMI MF1389) that provides the concentrations of III-V impurities in single crystal PV silicon, but requires single crystal silicon and does not provide the concentrations of other trace bulk impurities which may affect performance of the silicon solar cell.

2.6.4 Secondary ion mass spectrometry that can provide bulk trace elemental concentrations in PV Si for the entire periodic table at detection limits similar to or better than glow discharge mass spectrometry (GDMS), but is primarily not as cost effective compared to GDMS unless a small number of elements are of interest.

2.6.5 Steady state surface photovoltage (SEMI MF391) that provides the minority carrier diffusion length of PV silicon, and can provide iron concentrations in boron-doped PV silicon, but does not provide the elemental concentrations that may affect the minority carrier diffusion length (except for iron in boron-doped PV silicon.)

2.6.6 Photoconductivity decay (SEMI MF28) that provides the minority carrier lifetime in the bulk of the PV silicon, but does not provide the elemental concentrations that may affect the minority carrier lifetime.

2.6.7 Acid extraction followed by atomic absorption spectroscopy (SEMI MF1724) or inductively coupled mass spectrometry that provides elemental contamination on the surface of the PV silicon, but not in the bulk PV silicon.

2.6.8 Microwave photoconductive decay (SEMI MF1535) that provides the carrier recombination lifetime in the bulk of the PV Si, but does not provide the elemental concentrations that may affect the carrier recombination lifetime.

2.6.9 Test Method for Measuring Trace Elements in Silicon Feedstock for Silicon Solar Cells by High-Mass Resolution Glow Discharge Mass Spectrometry (SEMI PV1) that provides the concentrations of trace elements in bulk silicon.

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 The detection limit can be affected by the purity of the reagents.

3.2 Test sample preparation *and preparation of lab ware* can contaminate the test specimen if not performed correctly.

3.3 Materials in the ICP-MS instrument, particularly in the test sample introduction chamber/ion source, can introduce elemental contamination that gives false signals, not coming from the test sample. Analysis of a method blank test specimen can determine this.

3.4 Test samples of non-silicon matrices that are analyzed prior to the PV silicon test samples may introduce elemental cross-contamination in the ion optics of the detection scheme that may give false signals, not coming from the test sample. Analysis of a method blank can determine this.

3.5 Ions of atoms and molecular combinations of silicon, plasma gas (argon), atmospheric impurities (hydrogen, carbon, nitrogen, oxygen) and background from source components can interfere with the determination of the ion current of the selected isotopes at trace levels.

3.6 Bias in reference materials used to calibrate ICP-MS measurements introduces bias to the quantification. This can include errors in the assigned value of the impurity in the reference material or nonuniformity of the impurity in the reference material.

3.7 Mass and molecular interferences can introduce bias if the instrument mass resolution, or subsequent detection scheme, is not sufficient to exclude the interference. A discussion of well-known matrix interferences may be seen in Shabani, *et al.* Mater. Sci. Eng. B 2003, Vol. 102 pp.238–246.

3.8 The accuracy and precision of the measurement can degrade due to incomplete dissolution of the test sample in the acid mixture.

3.9 Characterization of mass interferences observed in ICP-MS systems manufactured by various vendors is of a scope beyond this Document. Care must be taken to avoid the reporting of mass interferences as an analyte. ICP-MS systems purchased from various instrument manufacturers may be used for this analysis.

4 Referenced Standards and Documents

4.1 SEMI Standards and Safety Guidelines

SEMI C10 — Guide for Determination of Method Detection Limits

SEMI MF28 — Test Method for Minority Carrier Lifetime in Bulk Germanium and Silicon by Measurement of Photoconductive Decay

SEMI MF43 — Test Method for Resistivity of Semiconductor Materials

SEMI MF84 — Test Method for Measuring Resistivity of Silicon Wafers with an In-Line Four-Point Probe

SEMI MF391 — Test Method of Minority Carrier Diffusion Length in Extrinsic Semiconductors by Steady-State Surface Photovoltage

SEMI MF397 — Test Method for Resistivity of Silicon Bars Using a Two-Point Probe

SEMI MF525 — Test Method for Measuring Resistivity of Silicon Wafers Using Spreading Resistance Probe

SEMI MF673 — Test Method for Measuring Resistivity of Semiconductor Wafers or Sheet Resistance of Semiconductor Films with a Noncontact Eddy-Current Gauge

SEMI MF1389 — Test Method for Photoluminescence Analysis of Single Crystal Silicon for III-V Impurities

SEMI MF1535 — Test Method for Carrier Recombination Lifetime in Silicon Wafers by Noncontact Measurement of Photoconductive Decay by Microwave Reflectance

SEMI MF1630 — Test Method for Low Temperature FT-IR Analysis of Single Crystal Silicon for III-V Impurities

SEMI MF1724 — Test Method for Measuring Surface Metal Contamination of Polycrystalline Silicon by Acid Extraction-Atomic Absorption Spectroscopy

SEMI PV1 — Test Method for Measuring Trace Elements in Silicon Feedstock for Silicon Solar Cells by High-Mass Resolution Glow Discharge Mass Spectrometry

4.2 ASTM Standards¹

ASTM E122 — Standard Practice for Calculating Sample Size to Estimate, With Specified Precision, the Average for a Characteristic of a Lot or Process

ASTM E135 — Standard Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

ASTM D1193 — Standard Specification for Reagent Water

4.3 ISO Standard²

ISO 14644-1 — Cleanrooms and Associated Controlled Environments – Part 1: Classification of Air Cleanliness by Particle Concentration

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

¹ American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959, USA; Telephone: 610.832.9585, Fax: 610.832.9555, <http://www.astm.org>

² International Organization for Standardization, ISO Central Secretariat, BIBC II, Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland; Telephone: +41.22.749.01.11, <http://www.iso.org>