Manufacturers of crystalline and micro-crystalline silicon used in solar cells purchase or produce their own silicon feedstock material. This silicon is often called Silicon Feedstock for Silicon Solar Cells and can take many physical forms, including, for example, granules, powders, polycrystalline silicon chunks, wafers, reclaimed silicon, and top and tail cuts from silicon boules.

The purity level of Silicon Feedstock for Silicon Solar Cells can affect solar cell efficiency, as well as the productivity of some processes used to transform the silicon into solar cells.

SEMI has many test methods that can be used to determine the purity level of PV Si Feedstock, depending upon its physical form and the elements of interest: SEMI MF397-02 for measuring net resistivity, SEMI MF1389-00 for measuring dopants by photoluminescence, SEMI MF1724-01 for measuring surface metal contamination on granules, chunks or powders by acid extraction followed by atomic absorption spectroscopy, SEMI MF1188-1105 for measuring interstitial oxygen by Fourier Transform Infrared Spectroscopy, SEMI MF1391-0704 for measuring substitutional carbon by Fourier Transform Infrared Spectroscopy, and SEMI MF1630-0704 for measuring dopants by low temperature Fourier Transform Infrared Spectroscopy. SEMI MF28-0707 can be used to indirectly measure the purity level using photoconductive decay.

However, the existing SEMI test methods do not provide for the measurement of a broad range of trace elemental impurities. Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) measures the element concentrations below 6N levels (or at ppbW level) for all elements (except the atmospherics C, O, N, H, and noble gases) including all the dopants (except for P) and metals, regardless of the state of the element (e.g., substitutional, interstitial, or located in a defect such as a grain boundary or the surface). The ICP-MS measurement can be made on PV Si Feedstock regardless of its physical form, i.e., granules, powders, polycrystalline silicon chunks, wafers, reclaimed silicon, and top and tail cuts from silicon boules. The ability of ICP-MS to detect impurities in the sub-6N level may be especially useful with the advent of silicon solar cell processing that getter impurities from the bulk so that PV feedstock with purity in the 6N region is acceptable.
Atomic Absorption Spectroscopy (AAS) test methods exist in SEMI for measuring impurities on the surface of electronic grade silicon (MF1724-00-1104) and there are a number of ASTM test methods for the analysis of silica, metals and alloys by ICP-MS (ASTM D 7439, ASTM C 1637 and ASTM C 26.05). There is no ASTM test method for the ICP-MS measurement of impurities in silicon.

Document 4675C is also being inter-committee ballot to Silicon Wafer committee for input.

### Review and Adjudication Information

<table>
<thead>
<tr>
<th>Group:</th>
<th>Task Force Review</th>
<th>Committee Adjudication</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date:</td>
<td>Tuesday, April 2, 2013</td>
<td>Wednesday, April 3, 2013</td>
</tr>
<tr>
<td>Time &amp; Timezone:</td>
<td>10:00-12:00</td>
<td>13:00-16:00</td>
</tr>
<tr>
<td>Location:</td>
<td>SEMI HQ</td>
<td>SEMI HQ</td>
</tr>
<tr>
<td>City, State/Country:</td>
<td>San Jose, CA/USA</td>
<td>San Jose, CA/USA</td>
</tr>
<tr>
<td>Leader(s):</td>
<td>Hugh Gotts (Balazs/Air Liquide)</td>
<td>Lori Nye (Brewer Science)</td>
</tr>
<tr>
<td>Standards Staff:</td>
<td>Kevin Nguyen (SEMI NA) 408.943.7997 <a href="mailto:knguyen@semi.org">knguyen@semi.org</a></td>
<td>Kevin Nguyen (SEMI NA) 408.943.7997 <a href="mailto:knguyen@semi.org">knguyen@semi.org</a></td>
</tr>
</tbody>
</table>

This meeting’s details are subject to change, and additional review sessions may be scheduled if necessary.

Check [www.semi.org/standards](http://www.semi.org/standards) for latest schedule and meeting location.
NEW STANDARD: TEST METHOD FOR THE MEASUREMENT OF
ELEMENTAL IMPURITY CONCENTRATIONS IN SILICON FEEDSTOCK
FOR SILICON SOLAR CELLS BY BULK DIGESTION, INDUCTIVELY
COUPLED-PLASMA MASS SPECTROMETRY

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 silicon 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 PV silicon feedstock to be used in either crystalline or multi-
crystalline 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 multi-crystalline 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 0.1-10,000
µg/kg (0.1-10,000 ppbW).

2.1.1 This test method does not include all the information needed to complete ICP-MS analyses. Sophisticated
crcomputer-controlled laboratory equipment, skillfully used by an experienced operator, is required to achieve the
desired sensitivity. This test method does cover the particular factors (for example, 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 75-125%, using Certified Reference Materials 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 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 non-uniformity 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

SEMI C10 — Guide for Determination of Method Detection Limits
SEMI MF28 — Test Methods for Minority Carrier Lifetime in Bulk Germanium and Silicon by Measurement of Photoconductive Decay
SEMI MF43 — Test Methods 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 Methods 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

4.2 ASTM Standards

ASTM E122 — Standard Practice for Calculating Sample Size to Estimate, With Specified Precision, the Average for a Characteristic of a Lot or Process¹
ASTM E135 — Standard Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials²
ASTM D1193 — Standard Specification for Reagent Water

4.3 Federal Standard³


---

² Annual Book of ASTM Standards, Vol 03.05.
NOTICE: Unless otherwise indicated, all documents cited shall be the latest published versions.

5 Terminology

5.1 Terminology in this test method is consistent with Terminology in ASTM E135. Required terminology specific to this test method, not covered in ASTM E135, is indicated in ¶ 5.2.

5.2 definitions

5.2.1 Acid Blank — a solution of acid used to establish the background spectrum and trace metal contamination of the acid mixture used in the procedure.

5.2.2 Certified Reference Material (CRM) — a NIST traceable single or multi-element solution standard.

5.2.3 high resolution — the designation of mass resolution above 4000.

5.2.4 Method Blank — a solution of acid prepared using the preparation method without a specimen or test sample used to establish the contribution of trace metal contamination from the laboratory environment, reagents or labware to the background.

5.2.5 PFA — perfluoroalkoxy.

5.2.6 PTFE — polytetrafluoroethylene.

5.2.7 PV Si Feedstock or Solar Grade Silicon — the designation given to a silicon solid material by a manufacturer or purchaser whereby the characteristics of that material are sufficient to produce silicon solar cells.

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

5.2.9 specimen — a suitably sized piece taken from a reference or test sample, prepared for introduction into the ICP-MS ion source, and analyzed.

5.2.10 test sample — material (silicon) to be analyzed for trace impurities by this ICP-MS method. Generally the test test sample is selected from a larger batch (lot, casting) of product and is intended to be representative of the batch.

6 Summary of Test Method

6.1 Inductively Coupled Plasma Mass Spectrometry is one the most convenient methods for determination of impurities in silicon, which occur in trace, mg/kg silicon mass fraction levels or lower. Detection limits for most elements are in the ppbW range in Si materials. The procedure consists of dissolution of the solid test sample with an acid mixture. The analysis should be performed in a cleanroom of ISO Class 5 (FED STD 209E Class 100) or better.

6.1.1 A standard weight of test sample is chosen in order to provide a consistent basis for the analysis.

6.1.2 Avoiding cross contamination, the test samples are loaded into clean PTFE or PFA bottles, covered with acid etchant consisting of a 1:1 HF/HNO₃ acid cocktail. It should be noted that finely divided silicon test samples will react very vigorously and exothermically! USE CAUTION!

6.1.3 After the test sample has dissolved, the test sample must be taken to dryness by heating to approximately 90°C in a fume hood to eliminate the silicon matrix and re-suspend in a dilute acid mixture. The final acid concentration should be approximately 5 wt.% HNO₃ (as appropriate to the elements to be analyzed).

6.1.4 An acid digest is introduced into the nebulizer. The aerosol generated are subsequently desolvated, atomized, partially ionized, and then focused as an ion beam through a quadrupole or magnetic-sector mass analyzer. The mass spectrum (the ion counts as a function of m/z) is collected as the magnetic field or the acceleration voltage, or the scanning of RF and DC voltages.

6.2 Contamination from the laboratory environment, apparatus, reagents, sampling techniques, and handling techniques is monitored statistically by the values for the method blank and Certified Reference Material (CRM).
6.2.1 The detection limit depends on the dilution factor, instrument sensitivity, variability of the blank signal, acid recovery efficiency, blank value, and method interferences.

6.2.2 The element composition of the test specimen is evaluated from the mass spectrum by comparison to a calibration curve generated by Certified Reference Material.

7 Apparatus


7.2 *Preparation Apparatus*, capable of preparing specimen.

8 Reagents and Materials

8.1 *Reagents* — Chemicals with less than 10 pptW contaminants shall be used in all tests.

NOTE 1: The contaminant levels for the chemicals may be relaxed dependent upon the precision requirements for the type of silicon material measured.

8.2 *Ultra-Pure Water* — Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to specification ASTM D1193.

8.3 *Certified Reference Material* — To the extent available, standards will be used to assess the calibration linearity and elemental recovery efficiency on the ICP-MS.

<table>
<thead>
<tr>
<th>Table 1 Example Suite of Impurity Elements in Si for Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron</td>
</tr>
<tr>
<td>Potassium</td>
</tr>
<tr>
<td>Chromium</td>
</tr>
<tr>
<td>Copper</td>
</tr>
<tr>
<td>Molybdenum</td>
</tr>
</tbody>
</table>

8.3.1 At least three concentration of reference materials are required to establish the calibration curve, including a method blank to establish the background contribution in analyses. Supporting data needs to be included to verify the method blank is below the detection limits of ICP-MS for the elements of interest.

9 Sampling

9.1 This procedure is destructive of the test sample, and therefore a sampling procedure must be used to evaluate the characteristics of a group of silicon materials. No general sampling procedure is included as part of this test method, because the most suitable sampling plan will vary considerably depending upon individual conditions. For referee purposes, a sampling plan shall be agreed upon before conducting the test. See ASTM Practice E122 for suggested choices of sampling plans.

10 Preparation of Reference Standards, Test Specimens, and Method Blank Solutions

10.1 The surface of the parent material may be included in the specimen analysis, especially in finely divided test specimens.

10.1.1 In order to obtain a representative bulk composition in a reasonable analytical time, chemical surface cleaning may be utilized to remove all contaminants without altering the composition of the specimen surface. The use of this procedure must be documented.

10.2 Prepare a method blank with the elements of interest below the expected detection limits.

11 Preparation of the ICP-MS Apparatus

11.1 The ICP-MS instrument must be accurately mass calibrated with CRM’s prior to measurements.
11.2 If the instrument uses different spectrometer settings to measure ion counts during the same analysis, the measurement efficiency of each setting relative to the others should be determined frequently as needed to guarantee proper performance of the detection system.

12 Instrument Quality Control

12.1 Analysis of a CRM must be performed at regular intervals during the analysis process to ensure spectrometer performance and data quality.

12.2 Plot validation analysis data from at least three elements with historic values in statistical process control (SPC) chart format to demonstrate that the analysis process is in statistical control. The equipment is suitable for use if the analysis data group is within the 3-sigma control limits and shows no non-random trends.

13 Procedure

13.1 Establish a suitable data acquisition protocol (DAP) appropriate for the ICP-MS instrument used for the analysis.

13.1.1 The protocol must include, but is not limited to, the measurement of elements tabulated in Table 2 and isotopes tabulated in Table 2. This selection of isotopes minimizes significant interference. Additional isotopes may be determined and reported, as agreed upon between all parties concerned with the analyses.

Table 2 Isotope Selections

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Element</th>
<th>Isotope Standard ICP-MS</th>
<th>Isotope Collision Cell ICP-MS</th>
<th>Isotope High Resolution ICP-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Aluminum</td>
<td>27</td>
<td>27</td>
<td>26.98</td>
</tr>
<tr>
<td>As</td>
<td>Arsenic</td>
<td>75</td>
<td>75</td>
<td>74.9216</td>
</tr>
<tr>
<td>B</td>
<td>Boron</td>
<td>11</td>
<td>11</td>
<td>11.009</td>
</tr>
<tr>
<td>Ca</td>
<td>Calcium</td>
<td>40</td>
<td>40</td>
<td>39.96</td>
</tr>
<tr>
<td>Cr</td>
<td>Chromium</td>
<td>52</td>
<td>52</td>
<td>51.94</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
<td>63</td>
<td>63</td>
<td>62.92</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron</td>
<td>56</td>
<td>56</td>
<td>55.93</td>
</tr>
<tr>
<td>K</td>
<td>Potassium</td>
<td>39</td>
<td>39</td>
<td>38.96</td>
</tr>
<tr>
<td>Mo</td>
<td>Molybdenum</td>
<td>98</td>
<td>98</td>
<td>97.9</td>
</tr>
<tr>
<td>Na</td>
<td>Sodium</td>
<td>23</td>
<td>23</td>
<td>22.99</td>
</tr>
<tr>
<td>Ni</td>
<td>Nickel</td>
<td>58</td>
<td>58</td>
<td>59.93</td>
</tr>
<tr>
<td>Sb</td>
<td>Antimony</td>
<td>121</td>
<td>121</td>
<td>120.9</td>
</tr>
<tr>
<td>Ti</td>
<td>Titanium</td>
<td>48</td>
<td>48</td>
<td>46.95, 47.94</td>
</tr>
<tr>
<td>Zn</td>
<td>Zinc</td>
<td>66</td>
<td>66</td>
<td>65.926</td>
</tr>
</tbody>
</table>

13.1.2 Instrumental parameters selected for isotope measurements must be appropriate for the analysis 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 interference.

13.2 Generate a Measurement DAP (MDAP) protocol including only the elements determined to be present in the test sample.

13.3 Measure the test sample at least two additional times using the MDAP protocol until the criteria of ¶ 14.1 is met.

13.4 Measure the method blank under the same conditions as the test specimen, before and after the test specimen.
14 Detection Limit Determination


15 Precision and Bias

15.1 Precision and bias will be determined at a later date through an inter-laboratory round robin comparison.

16 Report

16.1 Instrumental Settings — System must be optimized per the manufacturer’s recommendation.

16.2 Provide concentration data for the suite of elements listed in Table 2. Additional elements may be listed as agreed upon between all parties concerned with the analysis.

16.3 Elemental concentration shall be reported, typically, in units of µg per kg [µg/kg] or parts per billion by weight [ppbwt].

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

16.5 Non-detected elements shall be designated with a Limit of Detection.

17 Keywords

17.1 Silicon Feedstock for Silicon Solar Cells, crystalline and micro-crystalline silicon, inductively coupled plasma mass spectrometry (ICP-MS); purity analysis; trace element impurities, dopant.

NOTICE: Semiconductor Equipment and Materials International (SEMI) makes no warranties or representations as to the suitability of the Standards and Safety Guidelines set forth herein for any particular application. The determination of the suitability of the Standard or Safety Guideline is solely the responsibility of the user. Users are cautioned to refer to manufacturer’s instructions, product labels, product data sheets, and other relevant literature, respecting any materials or equipment mentioned herein. Standards and Safety Guidelines are subject to change without notice.

By publication of this Standard or Safety Guideline, SEMI takes no position respecting the validity of any patent rights or copyrights asserted in connection with any items mentioned in this Standard or Safety Guideline. Users of this Standard or Safety Guideline are expressly advised that determination of any such patent rights or copyrights, and the risk of infringement of such rights are entirely their own responsibility.