Background Statement for SEMI Draft Document 4558A
NEW STANDARD: TEST METHOD FOR MEASURING TRACE
ELEMENTS IN PHOTOVOLTAIC-GRADE SILICON BY HIGH-MASS
RESOLUTION GLOW DISCHARGE MASS SPECTROMETRY

Note: This background statement is not part of the balloted item. It is provided solely to assist the recipient in
reaching an informed decision based on the rationale of the activity that preceded the creation of this document.

Note: This document was prepared under the International PV Analytical Test Methods Task Force of the
Photovoltaic Technical Committee.

Note: Recipients of this document are invited to submit, with their comments, notification of any relevant patented
technology or copyrighted items of which they are aware and to provide supporting documentation. In this context,
“patented technology” is defined as technology for which a patent has been issued or has been applied for. In the
latter case, only publicly available information of the contents of the patent application is to be provided.

Background Statement:
Ballot results for Draft Document 4558 were reviewed by the PV Analytical Test Methods Task
Force on July 16, 2008, during SEMICON West in San Francisco. Recommendations of the
Task Force were that the negative submitted by Laszlo Fabry of Wacker Chemie AG was
accepted as technically persuasive and that the editorial comment submitted by Rafael Vargas-
Bernal of Instituto Tecnologico Superior de Irapuato concerning improvement of figures 1 and
2 be implemented. The ballot results and recommendation of the Task Force were adjudicated
by the PV Committee on July 16, 2008, and the Task Force recommendations were accepted.
Those changes have been implemented in this version of Draft Document 4558A.

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

The purity level of PV Si Feedstock can affect solar cell efficiency, as well as the productivity of
some processes used to transform the PV Si Feedstock 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
oxxygen 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 direct measurement of a broad
range of elemental impurities. Glow Discharge Mass Spectrometry (GDMS) directly 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 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 GDMS measurement can be made on PV Si Feedstock regardless of its physical form, i.e., granules, powders, polysilicon chunks, wafers, reclaimed silicon, and top and tail cuts from silicon boules. The ability of GDMS 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.

GDMS test methods exist in ASTM for measuring impurities in electronic grade aluminum (ASTM F 1593), electronic grade Al-Cu, Al-Si, and Al-Si-Cu alloys (ASTM F 1845), and in electronic grade Ti (ASTM F 1710). There is no ASTM test method for the GDMS measurement of impurities in silicon.

Document 4558A is also being lilac (intercommittee) ballot to Silicon Wafer committee for input.

Preliminary ballot results of this document will be reviewed by the International PV Analytical Test Methods Task Force on September 2, 2008, during the European Photovoltaic Solar Energy Conference in Valencia, Spain. Final ballot results will be adjudicated, if necessary, by PV Committee during their meetings in the Fall, 2008.
SEMI Draft Document 4558A
NEW STANDARD: TEST METHOD FOR MEASURING TRACE ELEMENTS IN PHOTOVOLTAIC-GRADE SILICON BY HIGH-MASS RESOLUTION GLOW DISCHARGE MASS SPECTROMETRY

1 Purpose
1.1 This test method can be used to monitor the bulk trace level elemental impurities in photovoltaic-grade (PV) 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 Si 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. This method can be used to evaluate the failure or reduced performance of crystalline or multi-crystalline silicon solar cells.
1.5 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.
1.6 For most elements the detection limit for routine analysis is on the order of 1-100 µg/kg (1-100 ppbwt).

2 Scope
2.1 This test method covers the determination of total bulk concentrations of most of the periodic table (exceptions are atmospheric C, O, N, H and noble gases due to high background signals) in PV silicon using a magnetic sector High-Mass Resolution (HR) Glow Discharge Mass Spectrometry (GDMS). This test method measures the total amount of each element, because this test method is independent of the element's chemistry or electrical activity in the PV silicon.
2.1.1 This test method does not include all the information needed to complete HR-GDMS 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 (for example, specimen preparation, setting of relative sensitivity factors, determination of detection limits) known to affect the reliability of direct trace element analysis.
2.2 This test method can be used for silicon in a range of physical forms, including polysilicon powders, granules, flakes, chunks, and single and multi-crystalline wafers and slugs.
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 ppbwt to ppmwt.
2.5 The limit of detection is determined by either the BLANK value or by count rate limitations, and may vary with instrumentation.
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).
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 polycrystalline 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 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 (expect 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 Si, 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.

NOTICE: This standard does not purport to address safety issues, 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 or other limitations prior to use.

3 Limitations

3.1 Sample preparation and preparation of supporting material (if used) can contaminate the test specimen if not performed correctly.

3.2 Materials in the GDMS instrument, particularly in the ion source/sample interaction chamber, can introduce elemental contamination that gives false signals, not coming from the test sample. Analysis of a BLANK test specimen (see ¶8.4.3) can determine this.

3.3 Test samples of non-Si matrices that are analyzed prior to the PV Si 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 BLANK test specimen and can determine this.

3.4 Ions of atoms and molecular combinations of silicon, plasma gas (argon), atmospheric impurities (hydrogen, carbon, nitrogen, oxygen) and background from source components (usually tantalum) can significantly interfere with the determination of the ion current of the selected isotopes at trace level mass fractions. These include for example the interferences listed in Table 1.

3.5 Bias in reference materials used to calibrate GDMS 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. This may be particularly important in reference materials made from multi-crystalline Si.

3.6 Mass interferences can introduce bias if the instrument mass resolution, or subsequent detection scheme, is not sufficient to exclude the interference.

3.7 The accuracy and precision of the measurement can degrade as the surface irregularities (for example, roughness or sharp edges) of the specimen surface increases. This degradation can be limited or avoided by suitable preparation of the sample surface and sample shape such as chemical-mechanical polishing, electrochemical polishing and acid etching.
Table 1 Examples of Mass Interferences in the GDMS measurement of PV silicon.

<table>
<thead>
<tr>
<th>Mass Interference</th>
<th>Interferes with</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{38}\text{Ar}^{+}$</td>
<td>$^{19}\text{F}^{+}$</td>
</tr>
<tr>
<td>$^{16}\text{O}^{16}\text{O}^{+}$</td>
<td>$^{32}\text{S}^{+}$</td>
</tr>
<tr>
<td>$^{36}\text{Ar}^{28}\text{Si}^{++}$</td>
<td>$^{32}\text{S}^{+}$</td>
</tr>
<tr>
<td>$^{30}\text{Si}^{1}\text{H}^{+}$</td>
<td>$^{31}\text{P}^{+}$</td>
</tr>
<tr>
<td>$^{38}\text{Ar}^{1}\text{H}^{+}$</td>
<td>$^{39}\text{K}^{+}$</td>
</tr>
<tr>
<td>$\text{SiO}^{+}$</td>
<td>$^{44}\text{Ca}^{+}$, $^{45}\text{Sc}^{+}$, $^{46}\text{Ti}^{+}$</td>
</tr>
<tr>
<td>$^{12}\text{C}^{16}\text{O}^{16}\text{O}^{+}$</td>
<td>$^{46}\text{Ca}^{+}$</td>
</tr>
<tr>
<td>$\text{SiOH}^{+}$</td>
<td>$^{45}\text{Sc}^{+}$, $^{46}\text{Ti}^{+}$</td>
</tr>
<tr>
<td>$\text{SiOH}_2^{+}$</td>
<td>$^{46}\text{Ti}^{+}$, $^{47}\text{Ti}^{+}$, $^{48}\text{Ti}^{+}$</td>
</tr>
<tr>
<td>$\text{SiOH}_3^{+}$</td>
<td>$^{47}\text{Ti}^{+}$, $^{48}\text{Ti}^{+}$, $^{49}\text{Ti}^{+}$</td>
</tr>
<tr>
<td>$\text{SiO}_2^{+}$</td>
<td>$^{54}\text{Cr}^{+}$</td>
</tr>
<tr>
<td>$\text{SiO}_2\text{H}^{+}$</td>
<td>$^{54}\text{Cr}^{+}$</td>
</tr>
<tr>
<td>$\text{SiO}_2\text{H}_2^{+}$</td>
<td>$^{54}\text{Cr}^{+}$</td>
</tr>
<tr>
<td>$\text{SiO}_2\text{H}_3^{+}$</td>
<td>$^{54}\text{Cr}^{+}$</td>
</tr>
<tr>
<td>$^{40}\text{Ar}^{12}\text{C}^{+}$</td>
<td>$^{52}\text{Cr}^{+}$</td>
</tr>
<tr>
<td>$^{40}\text{Ar}^{16}\text{O}^{+}$</td>
<td>$^{56}\text{Fe}^{+}$</td>
</tr>
<tr>
<td>$^{28}\text{Si}^{28}\text{Si}^{+}$</td>
<td>$^{56}\text{Fe}^{+}$</td>
</tr>
<tr>
<td>$\text{ArSi}^{+}$</td>
<td>$^{68}\text{Zn}^{+}$, $^{69}\text{Ga}^{+}$, $^{70}\text{Ge}^{+}$</td>
</tr>
<tr>
<td>$\text{ArArH}^{+}$</td>
<td>$^{77}\text{Se}^{+}$, $^{79}\text{Br}^{+}$</td>
</tr>
<tr>
<td>$^{31}\text{Ta}^{16}\text{O}^{+}$</td>
<td>$^{197}\text{Au}^{+}$</td>
</tr>
</tbody>
</table>

Note: For a purpose of this document the table of mass interferences is limited only to several common examples. Interferences should be always carefully scrutinized as they can vary from samples to sample due to varying level of impurities or purity of PV silicon.

4 Referenced Standards and Documents

4.1 SEMI Standards

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
E 122 — Practice for Choice of Sample Size to Estimate a Measure of Quality for a Lot or Process

E 135 — Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

F 1593 — Test Method for Trace Metallic Impurities in Electronic Grade Aluminum by High-Mass-Resolution Glow Discharge Mass Spectrometer


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 high resolution — the designation of mass resolution above 3500.

5.2.2 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.

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

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

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

6 Summary of Test Method

6.1 High-Mass Resolution Glow Discharge Mass Spectrometry is one of the most convenient methods for direct determination of impurities in Silicon, which occur in trace, mg/kg Si mass fraction levels or lower. Detection limits for most elements are in the atom-parts-per-billion range in Si materials. The procedure consists of forming the sample into rods with a cross-sectional area of 2 to 9 mm² and a length of 20 mm, or in the form of a plate or a disk of at least 15 mm in diameter. Powders, particulates, or small chunks (1-2 mm in size) are analyzed in the flat cell geometry after compacting the sample directly or pressing the sample into high purity (7N+) supporting medium, such as indium or graphite.

6.1.1 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 analyzer. The mass spectrum (the ion current) is collected as the magnetic field or the acceleration voltage, (or both) is scanned.

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

6.2.1 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.

6.3 The element composition of the test specimen is evaluated from the mass spectrum by applying a relative sensitivity factor (RSF ($X/M$)) for each element, $X$, compared to the matrix element, $M$. RSF’s are determined in a

---

1 Annual Book of ASTM Standards, Vol 14.02, ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428. Telephone: 610-832-9500, Fax: 610-832-9555, Website: www.astm.org

2 Annual Book of ASTM Standards, Vol 03.05.

separate analysis of a reference material performed under the same analytical conditions, source configuration, and operating protocol as for the test specimen.

6.4 The relative mass fractions of elements $X$ and $Y$ are evaluated from the relative isotopic ion currents $I(X_i)$ and $I(Y_j)$ in the mass spectrum, sometimes called the Ion Beam Ratio (IBR), 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:

$$\frac{(X)}{(Y)} = \frac{RSF(X/M) \times A(Y_j) \times I(X_i)}{RSF(Y/M) \times A(X_i) \times I(Y_j)}$$  \hspace{1cm} (1)$$

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

7  Apparatus

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

7.2 Machining Apparatus, capable of preparing specimen.

8  Reagents and Materials

8.1 Reagents — Reagent grade chemicals shall be used in all tests.

8.2 De-mineralized Water — Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to specification ASTM D 1193.

8.3 Tantalum Reference Sample — To the extent available, high purity tantalum material shall be used to verify the ion counting efficiency on the HR-GDMS detection system.

8.4 Si Reference Sample — To the extent available, Si reference materials shall be used to produce the HR-GDMS relative sensitivity factors for the various elements being determined as listed in Table 2.

8.4.1 As necessary, other Si based reference materials, for instance various silicides, may be used to produce the HR-GDMS relative sensitivity factors for the various elements being determined.

Table 2  Example Suite of Impurity Elements in Si for Analysis

<table>
<thead>
<tr>
<th>Lithium</th>
<th>Beryllium</th>
<th>Boron</th>
<th>Sodium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium</td>
<td>Aluminum</td>
<td>Phosphorus</td>
<td>Sulfur</td>
</tr>
<tr>
<td>Potassium</td>
<td>Calcium</td>
<td>Titanium</td>
<td>Vanadium</td>
</tr>
<tr>
<td>Chromium</td>
<td>Manganese</td>
<td>Iron</td>
<td>Cobalt</td>
</tr>
<tr>
<td>Nickel</td>
<td>Copper</td>
<td>Zinc</td>
<td>Germanium</td>
</tr>
<tr>
<td>Arsenic</td>
<td>Molybdenum</td>
<td>Silver</td>
<td>Cadmium</td>
</tr>
<tr>
<td>Antimony</td>
<td>Tungsten</td>
<td>Gold</td>
<td>Lead</td>
</tr>
<tr>
<td>Thorium</td>
<td>Uranium</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

8.4.2 Reference materials should be homogeneous (see ¶13.1).

8.4.3 At least two reference materials are required to establish the relative sensitivity factors, including a very high purity Si material (< 1 ppbw except for O and C) to establish the background contribution in analyses. The latter is called a BLANK herein. Supporting data needs to be included to verify the BLANK is below the detection limits of GDMS for the elements of interest.

8.4.4 The mass fraction of each analyte used for relative sensitivity factor determination should be at least a factor of 10 greater than the detection limit and at the same time smaller than 10 mg/kg (ppmwt) where possible.
8.4.5 To meet expected analysis precision, it is highly recommended that specimens of reference and test material present the same size and configuration (shape and exposed length, sampling orifice for flat pieces, powders and particulates in the glow discharge ion source.)

9 Sampling

9.1 Since this procedure is destructive in nature, 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 E 122 for suggested choices of sampling plans.

10 Preparation of Reference Standards, Test Specimens, and BLANK Specimens

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

10.2 The machined surface of the specimen must be cleaned prior to mounting the specimen and inserting it into the glow discharge ion source.

10.2.1 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.

10.2.2 To minimize the possibility of contamination, clean each specimen separately immediately prior to mounting in the glow discharge ion source.

10.3 Mount and insert the specimen into the glow discharge ion source, minimizing exposure of the cleaned surface to the laboratory environment.

10.3.1 Use a non-contacting gauge when mounting specimens in the analysis cell specimen holder to ensure the proper sample configuration in the glow discharge cell (see ¶8.4.5).

10.4 Sputter-etch the specimen surface in the glow discharge plasma for a period of time before data acquisition to ensure the cleanliness of the surface (see ¶14.3). Pre-analysis sputtering (or pre-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.

10.5 Prepare a BLANK specimen with the elements of interest below the expected detection limits.

11 Preparation of the GDMS Apparatus

11.1 The GDMS instrument must be accurately mass calibrated prior to measurements.

11.2 The GDMS instrument must be adjusted to the appropriate mass peak shape and mass resolving power for the required analysis.

11.3 If the instrument uses different ion collectors to measure ion currents during the same analysis, the measurement efficiency of each detector relative to the others should be determined frequently as needed to guarantee proper performance of the detection system.

12 Instrument Quality Control

12.1 A well-characterized specimen (preferably silicon) must be run on a regular basis to demonstrate the capability of the GDMS system as a whole for the required analyses.

12.2 A recommended procedure is the measurement of the relative ion currents of selected analytes and the matrix element in silicon reference samples.

12.3 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.
12.4 Upper and lower control limits for SPC must be within at least 20% of the mean of previously determined values of the relative ion currents.

13 Calibration

13.1 The calibration is by RSFs that are determined empirically from reference materials.

13.2 The HR-GDMS instrument should be calibrated using international recognized reference materials, preferably Si to the extent such reference samples are available.

13.2.1 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 sample.

13.2.2 RSF values must be determined for the suite of impurity elements for which specimens are to be analyzed (see Table 2) using selected isotopes for measurement and RSF calculation (see Table 3).

14 Procedure

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

14.1.1 The protocol must include, but is not limited to, the measurement of elements tabulated in Table 2 and isotopes tabulated in Table 3 for respective matrix. This selection of isotopes minimizes significant interference. Additional species may be determined and reported, as agreed upon between all parties concerned with the analyses. Table 1 lists significant spectral interference in this testing.

<table>
<thead>
<tr>
<th>Table 3 Isotope Selections</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>Ag</td>
</tr>
<tr>
<td>Al</td>
</tr>
<tr>
<td>As</td>
</tr>
<tr>
<td>B</td>
</tr>
<tr>
<td>Be</td>
</tr>
<tr>
<td>Bi</td>
</tr>
<tr>
<td>Ca</td>
</tr>
<tr>
<td>Co</td>
</tr>
<tr>
<td>Cr</td>
</tr>
<tr>
<td>Cs</td>
</tr>
<tr>
<td>Cu</td>
</tr>
<tr>
<td>Fe</td>
</tr>
<tr>
<td>K</td>
</tr>
<tr>
<td>Li</td>
</tr>
<tr>
<td>Mg</td>
</tr>
<tr>
<td>Mn</td>
</tr>
<tr>
<td>Mo</td>
</tr>
<tr>
<td>Na</td>
</tr>
<tr>
<td>Nb</td>
</tr>
<tr>
<td>Ni</td>
</tr>
<tr>
<td>Pb</td>
</tr>
<tr>
<td>Sb</td>
</tr>
<tr>
<td>Sc</td>
</tr>
<tr>
<td>Si</td>
</tr>
<tr>
<td>Sn</td>
</tr>
<tr>
<td>Ta</td>
</tr>
</tbody>
</table>
14.1.2 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.

14.2 Insert the prepared specimen into the HR GDMS ion source and initiate the glow discharge at pre-analysis sputtering conditions.

14.3 After pre-analysis sputtering, adjust the glow discharge ion source sputtering conditions to the conditions required for analysis if needed.

14.4 Analyze the specimen using the DAP protocol and accept as final only the mass fraction values, which are determined as detection limits.

14.5 Generate a Measurement DAP (MDAP) protocol including only the elements determined to be present in the sample (from results of ¶14.4).

14.6 Measure the sample at least two additional times using the MDAP protocol until the criteria of 14.6.1 is met.

14.6.1 If the mass fraction differences between the last two measurements are less than 5, 10 or 20%, depending on mass fractions (Table 4), the measurements are confirmed and the last two measurements are averaged.

Table 4 Required Relative Standard Deviation (RSD) for RSF Determinations, Pre-sputtering Period, and Plasma Stability Tests

<table>
<thead>
<tr>
<th>Analyte Content Range</th>
<th>Required RSD, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major (greater than 100 ppm)</td>
<td>5</td>
</tr>
<tr>
<td>Minor (between 100 ppm and 1 ppm)</td>
<td>10</td>
</tr>
<tr>
<td>Trace (between 1 ppm and 100 ppb)</td>
<td>20</td>
</tr>
</tbody>
</table>

14.6.2 The confirmed values from ¶14.6 and the detection limits determined from ¶14.4 are reported together as the result of the analysis.

14.7 Measure the BLANK under the same conditions as the test specimen.

15 Detection Limit Determination

15.1 Three types of detection limit determination are defined as follows.

15.1.1 Type I Detection Limit: If the analyte signal at the appropriate mass cannot be mass resolved from possible interfering ion signals, and the identification of the analyte signal cannot be confirmed by correlation with a similar signal from a related isotope, the analyte concentration calculated assuming that the entire signal or mass peak is due to the element in question constitutes an upper limit on the actual amount present.

15.2 Type II Detection Limit: If an analyte and an interfering ion are marginally mass resolvable, but there is no local minimum in the signal to confirm the presence of at least two separate contributions to the mass peak (analyte plus interfering ion), the upper limit on the concentration of the analyte is estimated by integrating the full ion signal over the half-mass peak width at half-maximum peak intensity (HWHM) mass range beginning at the mass position of the analyte and extending away from the mass of the interfering ion and then doubling the result (see Figure 1).
15.3 *Type III Detection Limit*: If the mass difference between an analyte and any possible interference ion is greater than 1.5 FWHM of the mass peak, and the analyte signal is superimposed on a signal dominated by detector noise or unstructured signals from ions of nearby masses (see Figure 2).

Details how to determine Type III detection limits are described in ASTM Test Method F1593, Section 13.

16 *Report*

16.1 Provide mass fraction 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.

16.2 Element mass fraction shall be reported, typically, in units of mg per kg [mg/kg] or parts per million by weight [ppmwt].

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

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

16.5 Unmeasured elements shall be designated with an asterisk (*) or other notation.
17 Precision and Bias

17.1 Precision and bias may be stated according to ASTM Test Method F 1593.

18 Keywords

18.1 PV silicon, solar grade silicon, high purity silicon; silicon feedstock, polysilicon, crystalline and micro-crystalline silicon, high-mass resolution glow discharge mass spectrometry (HR-GDMS); purity analysis; trace element impurities, dopant

NOTICE: SEMI makes no warranties or representations as to the suitability of the standards set forth herein for any particular application. The determination of the suitability of the standard 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. These standards are subject to change without notice.

By publication of this standard, Semiconductor Equipment and Materials International (SEMI) takes no position respecting the validity of any patent rights or copyrights asserted in connection with any items mentioned in this standard. Users of this standard 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.