SEMI PV1-0709
TEST METHOD FOR MEASURING TRACE ELEMENTS IN SILICON FEEDSTOCK FOR SILICON SOLAR CELLS BY HIGH-MASS RESOLUTION GLOW DISCHARGE 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 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 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 silicon feedstock processes and products, crystalline and multi-crystalline silicon growth processes.

1.4 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 silicon feedstock 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 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 silicon feedstock irrespective of all dopant species and concentrations.

2.4 This test method is especially designed to be used for bulk analysis of silicon feedstock 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.

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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 polysilicon unless a crystal is grown.

2.6.3 Photoluminescence (SEMI MF1389) that provides the concentrations of III-V impurities in single crystal 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 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 silicon, and can provide iron concentrations in boron-doped silicon, but does not provide the elemental concentrations that may affect the minority carrier diffusion length (expect for iron in boron-doped silicon).

2.6.6 Photoconductivity Decay (SEMI MF28) that provides the minority carrier lifetime in the bulk of the 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 silicon, but not in the bulk silicon.

2.6.8 Microwave Photoconductive Decay (SEMI MF1535) that provides the carrier recombination lifetime in the bulk of the 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 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 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.

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Table 1 Examples of Mass Interferences in the GDMS Measurement of Silicon Feedstock

$^{38}Ar^{++}$ interferes with $^{19}F^{+}$
$^{16}O^{16}O^{+}$ interferes with $^{32}S^{+}$
$^{36}Ar^{28}Si^{++}$ interferes with $^{32}S^{+}$
$^{30}Si^{1}H^{+}$ interferes with $^{31}P^{+}$
$^{38}Ar^{1}H^{+}$ interferes with $^{39}K^{+}$
SiO^{+} interferes with $^{44}Ca^{+}$,$^{45}Sc^{+}$, $^{46}Ti^{+}$
$^{12}C^{16}O^{16}O^{+}$ interferes with $^{44}Ca^{+}$
$SiOH^{+}$ interferes with $^{45}Sc^{+}$, $^{46}Ti^{+}$, $^{47}Ti^{+}$
$SiOH_2^{+}$ interferes with $^{46}Ti^{+}$, $^{47}Ti^{+}$, $^{48}Ti^{+}$
$SiOH_3^{+}$ interferes with $^{47}Ti^{+}$, $^{48}Ti^{+}$, $^{49}Ti^{+}$
SiO_2^{+} interferes with $^{60}Ni^{+}$, $^{61}Ni^{+}$, $^{62}Ni^{+}$
SiO_2H^{+} interferes with $^{61}Ni^{+}$, $^{62}Ni^{+}$, $^{63}Cu^{+}$
$SiO_2H_2^{+}$ interferes with $^{62}Ni^{+}$, $^{63}Cu^{+}$, $^{64}Zn^{+}$
$SiO_2H_3^{+}$ interferes with $^{63}Cu^{+}$, $^{64}Zn^{+}$, $^{65}Cu^{+}$
$^{40}Ar^{12}C^{+}$ interferes with $^{52}Cr^{+}$
$^{40}Ar^{16}O^{+}$ interferes with $^{56}Fe^{+}$
$^{28}Si^{28}Si^{+}$ interferes with $^{56}Fe^{+}$
$ArSi^{+}$ interferes with $^{68}Zn^{+}$, $^{69}Ga^{+}$, $^{70}Ge^{+}$
$ArArH^{+}$ interferes with $^{77}Se^{+}$, $^{79}Br^{+}$
$^{181}Ta^{16}O^{+}$ interferes with $^{197}Au^{+}$

#1 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 silicon feedstock.

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

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