

SEMI PV88-1018 (Reapproved 0124) TEST METHOD FOR DETERMINATION OF HYDROGEN IN PHOTOVOLTAIC (PV) POLYSILICON BY INERT GAS FUSION INFRARED ABSORPTION METHOD

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NOTICE: Paragraphs entitled ‘NOTE:’ are not an official part of this Standard or Safety Guideline and are not intended to modify or supersede the official Standard or Safety Guideline. These have been supplied by the global technical committee to enhance the usage of the Standard or Safety Guideline.

1 Purpose

1.1 The purpose of this Test Method is to standardize analytical protocols for the determination of hydrogen content in photovoltaic (PV) polysilicon which may affect the safety of casting process for polycrystalline silicon ingot and the quality of polysilicon ingot relating to the subsequent properties and performances of PV solar products. This will facilitate comparison of test results among worldwide laboratories used for monitoring or qualifying PV polysilicon and other PV silicon materials.

2 Scope

2.1 This Test Method can be used to analyze hydrogen content in polysilicon for PV applications, involving all types of PV polysilicon; for example, granular polycrystalline silicon produced by fluidized bed process or PV polysilicon wafers and slugs, etc.

2.2 Based on the same matrix and instruments, the test method may also be used for determining hydrogen content in other silicon materials covering PV monosilicon, semiconductor monosilicon and semiconductor polysilicon, silicon raw materials including metal silicon and silicon powder, etc.

2.3 This Test Method is for use with commercially available hydrogen analyzers which are based on the inert gas fusion principle and use infrared detector as the measuring technique.

2.4 The detection range of the method described will depend upon the detection range of individual hydrogen analyzers. For the one hydrogen analyzer, the detection range when expressed as a mass percentage (% *m/m*) could be changed by different weight of sample. For example, three of commercially available hydrogen analyzers, the detection range of the First is between 0.0001 mg hydrogen and 2.5 mg hydrogen (i.e., between 0.00001% (*m/m*) and 0.2500% (*m/m*) for 1 g sample or between 0.00007% (*m/m*) and 1.666% (*m/m*) for 0.15 g sample), the Second is between 0.0001 mg hydrogen and 1.0 mg hydrogen (i.e., between 0.00001% (*m/m*) and 0.1000% (*m/m*) for 1 g sample or between 0.00007% (*m/m*) and 0.666% (*m/m*) for 0.15 g sample), while the Third is between 0.00008 mg hydrogen and 2.5 mg hydrogen (i.e., between 0.000008% (*m/m*) and 0.2500% (*m/m*) for 1 g sample or between 0.00006% (*m/m*) and 1.666% (*m/m*) for 0.15 g sample).

2.5 Silicon samples in a range of physical forms can be used, including polysilicon powders, granules, chunks, single and multicrystalline wafers and slugs.

2.6 The hydrogen determinations described in this test method can be used irrespective of all dopant species and concentrations.

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 Not all the information needed to determine the hydrogen content in PV polysilicon is included in this Test Method. For instance, determination of the optimum temperatures for measuring the hydrogen content in a variety of silicon samples or optimization of the hydrogen peak parameters are not described in this Test Method.

3.2 The limit of detection is determined by the instrumental blank value limitations, and may vary with instrumentation and preparation techniques.

3.3 Some impurities from a lower grade flux can cause some adsorption of released hydrogen. It is recommended to use only high purity flux.

3.4 Temperature fluctuations in single graphite crucibles may affect the measurement. This can be significantly reduced by using inner crucibles referred further as double-wall crucibles.

4 Referenced Standards and Documents

4.1 SEMI Standards and Safety Guidelines

SEMI PV17 — Specification for Virgin Silicon Feedstock Materials for Photovoltaic Applications

SEMI PV22 — Specification for Silicon Wafers for Use in Photovoltaic Solar Cells

SEMI PV43 — Test Method for the Measurement of Oxygen Concentration in PV Silicon Materials for Silicon Solar Cells by Inert Gas Fusion Infrared Detection Method

4.2 ASTM® Standards¹

ASTM E50 — Standard Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials

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 E1447 — Standard Test Method for Determination of Hydrogen in Titanium and Titanium Alloys by Inert Gas Fusion Thermal Conductivity/Infrared Detection Method

4.3 ISO® Standards²

ISO 5725-2 — Accuracy (Trueness and Precision) of Measurement Methods and Results - Part 2: Basic Method for the Determination of Repeatability and Reproducibility of a Standard Measurement Method

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 *carbon steel reference material* — carbon steel sample known hydrogen content (% m/m) with certification.

5.2.2 *graphite crucible* — crucibles made of high purity graphite grades in order to ensure good heating characteristics with minimal dusting.

5.2.3 *inert gas fusion with infrared absorption method* — the designation is given to the analytical method in accordance to the definition “inert gas fusion with infrared detection” in SEMI PV43. It is an analytical method in

¹ ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959, USA; Telephone: +1.610.832.9585, Fax: +1.610.832.9555, <http://www.astm.org>. ASTM trademark is owned by ASTM International.

² International Organization for Standardization, ISO Central Secretariat, Chemin de Blandonnet 8, CP 401-1214 Vernier, Geneva, Switzerland; Telephone: +41.22.749.01.11, Fax: +41.22.733.34.30, <http://www.iso.org>. ISO trademark is owned by International Organization for Standardization.

which the analyzed sample is fused in single-use graphite crucible under inert gas flow at a temperature sufficient to release gases, which are then measured using infrared detection.

5.2.4 polysilicon for photovoltaic applications — the designation is given to silicon solid materials in accordance to SEMI PV17 and SEMI PV22.

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

5.2.6 test portion — a portion of the test sample to be tested for hydrogen content by this method.

5.2.7 test sample — material (silicon) to be analyzed for hydrogen content by this method. Generally, the test sample is selected from a large batch of silicon materials and is intended to be representative of the batch.

6 Summary of Test Method

6.1 The principle of this Test Method is the same with the standard ASTM E1447.

6.2 The test portion, contained in a single-use double-wall graphite crucible, is fused in a flowing carrier gas atmosphere. Hydrogen present in the sample is released as molecular hydrogen into the flowing gas stream. The hydrogen is converted to water by passing the gas stream over heated copper oxide (rare earth base) and subsequently measuring in an appropriate infrared (IR) absorption cell.

6.3 This Test Method is written for use with commercial analyzers equipped to perform the above operations automatically and is calibrated using reference materials of known hydrogen content.

7 Apparatus

7.1 Fusion and Measurement Apparatus — There are several instruments available commercially, which are having the same general features that are suitable for this test method. Automatic hydrogen determinator, consisting of an electrode furnace or induction furnace; analytical gas stream impurity removal systems; auxiliary purification systems and an infrared hydrogen measurement system (i.e., IR-detection instruments).

7.2 Electronic Balance(s) — 0.1 mg accuracy.

7.3 Graphite Crucible — The double-wall crucibles must be machined from high-purity graphite and should meet the specifications recommended by the manufacturers of the instruments.

7.4 Crucible Tongs — Capable of handling recommended crucibles.

7.5 Tweezers or Forceps — For contamination-free sample handling.

7.6 Sample Preparation Equipment — Capable of processing a sample into the shape and size required by the instruments; for example, cutting machine, polishing machine, etc.

8 Reagents and Materials

8.1 Inert Gas — Helium (99.99%) or argon in the purity range specified by the instrument manufacturer.

8.2 Pneumatic — Nitrogen (99.9%) or compressed air which source must be oil and water free.

8.3 Copper Oxide (Rare Earth Base) — To convert hydrogen to water in IR-detection instruments. Characteristics specified by the instrument manufacturer.

8.4 Sodium Hydroxide on Non-Fibrous Silicate Carrier — Used in instruments to absorb residual CO₂ in the inert gas stream. Purity as specified by the instrument manufacturer.

8.5 Anhydrous Magnesium Perchlorate — Used in the instruments for moisture absorption. Purity as specified by the instrument manufacturer.

8.6 High-Purity Nickel Capsule (Low Hydrogen) — Use the purity as recommended by the instrument manufacturer with hydrogen content below the limit of detection of the instrument.

8.7 Calibration Reference Materials — If available, prior to silicon reference materials containing certified amounts of hydrogen, or select carbon steel reference materials known hydrogen content (% m/m) with certification.