

SEMI AUX019-0211
RESEARCH REPORT ON INTERLABORATORY STUDY TO
ESTABLISH PRECISION STATEMENTS FOR SEMI PV1, 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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Abstract

SEMI PV1 is an analytical test method, and the goal has always been to add a precision statement based upon an Interlaboratory Study, sometimes called a Round Robin Test. The Interlaboratory Study (ILS) was planned and executed over a period of between one and two years. Eight laboratories participated from Europe, U.S.A., and China. This final report includes the rationale behind the design of this ILS, all data from all eight laboratories, the selection process used to exclude some data and two laboratories, and the final precision statement. The statistical approach followed ASTM E691-09, "Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method." In addition to the GDMS data, SIMS data from one laboratory (Evans Analytical Group, Sunnyvale, CA) was included for comparison, but not included in the precision statement.

1. Introduction:

An Interlaboratory Study was conducted to establish a precision statement for SEMI PV1, Test Method for Measuring Trace Elements in Silicon Feedstock for Silicon Solar Cells by High-Mass Resolution Glow Discharge Mass Spectrometry.

2. Test Method:

The Test Method used for this inter-laboratory study (ILS) is SEMI PV1 and is currently under jurisdiction of SEMI. To obtain a copy of this standard, go to SEMI's website, www.semi.org or contact SEMI Global Headquarters, San Jose, 3081 Zanker Road, San Jose, CA 95134, USA, Tel: 1.408.943.6900.

3. Participating Laboratories:

The following laboratories and key personnel participated in this interlaboratory study:

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4. Background

Heretofore, the calibration of GDMS measurements of trace elements in silicon has used one or more of the following procedures:

- i) NIST SRM 57a (or the latest release of SRM 57b) of metallurgical grade silicon (MG-Si).

This procedure provides calibration of a wide range of elements in silicon. However, the accuracy of the calibration is affected by the matrix difference between MG-Si, which is 2N (99%) pure, and “Silicon feedstock” purity, which can be within the range of 5N to 11N. The bias in using SRM 57a to calibrate the measurement for silicon feedstock materials is normally estimated to be within a factor 2X but this is an estimate only.

- ii) Research studies of the axial distribution of elements in directional solidified (DS) silicon ingots that have been intentionally melt-doped with known amounts of selected elements.

This calibration is derived from knowing the elemental segregation coefficients along with the measured axial distribution. However, the effective segregation coefficients are not *a priori* known since they can be affected by growth rate, mixing, and back-diffusion.

- iii) Comparison to Secondary Ion Mass Spectrometry (SIMS) measurements in matched samples where the SIMS calibrations are traceable to silicon reference materials.

However, the only NIST SRMs applicable in this case are for B and P in silicon. Other element calibrations are traceable to electronic grade silicon implanted with known doses of the elements of interest, but these are not industry consensus reference materials in the sense of SEMI MF1569.

5. Test Sample Set Design Considerations

The above mentioned calibration issue has made it difficult to design a set of appropriate test samples and implement an ILS for a wide range of trace impurities in silicon. Several approaches were considered:

- i) Melt-doping Cz-grown silicon ingots with a range of transition metals where the effective segregation coefficients are well-known in the Cz-Si growth process. The difficulty in this case was the concentration of the transition metal impurities in the bulk of the material would be near or below the detection limits, so that the interlaboratory precisions would be dominated by the variability of individual measurements. In addition, obtaining the agreement for a Cz-Si crystal grower to dope with transition metals was expected to be nil.

- ii) Melt-doping directional-solidified (DS) grown multi-crystalline silicon ingots with a range of transition metals where the effective segregation coefficients were estimated in order to achieve a high doping concentration to avoid the variability issue in i). This kind of material appeared available in the PV industry, but input from a range of experts suggested the transition metals would not be very homogeneous in the silicon so that providing matched, hub-and-spoke sample sets was unlikely.

- iii) Using already available Cz-grown electronic grade silicon doped with either B or P (no compensation) where the uniformity was consistent with electronic grade silicon and the

uncompensated resistivity would provide an independent measure of the dopant concentration. This approach was limited to B and P elements.

iv) Melt-doping DS grown silicon ingots but using only B and P doping instead of transition metals. This would only be acceptable if it could be shown the B and P levels were homogeneous enough to provide matched, hub-and-spoke sample sets. However, resistivity alone would not provide an accurate dopant concentration due to the high compensation. This approach would be limited to B and P, but if UMG-Si was used, it was expected that the element Ge could be also included because Ge is a common element and uniform at the ppmw level in UMG-Si.

6. Description of Samples:

Ten Silicon samples of varying dopant contents were selected as test specimen for this study. Samples were selected to represent high, medium and low dopant levels currently in use for manufacturing silicon based photovoltaic cells. They contained varying amounts of the major scope elements, such as Boron and Phosphorus, some of which represent the working range of what is typically found in Si feedstocks for Si solar cells. The materials were also selected to investigate possible method issues such as spectral overlaps or problems with sample preparation. The samples are such as might be typically encountered in a laboratory performing qualification test on Silicon feedstocks for the photovoltaic industry. A description of the samples selected for this ILS for each sample is given below. Note that all B-doped Cz-Si samples were doped with ^{11}B , and the ^{10}B content was anomalously low (isotopic ratios were abnormal). Note the first four samples have resistivity data provided by the supplier, and the ^{11}B atomic concentrations are calculated assuming the ^{10}B atomic concentration is a negligible contribution to the resistivity. In addition, the UMG-Si samples had detectable Ge atomic concentrations.

1. EGS5: Cz-Si, ^{11}B -doped, resistivity 0.369 ohm-cm (^{11}B calculated $4.6 \times 10^{16}/\text{cm}^3$)
2. EGS3: Cz-Si, ^{11}B -doped, resistivity 0.592 ohm-cm (^{11}B calculated $2.6 \times 10^{16}/\text{cm}^3$)
3. EGS2: Cz-Si, ^{11}B -doped, resistivity 0.707 ohm-cm (^{11}B calculated $2.1 \times 10^{16}/\text{cm}^3$)
4. EGS1: Cz-Si, ^{11}B -doped, resistivity 2.274 ohm-cm (^{11}B calculated $0.60 \times 10^{16}/\text{cm}^3$)
5. EGSP: Cz-Si, ^{11}B at $2.65 \times 10^{13}/\text{cm}^3$, $^{10}\text{B} < 1 \times 10^{13}/\text{cm}^3$, $\text{P} < 1 \times 10^{14}/\text{cm}^3$ all by SIMS
6. RSHB: Cz-Si, ^{11}B at $1.39 \times 10^{15}/\text{cm}^3$, ^{10}B at $1.45 \times 10^{13}/\text{cm}^3$, $\text{P} < 1 \times 10^{13}/\text{cm}^3$ all by SIMS
7. RSHC: Cz-Si, ^{11}B at $9.2 \times 10^{14}/\text{cm}^3$, ^{10}B at $2.3 \times 10^{13}/\text{cm}^3$, $\text{P} < 1 \times 10^{13}/\text{cm}^3$ all by SIMS
8. UMG1 – top of directional solidified UMG-Si ingot
Provided by Becancour Silicon, Inc.
9. UMG2 – middle of directional solidified UMG-Si ingot
Provided by Becancour Silicon, Inc.
10. UMG3 – bottom of ingot
Provided by Becancour Silicon, Inc.

7. Interlaboratory Study Instructions

Note: The participant laboratories were not told which samples had anomalously low ^{10}B atomic concentrations in order to assess the ability to detect very low boron, or in some cases the boron background level.

The following instructions were sent to the participating laboratories.

To All:

We are finally ready for a GDMS round robin. I have explained the ideal RR below in the Appendix. We do not have samples for the ideal RR, but we have samples that will allow us to make a precision and repeatability statement for the GDMS analysis of dopants in PV Si. The samples include slugs of electronic grade silicon which provides very uniform dopant distributions and directional solidified UMG-Si that was processed in a special manner to make the dopants fairly uniform.

The proposal is to measure the following elements: ^{10}B , ^{11}B , ^{31}P and Ge. Both ^{10}B and ^{11}B are included because some of the samples are intentionally doped with $^{10}\text{B}/^{11}\text{B}$ ratios that are not normal isotopic ratios.

There are a total of 10 samples.

I propose that each laboratory analyze the 10 samples three (3) times per day for four (4) separate days. Since the analysis only requires four elements, each analysis can be short. Please let me know if this proposal is acceptable.

*Thanks,
Dick Hockett*

Appendix

The ideal RR is something like the following:

Samples: N samples that have element concentrations which cover the range of the test method scope and which are uniform so that each lab receives an equivalent set of N samples..

Test: M laboratories which will make the tests

Measurements: Each of N samples is analyzed P times in one day for Q days

Data Reduction: ASTM data reduction method performs a statistical evaluation to determine within-lab repeatability, between-lab repeatability, and statistical metrics which reveals confidence limits on statistically valid “differences.”

Results evaluation: This is to determine if some data should be ignored and is based on the statistical data reduction or a determination from a lab that something was wrong.

Report: Each lab receives a report of the results indicating which data corresponds to that lab. To identify of which data corresponds to which other lab is normally kept confidential.

The numbers of N samples, M labs, P number of measurements in one day, and the Q number of days are often compromised based upon what samples can be obtained and what time is available in the labs for the measurements.

The biggest challenge for the GDMS RR is the uniformity of element concentration in the N samples. For this reason I am thinking of the following approach. I have a set of Cz-Si samples with different B and P concentrations. These samples are “electronic grade” silicon and the concentrations are uniform. These samples will provide a good analysis of within-lab and between-lab repeatability. In addition B and P are the most important elements for Si PV feedstock evaluation.

However, it would be valuable to include some PV Si samples, such as mc-Si slugs, in the RR even though these samples may not be uniform. These samples will normally have other elements that will be detectable by GDMS. A comparison between the results using the Cz-Si and the mc-Si can be made.

8. Description of the Fast Flow GDMS Equipment:

For information on the GDMS instrument used by each laboratory, please see Annex XX (Source: <http://www.thermoscientific.com/wps/portal/ts/products/detail?productId=11962735>) This Annex also contains the data on instrument sensitivity and mass precision.

9. Data Report Forms:

Each laboratory was provided with a data report Excel file containing the designated cells for each material. This data was copied and pasted into a summary page for each laboratory. A copy of this completed summary for each laboratory is provided in Tables 1-01 through 1-10.

Please note: The laboratories have been randomly coded and cannot be identified herein.

10. Statistical Data Summary/Discussion:

The statistical evaluation of the submitted results was completed according to ASTM E691-09 “Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method”. This statistical analysis was supervised by Martin Kasik (EAG-NY). The ASTM E691 methodology was programmed into Excel’s VBA language (by Martin Kasik).

According to ASTM E691, Section 15.1, the analysis and treatment of the test results have three purposes:

- (1) to determine whether the collected data are adequately consistent to form the basis for a test method precision statement,
- (2) to investigate and act on any data considered to be inconsistent, and
- (3) to obtain the precision statistics on which the precision statement can be made.

The first purpose is to evaluate the consistency of the data. This is done by calculating for each test cell -- two parameters called k-values and h-values from the test data. The “k-value” is a measure of the consistency of the within-laboratory results. The “h-value” is a measure of the consistency between laboratories, and can be either negative or positive. The h-values and k-values have no dimensions. The derivations of the h- and k-values are given in ASTM E691. Note that k and h values are not part of the final precision statement, but are a means to screen the test results for inconsistencies on a statistical basis. A poor k-value indicates that a particular laboratory has a poor internal consistency for a test result. A poor h-value indicates a particular laboratory has a poor lab-to-lab consistency for a test result.

The determination of whether a k-value or an h-value is “poor” or “unacceptable” is done by comparing them with what is called an appropriate Critical Value as discussed next. The methods for determining Critical Values are given in the ASTM E691.

The Critical Value for a k-value is determined by two things: (1) the number of laboratories in the Study, and (2) the number of the replicate test results per laboratory per material. For our ILS with the final 6 participating laboratories and 4 replicates the Critical Value (CV) for a k-value is 1.84. (Note: the initial CV before some of the labs were eliminated was higher than 1.84). A k-value that is greater than 1.84 is considered an outlier and indicates major inconsistency. A k-value between $2/3^{\text{rd}}$ and 1 times the CV indicates substandard degree of consistency. A k-value between $1/3^{\text{rd}}$ and $2/3^{\text{rd}}$ times the CV indicates an average degree of consistency. A k-value below $1/3^{\text{rd}}$ times the CV indicates excellent consistency.

The Critical Value for an h-value is determined only by the number of laboratories in the Study. For our Study with the final 6 participating laboratories the Critical Value (CV) for the absolute value of an h-value is 1.92. (Note: the initial CV before some of the labs were eliminated was higher than 1.92). An h-value with absolute value that is greater than 1.92 is considered an outlier and indicates major inconsistency. An h-value with absolute value between $2/3^{\text{rd}}$ and 1 times the CV indicates substandard degree of consistency. An h-value with absolute value between $1/3^{\text{rd}}$ and $2/3^{\text{rd}}$ times the CV indicates an average degree of consistency. An h-value with absolute value below $1/3^{\text{rd}}$ times the CV indicates excellent consistency.

The statistical evaluation Excel workbook contains all the submitted results in separate calculation worksheets for each lab. The calculated values of h and k were also included in separate worksheets for each lab, and the same for the repeatability standard deviations and the reproducibility standard deviations. In addition, all of this in color coded tables and graphs allowing carefully examination of all data and exhibiting the statistical results in an easily readable format.

11.1 Summary Statistics

Tables 1-01 through 1-10 present summaries of all data collected from each of the 10 labs (9 GDMS labs, 1 SIMS lab), for each material type, and the k- and h-statistics calculated in accordance with the requirements for ASTM E691-09. This data will be used to establish the precision statement to be published with the PV1 test method.

11.2 Color coding in tables

Color coding of the cells is different between the measurement data and the k or h-values. The following explains this difference.

For the cells with measurement data:

Green indicates data lying within $\pm$ one standard deviation (SD) of the mean of the all the results for that material by that lab. Yellow corresponds to between 1SD and 2SD, and Red corresponds to greater than 2SD.

For the cells with the k or h-values:

Bright green indicates values ≤ 0.33 times the CV. Light green indicates values between 0.33 and 0.66 times the CV. Yellow indicates values between 0.66 and 1 times the CV. Red indicates values greater than the CV. Red in a k-value or an h-value represents a major inconsistency. Yellow is substandard. Light green is good. Bright green is excellent.

11.3 Discussion:

The following three sections below discuss a variety of details relating to the statistical calculations and present observations concerning the quality of the data obtained using the PV1 test method:

Section 1: General Observations

The first set of submitted data clearly pointed towards that the overall Mean from this study will not necessarily be the "right representative number" since there were obvious differences in instrumental parameters between the labs. Additionally, there was an indication that some of the labs had not been using reference samples for verifying the observed results. Despite these issues it is useful to judge the individual laboratory's performance by the measures described by ASTM E 691, the "k" and "h" statistics using all of the test specimen, including those, in which the analytes are very close or below the techniques' sensitivity.

Section 2: Test for outlying results/laboratories

The obvious typos and some errors in the submitted raw data were first corrected in coordination with the participating labs before these were statistically evaluated. For this the participants were contacted for additional information and/or clarifications.

The Cz-Si samples (EG and RSH samples) were found not to be useful in this ILS in the sense of providing a precision statement. The reasons are as follows. They did not contain P, Ge, or ^{10}B above the detection limits of GDMS. With the exception of ESG5, they did not obtain ^{11}B at a high enough level to get a reasonable detection; and even for ESG5, the ^{11}B was not high enough to provide a useful precision. Thus, the measurement data for the Cz-Si samples were excluded in this ILS in terms of developing a precision statement.

The measurement data for the Cz-Si samples did, however, highlight instrumental or procedural problems at some of the labs, particularly for detecting low levels of B. An example was the detection of the $^{40}\text{Ar}^{+4}$ mass interference of ^{10}B . The GDMS instrument can mass separate these two species, but the procedure used by some labs did not evaluate for this interference, and they reported the mass interference. This was a problem for some labs in detecting ^{10}B in the UMG-Si samples, and those data were excluded. Likewise, some labs had higher backgrounds for P than other labs due to some instrumental differences; but this problem was only an issue for low levels of P, and not a problem for the UMG-Si samples. The UMG-Si samples became a useful set of samples to developing a precision statement for the PV1 test method.

With understanding that the Cz-Si sample data were to be excluded in the k- and h- screening of the UMG-Si sample data, the following were the decisions made on the labs' data.

Lab #1: Table 1 – 01: All test results accepted as received and included for calculations in the precision statement.

Lab #2: Table 1 – 02: All test results accepted as received and included for calculations in the precision statement.

Lab #3: Table 1 – 03: The submitted results exhibited large discrepancies and differences as compared to the expected B mass fraction ranges. This pointed towards serious instrument setup and/or methodology related problems. Therefore these set of data were excluded from the final statistical evaluations.

Lab #4: Table 1 – 04: There were some outliers in the submitted samples on ^{10}B , but all at or below the sensitivity of the instrument as operated or below the scope of this test method. The ^{10}B data were excluded. All other test results within the scope of this method were accepted as received and included calculations in the precision statement.

Lab #5: Table 1 – 05: Except for one test result of ^{10}B below the scope of this test method the test results were accepted as received and included in the calculations in the precision statement.