

SEMI PV25-1011

TEST METHOD FOR SIMULTANEOUSLY MEASURING OXYGEN, CARBON, BORON AND PHOSPHORUS IN SOLAR SILICON WAFERS AND FEEDSTOCK BY SECONDARY ION MASS SPECTROMETRY

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1 Purpose

1.1 Secondary ion mass spectrometry (SIMS) can measure the total bulk concentrations of oxygen, carbon, boron and phosphorus in polished solar silicon wafers and silicon feedstock. Bulk carbon is important because it can form carbon-related defects, such as SiC inclusions. Bulk oxygen is important in boron-doped silicon because a BO_x defect can degrade cell efficiency. Boron and phosphorus are common dopants in solar Si wafers, and are difficult to measure directly in solar Si wafers, especially in highly compensated silicon.

1.2 The measurement of all four elemental concentrations can be accomplished in one test and using one SIMS instrument equipped with a cesium primary ion source.

1.3 The SIMS method can be used at three stages of solar Si wafers and silicon feedstock: research and development; process check; and verification at the commercial sales/purchase interface.

2 Scope

2.1 This Test Method covers the simultaneous determination of total oxygen, carbon, boron and phosphorus concentrations in the bulk of silicon samples that are prepared from solar silicon wafers or solar silicon feedstock using SIMS.¹

2.2 This Test Method can be used for silicon in which the dopant concentrations are less than 0.2% (1×10^{20} atoms/cm³) for carbon, oxygen, boron, and phosphorus.

2.3 This Test Method can be used for silicon irrespective of the amount of compensation in the silicon.

2.4 This Test Method can be used for either multicrystalline or single crystal silicon wafers.

2.5 This Test Method is for bulk analysis where the oxygen, carbon, boron and phosphorus concentrations are constant with depth.

2.6 This Test Method can be used for silicon in which the oxygen, carbon, boron and phosphorus contents are respectively $\geq 5 \times 10^{16}$ atoms/cm³; $\geq 1 \times 10^{16}$ atoms/cm³; $\geq 1 \times 10^{14}$ atoms/cm³; and $\geq 2 \times 10^{14}$ atoms/cm³.

2.7 Calibration of the SIMS measurement of boron and phosphorus in silicon is traceable to NIST reference materials. Calibration for the oxygen measurement is indirectly traceable to NIST reference material through FTIR correlation. Calibration for the carbon measurement is completed using carbon-implanted silicon wafer reference materials.

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 Oxygen and carbon on or in the surface silicon oxide can interfere with the bulk oxygen and carbon measurements. This can be minimized by baking the samples before analysis.

3.2 Oxygen and carbon adsorbed on the test specimen surface from the SIMS instrument chamber and fixtures interfere with the bulk oxygen and carbon measurements by raising the background signals. The vacuum quality of the SIMS instrument can be used to minimize this.

¹ Hockett, R. S. "Solar Grade Si Impurity Evaluations Using GDMS and SIMS." 3rd International Workshop on Crystalline Silicon Solar Cells, SINTEF/NTNU, Trondheim Norway, June 3–5, 2009.

3.3 Oxygen or carbon in the SIMS primary Cs beam may be implanted into the silicon specimen as CsO or CsC and thereby increase the oxygen and carbon background concentrations. A primary beam mass filter may be used to reduce this interference, but in this case, the reduced Cs beam current density will reduce the sputter rate which may increase the oxygen and carbon background signals.

3.4 $^1\text{H}^{30}\text{Si}$ at mass 31 can interfere for detecting phosphorus ^{31}P . This must be avoided by using SIMS equipment with mass resolution of 4000.

3.5 The specimen surface must be flat in the specimen holder window so that the inclination of the specimen surface with respect to the ion collection optics is constant from specimen to specimen. Otherwise, the accuracy and precision can be degraded. This is accomplished by mechanical polishing the silicon specimen.

3.6 Calibration of the carbon measurement in silicon by SIMS is not traceable to a NIST reference material. Instead carbon implantation into silicon is used for reference. Bias in the assigned carbon areal density of the calibration specimen can introduce bias into the SIMS carbon measurement.

3.7 Variability from the calibration measurement of any of the four elements may increase the measurement precision of the test specimen.

3.8 Bias in the assigned carbon areal density of the calibration specimen can introduce bias into the SIMS measured carbon.

3.9 The detection capability depends upon the SIMS instrumental backgrounds and the precision of the measurements.

3.10 The analytical volume of this test method is on the order of 100's of micrograms, so that heterogeneity of oxygen, carbon, boron, or phosphorus concentrations on scales greater than this analytical volume may degrade the inherent precision of the Test Method.

4 Referenced Standards and Documents

4.1 SEMI Standards and Safety Guidelines

SEMI MF2139 — Test Method for Measuring Nitrogen Concentration in Silicon Substrates by Secondary Ion Mass Spectrometry

4.2 ASTM Standards²

ASTM E122 — Practice for Calculating Sample Size to Estimate, With a Specified Tolerable Error, the Average for a Characteristic of a Lot or Process

ASTM E673 — Terminology Relating to Surface Analysis

NOTICE: Unless otherwise indicated, all documents cited shall be the latest published versions.

5 Terminology

5.1 *Definitions* — All terms in this Test Method are in accordance with those given in ASTM E673.

6 Summary of Test Method

NOTE 1: This Test Method is almost identical to SEMI MF2139 except for the elements to be measured.

6.1 SIMS is utilized to determine the bulk concentration of oxygen, carbon, boron and phosphorus in multicrystalline or single crystal silicon. Specimens of silicon are mechanically polished to provide a flat analysis surface. The polished silicon specimen (one or more calibration specimen and the test specimens) are loaded into a sample holder. The holder with the specimens is baked at 100°C in air for 1 hour and then transferred into the analysis chamber of the SIMS instrument.

6.2 The calibration samples are analyzed using a cesium (Cs) primary ion beam and negative ion spectrometry of ^{16}O , ^{12}C , ^{31}P , and $^{11}\text{B}^{28}\text{Si}$ to determine a relative sensitivity factor (RSF) of oxygen, carbon, phosphorus and boron in silicon.

² 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>

6.3 Each test specimen in the sample holder is sputtered by the primary cesium ion beam, without analyzing secondary ion intensities, in order to reduce the oxygen and carbon backgrounds. The amount of time required for this pre-analysis sputtering depends upon the instrumentation and the desired background oxygen and carbon concentrations.

6.4 For the analysis of the test specimens, a cesium primary ion beam is used to bombard each test specimen at two different sputter rates, by reducing the beam raster area for the second sputter rate, while at the same time maintaining a constant detected area. This beam raster change technique is used for two reasons. Firstly, this technique reduces the background oxygen and carbon contributions from the sample surface. Secondly, this technique allows the determination of both the instrumental oxygen and carbon backgrounds and the real bulk oxygen and carbon concentrations in each test specimen measurement without the use of a separate blank specimen, and due to averaging is capable of separating the bulk oxygen and carbon from the instrumental oxygen and carbon even if the bulk oxygen and carbon are less than the instrumental oxygen and carbon.³

6.5 The two sputter rates, and the amount of time they are applied in each measurement, are chosen to optimize the detection capability; the values depend on the instrumentation being used. However, the second sputter rate is typically the maximum sputter rate of the instrumentation, and the first sputter rate is typically less than half that of the second sputter rate.

6.6 The negative secondary ions of ^{12}C , ^{16}O , ^{31}P , and $^{11}\text{B}^{28}\text{Si}$ are mass analyzed by a mass spectrometer, and detected by an electron multiplier (EM) or equivalent high-sensitivity ion detector as a function of time. The matrix negative secondary ion count for silicon such as ^{28}Si is measured by a Faraday cup (FC) or appropriate detector during the profile. If multiple detectors are used during the test, the relative sensitivities of the detectors are determined by measuring standard ion signals (either the same negative secondary ion count rate or ion count rates of known relative intensity such as natural $^{28}\text{Si}/^{30}\text{Si}$) on each detector.

6.7 For illustration purposes an example data profile is shown in Figure 1 where the log of counts of ^{12}C , ^{16}O , ^{31}P , and $^{11}\text{B}^{28}\text{Si}$ and ^{28}Si is plotted versus cycle time. One cycle is the time it takes the SIMS detection scheme to cycle the mass spectrometer in order to mass analyze all four elements; this is typically a few seconds per cycle for a magnetic sector spectrometer. At about 12 cycles in the plot, the Cs beam raster area was changed from $250\text{ }\mu\text{m} \times 250\text{ }\mu\text{m}$ down to $100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$, resulting in an increase in signal intensities, because the volume of material analyzed per second has increased. At about 24 cycles, the Cs beam raster area was reversed back to the first condition, and the signal intensities are seen to be reduced back to the original levels. Since the surface analysis area was kept constant during the raster change (i.e., the actual surface area detected is independent of the raster area), the signal intensities have two separate contributions, one from elements that are adsorbed to the surface and one from elements in the volume of material analyzed each second. There is some oxygen and carbon that is adsorbed to the surface from the local environment outside of the silicon, and there is some oxygen and carbon that is from the bulk silicon. A key point is that if there is no oxygen or carbon in the bulk silicon, the oxygen or carbon signal intensity does not change as a result of the change in sputter rate, because the adsorbed oxygen or carbon (i.e., instrumental oxygen or carbon signal) is only dependent on the analysis area, which has been held constant. This understanding leads to the following equations for each of the four elements:

$$\frac{I_n}{I_{si}} \times RSF = [N_b] + [N] \quad (1)$$

$$\frac{I_N}{I_{SI}} \times RSF = [N_B] + [N] \quad (2)$$

$$[N_b] = \frac{I_B}{I_{si}} \times RSF \quad (3)$$

$$[N_B] = \frac{I_B}{I_{SI}} \times RSF \quad (4)$$

³ Ishitani, A., Okuno, K., Karen, A., Karen, S. and Soeda, F. "Improvement of Oxygen Detection Limit in Silicon by Use of the Secondary Ion Energy Distribution and Background Subtraction." in *Proceedings of the International Conference of Materials and Process Characterization for VLSI, 1988 (ICMPC'88)*, edited by X-F Zong, Y-Y Wang, and J. Chen, World Scientific, New Jersey (1988): pp. 124–129.