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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Method for Measuring Oxygen Concentration in Heavily Doped Silicon Substrates by Secondary Ion Mass Spectrometry¹

This standard is issued under the fixed designation F 1366; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

^{ε1} NOTE—Keywords were added editorially in April 1998.

1. Scope

1.1 This test method covers the determination of total oxygen concentration in the bulk of single crystal silicon substrates using secondary ion mass spectrometry (SIMS).

1.2 This test method can be used for silicon in which the dopant concentrations are less than 0.2 % (1×10^{20} atoms/cm³) for boron, antimony, arsenic, and phosphorus (see Test Method F 723). This test method is especially applicable for silicon that has resistivity between 0.0012 and 1.0 Ω -cm for *p*-type silicon and between 0.008 and 0.2 Ω -cm for *n*-type silicon (see Test Methods F 43).

1.3 This test method can be used for silicon in which the oxygen content is greater than the SIMS instrumental oxygen background as measured in a float zone silicon sample, but the test method has a useful precision especially when the oxygen content is much greater (approximately 10 \times to 20 \times) than the measured oxygen background in the float zone silicon.

1.4 This test method is complementary to infrared absorption spectroscopy that can be used for the measurement of interstitial oxygen in silicon that has resistivity greater than 1.0 Ω -cm for *p*-type silicon and greater than 0.1 Ω -cm for *n*-type silicon (see Test Method F 1188). The infrared absorption measurement can be extended to between 0.02 and 0.1 Ω -cm for *n*-type silicon with minor changes in the measurement procedure.²

1.5 In principle, different sample surfaces can be used, but the precision estimate was taken from data on chemical-mechanical polished surfaces.

1.6 *This standard does not purport to address all of the safety concerns, 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 limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:

¹ This test method is under the jurisdiction of ASTM Committee F-01 on Electronics and is the direct responsibility of Subcommittee F01.06 on Silicon Materials and Process Control.

Current edition approved Jan. 15, 1992. Published March 1992.

² Hill, D. E., "Determination of Interstitial Oxygen Concentration in Low-Resistivity *n*-type Silicon Wafers by Infrared Absorption Measurements," *Journal of the Electrochemical Society*, Vol 137, 1990, p. 3926.

E 122 Practice for Choice of Sample Size to Estimate a Measure of Quality for a Lot or Process³

F 43 Test Methods for Resistivity of Semiconductor Materials⁴

F 723 Practice for Conversion Between Resistivity and Dopant Density for Arsenic-Doped, Boron-Doped, and Phosphorus-Doped Silicon⁴

F 1188 Test Method for Interstitial Atomic Oxygen Content of Silicon by Infrared Absorption⁴

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

3.1.1 *ion mass spectrometry*—the separation and counting of ions by their mass-to-charge ratio.

3.1.2 *primary ions*—ions created and focussed by an ion gun onto the specimen surface to sputter ionize surface atoms.

3.1.3 *secondary ions*—ions that leave the specimen surface as a result of the primary ion beam sputter ionizing the specimen surface atoms.

3.1.4 *secondary ion mass spectrometry*—mass spectrometry performed upon secondary ions from the specimen surface.

4. Summary of Test Method

4.1 SIMS is utilized to determine the bulk concentration of oxygen in single crystal silicon substrate. Specimens of single crystal silicon (one float-zone silicon specimen, two calibration specimens, and the test specimen) are loaded into a sample holder. The holder with the specimens is baked at 100°C in air for 1 h and then transferred into the analysis chamber of the SIMS instrument. A cesium primary ion beam is used to bombard each specimen. The negative secondary ions are mass analyzed. The specimens are presputtered sequentially to reduce the instrumental oxygen background. The specimens are then analyzed, in locations different from the presputtering locations, for oxygen and silicon in a sequential manner throughout the holder. Three measurement passes are made through the holder. The ratio of the measured oxygen and silicon secondary ion intensities (O^-/Si^-) is calculated for each specimen. The relative standard deviation (RSD) of the ratio is

³ *Annual Book of ASTM Standards*, Vol 14.02.

⁴ *Annual Book of ASTM Standards*, Vol 10.05.

then calculated for each specimen. If any specimen other than the float zone specimen has a RSD of the ratio greater than 3 %, more analyses are performed. The SIMS average O/Si ratios are then converted to infrared-equivalent concentrations by utilizing either the load-line calibration method^{5,6} or the load factor calibration method⁶ with the calibration specimens in the load.

5. Significance and Use

5.1 SIMS can measure the oxygen concentration in heavily-doped silicon substrates used for epitaxial silicon where the free carrier concentration obscures the infrared absorption and prevents the normal use of the infrared measurement as a characterization technique for the commercial production of silicon.

5.2 The SIMS measurement allows for the production of controlled oxygen content in heavily-doped silicon crystals.

5.3 This test method can be used for process control, research and development, and materials acceptance purposes.

6. Interferences

6.1 Oxygen from silicon oxide, carbon oxide, and water on the surface can interfere with the oxygen measurement.

6.2 Oxygen adsorbed from the SIMS instrument chamber to the surface can interfere with the oxygen measurement.

6.3 There are no effects upon the oxygen ion yield from the dopants for dopant densities less than 1×10^{20} atoms/cm³.⁷

6.4 The SIMS oxygen instrumental background as measured on the float zone silicon specimen should be as low as possible and stable before the analyses are begun.

6.5 The specimen surface must be flat in the specimen holder windows 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.

6.6 The accuracy and precision of the measurement significantly degrade as the roughness of the specimen surface increases. This degradation can be avoided by using chemical-mechanical polished surfaces.

6.7 Variability of oxygen in the calibration standards can limit the measurement precision.

6.8 Bias in the assigned oxygen of the calibration standards can introduce bias into the SIMS measured oxygen.

7. Apparatus

7.1 *SIMS Instrument*, equipped with a cesium primary ion source, electron multiplier detector and Faraday cup detector, and capable of measuring negative secondary ions.

⁵ Goldstein, M., and Makovsky, J., "The Calibration and Reproducibility of Oxygen Concentration in Silicon Measurements Using SIMS Characterization Techniques," *Semiconductor Fabrication: Technology and Metrology*, ASTM STP 990, Dinesh C. Gupta, Ed., ASTM, 1988, pp. 350–360.

⁶ Makovsky, J., Goldstein, M., and Chu, P., "Progress in the 'Load Line Calibration' Method for Quantitative Determination of [O] in Silicon by SIMS," *Seventh International Meeting on Secondary Ion Mass Spectrometry, SIMS VII*, John Wiley and Sons, 1990, p. 487.

⁷ Bleiler, R. J., Chu, P. K., Novak, S. W., and Wilson, R. G., "Study of Possible Matrix Effects in the Quantitative Determination of Oxygen in Heavily Doped Czochralski Silicon Crystals," *Seventh International Meeting on Secondary Ion Mass Spectrometry, SIMS VII*, John Wiley and Sons, 1990, p. 507.

7.1.1 The SIMS instrument should be adequately prepared (that is, baked) so as to provide the lowest possible instrumental background.

7.2 *Cryopanel*, liquid nitrogen- or liquid helium-cooled, which surrounds the test specimen holder in the analysis chamber.

7.3 *Test Specimen Holder*.

7.4 *Oven*, for baking test specimen holder.

8. Sampling

8.1 Since this procedure is destructive in nature, a sampling procedure must be used to evaluate the characteristics of a group of silicon wafers. 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 Practice E 122 for suggested choices of sampling plans.

9. Specimen Requirements

9.1 Sample specimens must be flat and smooth on the side used for analysis.

9.2 Sample specimens must be cleaved or diced to fit within the sample specimen holder.

10. Calibration

10.1 The two calibration standards in each load must be lightly doped Czochralski silicon⁸ in which the oxygen concentration is measured by infrared absorption spectroscopy (see Test Method F 1188), and the measured values of the two standards bracket the expected values for the test specimen (that is, one calibration standard is higher in oxygen and one is lower, compared to the expected value in the test specimen).

10.2 The calibration standards must be measured by infrared absorption to determine the concentration and homogeneity of the oxygen within the standards; each standard is assigned the averaged infrared absorption oxygen value for the substrate.

10.3 Calibration standards that are included in the SIMS analyses must be taken from that portion of the wafer that provided a homogeneous measurement in the Fourier transform infrared spectrophotometer, (FT-IR) analysis; this portion is typically the central portion of the wafer.

10.4 Each calibration standard specimen must be the same size and have the same polished surface as the test specimen.

10.5 The float zone specimens that are included in the SIMS analysis to measure the instrumental oxygen background must be measured by infrared absorption to determine if the oxygen concentration is low enough to measure the instrumental SIMS background. Oxygen concentrations below 0.5 ppma (see Test Method F 1188) in the float zone specimen are normally sufficient.

10.6 Each float zone specimen must be the same size and have the same polished surface as the test specimen.

11. Procedure

11.1 Specimen Loading:

⁸ Czochralski silicon is available from most silicon substrate suppliers.

11.1.1 Load the specimens into the SIMS sample holder, checking to see that the specimens are flat against the backs of the windows and cover the windows as much as is possible. A specimen load includes one float zone silicon specimen, two or more standard specimens, and the test specimen.

11.1.2 Bake the loaded sample holder at $100 \pm 10^\circ\text{C}$ for a minimum of 1 h in air.

11.2 *Instrument Tuning:*

11.2.1 Turn on the instrument in accordance with the manufacturer's instructions.

11.2.2 Fill the liquid nitrogen or helium cold trap.

11.2.3 *Analytical Conditions:*

11.2.3.1 Use a cesium primary ion current and focus, which maximizes the ion count rate for an appropriate silicon isotope.

11.2.3.2 Typical analytical conditions are 250μ by 250μ raster and 1-s integrations. Choose apertures to keep the oxygen count rate on the electron multiplier detector below 1×10^5 counts per second for the test specimen.

11.3 *Analysis of Specimen:*

11.3.1 Position the specimen holder so that the sputtered crater in the specimen will form near the center of the window.

11.3.2 Center the primary ion beam and begin a SIMS profile.

11.3.3 Repeat 11.3.1 and 11.3.2 for all the specimens in the holder until all the specimens have been presputtered. This is called a presputtering round and is intended to reduce the instrumental oxygen background. No oxygen data are taken or used from these profiles.

11.3.4 Now make a second round of measurements on all the samples according to 11.3.1 and 11.3.2, but in locations near the presputtered craters of the specimen. Do not make the second round of measurements in the same craters as the presputter craters.

11.3.5 At the end of each profile in the second round of craters, measure and record the $^{16}\text{O}^-$ count rate on the electron multiplier detector and the $^{30}\text{Si}^-$, or other Si isotope as appropriate, matrix ion count rate on the Faraday cup detector.

11.3.6 Repeat 11.3.4 and 11.3.5 for a third and fourth round of measurements, all in their own separate craters. Group all the analyses for each specimen near the center of the window but do not overlap. The raster area for each analysis must be the same.

11.3.7 Calculate the ratio $S(\text{O}^-/\text{Si}^-)$ of oxygen count rate to silicon count rate using the recorded secondary ion intensities at the end of each profile in the second, third, and fourth rounds of profiles, thus obtaining three ratios per specimen.

11.3.8 Calculate the average $S_{\text{avg}}(\text{O}^-/\text{Si}^-)$ of the three ratios for each specimen in the holder.

11.3.9 Compare the average ratio $S_{\text{avg fz}}(\text{O}^-/\text{Si}^-)$ for the float zone specimen to the average ratio $S_{\text{avg sp}}(\text{O}^-/\text{Si}^-)$ of the other specimens. If the average ratio for the float zone specimen is not much less (approximately $10\times$ less) than the average ratio for the other specimens, then the precision of the measurement may be degraded. In this case, depending upon the desired precision, it may be necessary to either abort the analysis and find the cause of the high instrumental background, or to increase the number of measurements per specimen.

11.3.10 Calculate the relative standard deviation (RSD percent) of the ratio $S(\text{O}^-/\text{Si}^-)$ for each specimen, including the calibration specimen, the float zone specimen, and the test specimen.

11.3.11 Repeat the analysis of oxygen for specimens (other than float zone specimens) with a RSD percent greater than 3 %.

11.3.12 Record the specimen identification, O^-/Si^- ratios, average, standard deviation, and relative standard deviation in a table and include the same for the float zone silicon specimen.

12. Calculation

12.1 *Load Line Calibration Procedure:*

12.1.1 Calculate the slope m and intercept b of the load calibration line of infrared absorption oxygen values F versus the SIMS average O^-/Si^- ratios S for the standards as follows:

$$F = mS + b \tag{1}$$

where m and b are calculated from the assigned infrared absorption oxygen values F_1 and F_2 of the two calibration standards and S_1 and S_2 are the measured average ratios of the O^-/Si^- for the two calibration standards.

$$m = \frac{(F_1 - F_2)}{(S_1 - S_2)} \tag{2}$$

$$b = \frac{(F_1S_2 - F_2S_1)}{(S_2 - S_1)} \tag{3}$$

12.1.2 Convert the SIMS O^-/Si^- ratios S_u for each test specimen and for the float zone specimen to the infrared absorption equivalent value F_u based on the calibration line (Eq 1) and as illustrated in Fig. 1.

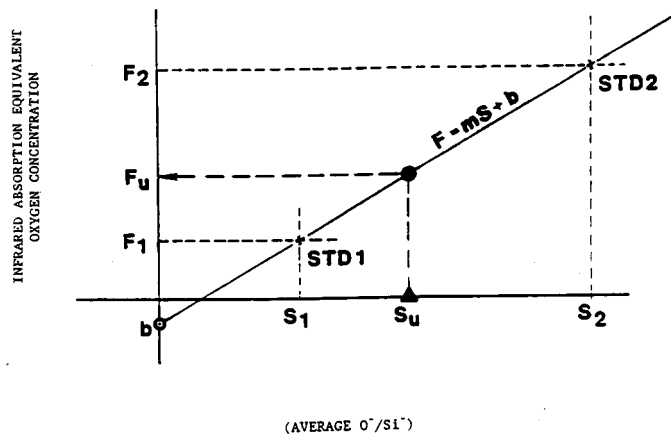
12.2 *Load Factor Calibration Procedure:*

12.2.1 Calculate the calibration load factors, $LF_1 = F_1/S_1$ and $LF_2 = F_2/S_2$, of the assigned infrared absorption oxygen F to the S ratio O^-/Si^- from the standard samples using the average ratios of the O^-/Si^- from the calibration standards.

12.2.2 Calculate the average load factor, LF_{avg} , as follows:

$$LF_{\text{avg}} = \frac{(LF_1 + LF_2)}{2} \tag{4}$$

12.2.3 Convert the SIMS O^-/Si^- ratios S_u for each test specimen to the infrared absorption equivalent value F_u by



SIMS AVERAGE RATIO OF OXYGEN COUNT RATE TO SILICON COUNT RATE
FIG. 1 Load Line Calibration for SIMS Bulk Oxygen Analysis

multiplying the S_u by the average load factor LF_{avg} derived from the calibration standards, as follows:

$$F_u = S_u \times LF_{avg} \quad (5)$$

13. Report

13.1 Report the following information:

13.1.1 The instrument used, the operator, and the date of the measurements,

13.1.2 Identification of test and standard specimens,

13.1.3 Calibration procedure used,

13.1.4 The infrared absorption equivalent oxygen values for the test specimen and the float zone silicon specimen, and

13.1.5 The relative standard deviations (RSD percent) of the oxygen values for the test specimen and the float zone silicon specimen.

14. Precision

14.1 The precision was estimated for both the load line

calibration and average load factor calibration procedures using 191 samples from one silicon wafer and measured in 191 different loads over a two-month period. The one standard deviation was 0.38 ppma (FT-IR equivalent to Test Method F 1188) for both methods for an oxygen level of 18 ppma (Test Method F 1188). The annex gives the data.

14.2 The load line and average load line methods to quantification gave equivalent accuracy and precision in the test mentioned in 12.1. The reason one is used versus another is more conceptual than empirical if the oxygen values for the standards bracket the oxygen values of the test specimens.

15. Keywords

15.1 FTIR; oxygen; secondary ion mass spectrometry; silicon

ANNEX

(Mandatory Information)

A1. ANALYSIS OF DATA FROM THE MULTI-INSTRUMENT EXPERIMENT

A1.1 The precision estimate was taken from data generated in one laboratory using three instruments and ten instrument operators. All the instruments were CAMECA IMS 3f or 4f SIMS instruments. The test specimens were all taken from one silicon wafer that was lightly doped and verified by infrared absorption spectroscopy to have uniform interstitial oxygen levels across the central region where the test specimens were taken. The test specimens were chemically mechanically polished on one side. The standards had oxygen levels that bracketed the expected level of oxygen of the test specimen.

A1.2 The measurements were made in 191 loads over a two-month period.

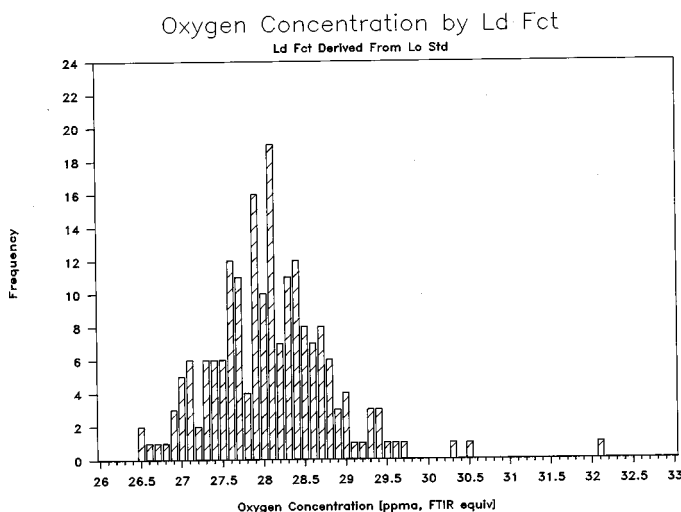


FIG. A1.1 Frequency Distribution of SIMS Measured Oxygen Using the Load Line Calibration Method

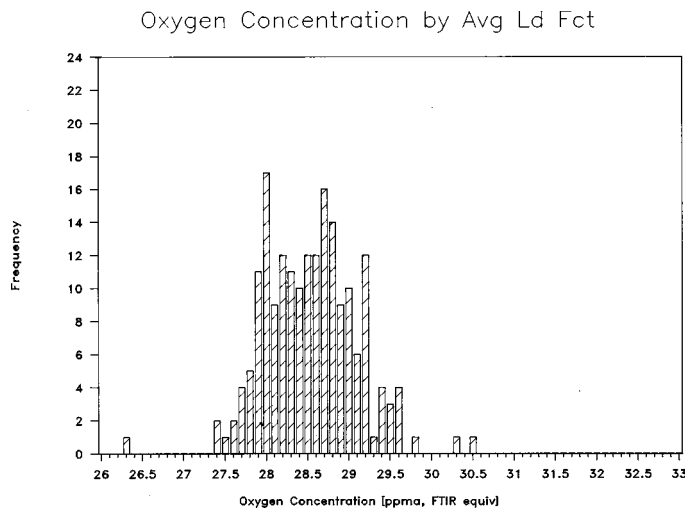


FIG. A1.2 Frequency Distribution of SIMS Measured Oxygen Using the Average Load Factor Calibration Method

A1.3 Both the load line calibration and the average load factor calibration methods were used to convert the SIMS data to infrared absorption equivalent oxygen. The load line calibration method gave an average oxygen level of 18.64 ppma (Test Method F 1188), a one standard deviation of 0.39 ppma, and a relative standard deviation of 2.09 %. A frequency distribution is shown in Fig. A1.1. The average load factor calibration method gave an average oxygen level of 18.61 ppma (Test Method F 1188), a one standard deviation of 0.365 ppma, and a relative standard deviation of 1.97 %. A frequency distribution is shown in Fig. A1.2.

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