

SEMI MF2139-1103 (Reapproved 1110) TEST METHOD FOR MEASURING NITROGEN CONCENTRATION IN SILICON SUBSTRATES BY SECONDARY ION MASS SPECTROMETRY

This standard was technically approved by the global Silicon Wafer Committee. This edition was approved for publication by the global Audits & Reviews Subcommittee on August 27, 2010. Initially available at www.semi.org in October 2010. Originally published by ASTM International as ASTM F2139-01; previously published November 2003.

1 Purpose

1.1 Secondary ion mass spectrometry (SIMS) can measure in un-annealed, polished Czochralski (CZ) silicon substrates the nitrogen concentration that may be intentionally introduced to: (1) increase the V/G tolerance for grown-in defects free region, where V is the pull rate and G is the crystal temperature gradient at the solid-liquid interface;¹ (2) increase the void-free denuded zone depth and the bulk micro-defect density after annealing in hydrogen or argon;^{2,3} (3) reduce the crystal originated particle (COP) size after annealing;^{2,3} or (4) enhance the precipitation of oxygen in epitaxial substrates under reduced temperature processing.⁴

1.2 SIMS can measure total bulk nitrogen in CZ-silicon, whereas infrared spectroscopy is negatively affected by the chemical state in oxygen-containing silicon.⁵ In addition, SIMS can measure the total bulk nitrogen in $p^+(B)$ and $n^+(Sb)$ substrates used for epitaxial silicon, whereas infrared spectroscopy cannot due to free electron absorption interferences.

1.3 SIMS can measure in un-annealed, polished Float-zoned (FZ) silicon substrates the nitrogen concentration that may be introduced to strengthen low oxygen substrates.

1.4 The SIMS method can be used for process check of crystal doping, and for research and development.

2 Scope

2.1 This test method covers the determination of total nitrogen concentration in the bulk of single crystal substrates using secondary ion mass spectrometry (SIMS).^{6,7}

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 boron, antimony, arsenic, and phosphorus.

2.3 This test method is for bulk analysis where the nitrogen concentration is constant with depth.

2.4 This test method can be used for silicon in which the nitrogen content is 1×10^{14} atoms/cm³ or greater. The detection capability depends upon the SIMS instrumental nitrogen background and the precision of the measurement.

2.5 This test method is complementary to infrared spectroscopy, electron paramagnetic resonance, deep level transient spectroscopy, and charged particle activation analysis.⁸ The infrared spectroscopy method detects nitrogen

1 Iida, M., Kusaki, W., Tamatsuka, M., Iino, E., Kimura, M., and Muraoka, S., "Effects of Light Element Impurities on the Formation Grown-In Defects Free Region of Czochralski Silicon Single Crystal," in *Defects in Silicon III*, edited by W. M. Bullis, W. Lin, P. Wagner, T. Abe, and S. Kobayashi, The Electrochemical Society Proceedings Series PV99-1, The Electrochemical Society, Pennington, NJ, 1999: pp. 499–510.

2 Tamatsuka, M., Kobayashi, N., Tobe, S., and Masui, T., "High Performance Silicon Wafer with Wide Grown-in Void Free Zone and High Density Internal Gettering Site Achieved via Rapid Crystal Growth with Nitrogen Doping and High Temperature Hydrogen and/or Argon Annealing," *ibid.*, pp. 456–467.

3 Minami, T., Takeda, R., Saito, H., Hirano, Y., Suzuki, O., Nitta, S., Kashima, K., and Matsushita, Y., "Influence of Void Size on the Formation of Defect Free Regions in Hydrogen Annealed CZ Silicon Wafers," ECS Extended Abstract No. 514, 197th Meeting of the Electrochemical Society, The Electrochemical Society, Pennington, NJ, 2000.

4 Shimura, F., and Hockett, R. S., "Nitrogen effect on oxygen precipitation in Czochralski silicon," *Appl. Phys. Lett.*, (1986): pp. 224–226.

5 Abe, T., Kikuchi, K., Shirai, S., and Muraoka, M., in *Semiconductor Silicon 1981*, edited by H. R. Huff, R. J. Kriegler and Y. Takeishi, The Electrochemical Society, Pennington, NJ, 1981: pp. 54–71.

6 Hockett, R. S., Evans, Jr., C. A., and Chu, P. K., "The SIMS Measurement of Nitrogen in Nitrogen-Doped CZ-Silicon," in *Secondary Ion Mass Spectrometry SIMS VI*, edited by A. Benninghoven, A. M. Huber, and H. W. Huber, John Wiley & Sons, New York, 1988: pp. 441–444.

7 Hockett, R. S. and Sams, D. B., "The Measurement of Nitrogen in Silicon Substrates by SIMS," in *High Purity Silicon VI*, edited by C. L. Claeys, P. Rai-Choudhury, M. Watanabe, P. Stallhofer, and H. J. Dawson, ECS Proceedings Vol. PV 2000-17, The Electrochemical Society, Pennington, NJ, 2000: pp. 584–595.

in specific vibrational states, rather than total nitrogen, and is limited to silicon with doping concentrations less than about 1×10^{17} atoms/cm³. The charged particle activation analysis detection capability is limited by an interference from boron.

NOTICE: This standard does not purport to address safety issues, if any, associated with its use. It is the responsibility of the users 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 Nitrogen on or in the surface silicon oxide can interfere with the bulk nitrogen measurement.

3.2 Nitrogen adsorbed on the test specimen surface from the SIMS instrument chamber and fixtures interfere with the bulk nitrogen measurement by raising the background signal. The vacuum quality of the SIMS instrument can be used to minimize this.

3.3 Nitrogen in the SIMS primary Cs beam may be implanted into the silicon specimen as CsN and thereby increase the nitrogen background concentration. A primary beam mass filter may be used to reduce this interference, but in this case, a reduced Cs beam current density is needed to maximize the sputter rate.

3.4 Anomalous nitrogen intensity spikes can interfere with the averaging of signal intensity which is assumed to be random (see ¶ 6.9).

3.5 Carbon introduces an interference as $^{12}\text{C}^{30}\text{Si}$ at mass 42 for detecting nitrogen as $^{14}\text{N}^{28}\text{Si}$. This can be avoided by detecting the nitrogen as $^{14}\text{N}^{29}\text{Si}$ at mass 43, but the signal rate is reduced greatly, about a factor of 20 when the minor isotope of silicon is used. There are methods to measure the carbon interference, and subtract this interference. One of the methods to measure the carbon interference can have its own interference from high levels of boron dopant.

3.6 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.

3.7 The bias 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 wafers.

3.8 Variability of nitrogen in the calibration specimen can limit the measurement precision.

3.9 Variability from the calibration measurement may increase the measurement precision of the test specimen.

3.10 Bias in the assigned nitrogen concentration of the calibration specimen can introduce bias into the SIMS measured nitrogen.

3.11 Thermal processing above 800°C of the silicon substrate may cause diffusion of the nitrogen, so that the nitrogen concentration is not constant with depth, a key assumption of this test method.

3.12 Thermal processing of the silicon substrates in a nitrogen-containing ambient can introduce large amounts of nitrogen from the ambient deep into the silicon crystal.⁶

4 Referenced Standards and Documents

4.1 ASTM Standards⁹

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.

8 Stein, Herman J., "Nitrogen in Crystalline Si," in Materials Research Society Symposia Proceedings Vol. 59, *Oxygen, Carbon, Hydrogen and Nitrogen in Crystalline Silicon*, edited by J. C. Mikkelsen, Jr., S. J. Pearton, J. W. Corbett, and S. J. Pennycook, Materials Research Society, Pittsburgh, PA, 1986: pp. 523–535.

9 American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, Pennsylvania 19428-2959, USA. Telephone: 610.832.9585; Fax: 610.832.9555; <http://www.astm.org>

5 Terminology

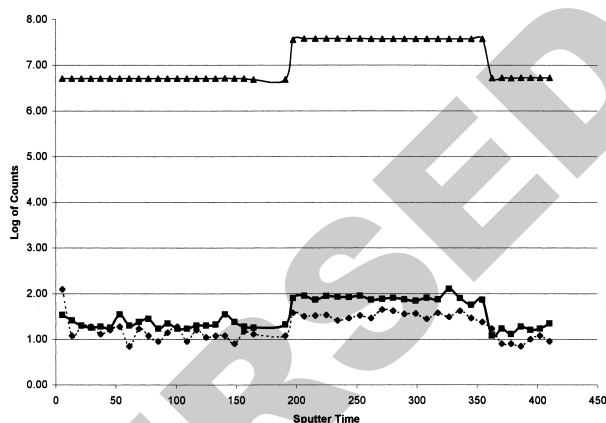
5.1 *Definitions* — All terms in this test method are in accordance with those given in ASTM E673.

6 Summary of Test Method

6.1 SIMS is utilized to determine the bulk concentration of nitrogen in single crystal silicon substrate. Specimens of single crystal silicon (one 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 sample is analyzed using a cesium (Cs) primary ion beam and negative ion spectrometry of $^{14}\text{N}^{28}\text{Si}$, or $^{15}\text{N}^{28}\text{Si}$, depending upon the nitrogen isotope in the calibration sample, to determine a relative sensitivity factor (*RSF*) of nitrogen in silicon.

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 nitrogen background. The amount of time required for this pre-analysis sputtering depends upon the instrumentation and the desired background nitrogen concentration.



NOTE: Top curve (▲) Mass 30 (^{30}Si); middle curve (■) Mass 42 ($^{14}\text{N}^{28}\text{Si}$), bottom curve (◆) Mass 40 ($^{12}\text{C}^{28}\text{Si}$)

Figure 1
SIMS Signals in Nitrogen-Doped Silicon, Log Scale

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 nitrogen contribution from the sample surface. Secondly, this technique allows the determination of both the instrumental nitrogen background and the real bulk nitrogen concentration in each test specimen measurement without the use of a separate blank specimen, and due to averaging is capable of separating the bulk nitrogen from the instrumental nitrogen even if the bulk nitrogen is less than the instrumental nitrogen.¹⁰

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 ion of $^{14}\text{N}^{28}\text{Si}$ is 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 (^{28}Si , ^{29}Si , ^{30}Si , or a dimer such as $^{30}\text{Si}_2$) 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

¹⁰ 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.