

SEMI MF1630-1107 (Reapproved 0912) TEST METHOD FOR LOW TEMPERATURE FT-IR ANALYSIS OF SINGLE CRYSTAL SILICON FOR III-V IMPURITIES

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NOTICE: This Document was reapproved with minor editorial changes.

1 Purpose

- 1.1 Electronic grade polysilicon producers and users rely on low temperature Fourier transform infrared (LTFT-IR) spectroscopy to evaluate polysilicon for quality assurance and research purposes.
- 1.2 LTFT-IR spectroscopy identifies and quantitates boron, phosphorus, aluminum, arsenic, indium, antimony, and gallium.
- 1.3 LTFT-IR spectroscopy can be applied to FZ, CZ, or other single crystal silicon (either doped or undoped) up to the concentration limits given in § 2.2.
- 1.4 The measurement of carbon in silicon at low temperature can be accomplished concurrently in accordance with SEMI MF1391. The carbon can be measured at lower concentrations at <15 K than is possible at room temperature because the two-phonon band transmission is increased by a factor of two allowing greater throughput to the detector that results in an increased signal to noise ratio. Also the carbon adsorption band narrows from a full width half maximum (FWHM) of 5 to 6 cm^{-1} to a FWHM of 2.5 to 3.0 cm^{-1} at these low temperatures.

2 Scope

- 2.1 This Test Method covers the determination of electrically active boron, phosphorus, arsenic, aluminum, antimony, and gallium concentration in single crystal silicon.
- 2.2 This Test Method can be used for silicon in which the impurity/dopant concentrations are between 0.01 and 5 ppba for each of the electrically active elements.
- 2.3 The concentration for each impurity/dopant can be obtained by application of Beer's Law. Calibration factors are given for each element.

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 The sample specimen must be colder than 15 K for measurement of electrically active species. If the sample specimen is mounted on a cold finger, care must be taken to obtain good contact between the sample specimen and the cold finger for efficient heat transfer. The oxygen absorption lines at 1136 cm^{-1} and 1128 cm^{-1} are sensitive to temperature and can be used to determine the specimen temperature.¹ When the sample specimen is less than 15 K the net absorbance at 1136 cm^{-1} is three times larger than the net absorbance at 1128 cm^{-1} . A ratio of greater than three is obtained for temperatures below 15 K.
- 3.2 Without sufficient incident white light the compensated donors and acceptors will not absorb. Therefore, the white light intensity must be great enough to completely neutralize all the compensated donors and acceptors. The intensity of the white light necessary must be determined for each system. The user should increase the intensity of the white light until further increase in intensity no longer affects the area/height of the electrically active impurity/dopant peaks.

¹ Rome, J. J. "Calibration Relationships for Optically Measuring the Concentrations of Boron, Gallium and Indium in Silicon." Thesis, School of Engineering, Air Force Institute of Technology (1982): pp. 46–47.

3.3 Water vapor absorption interferes with the measurement of several peaks. Consequently, the background spectrum should be collected at least daily. The entire light path, including the sample chamber, must be purged to remove moisture. Special care should be taken whenever a sample specimen is changed so that the moisture level in the sample chamber or elsewhere in the light path is not affected.

3.4 Oxygen level in Czochralski silicon can be high enough to exhibit thermal donor absorption lines. These lines fall between 400 cm^{-1} and 550 cm^{-1} and can interfere with aluminum (473 cm^{-1}), gallium (548 cm^{-1}), and occasionally arsenic (382 cm^{-1}). Thermal donors can be removed by annealing the sample specimen.

3.5 Multiple internal reflections can produce a secondary interferogram and baseline oscillations. Changing the sample specimen thickness, the surface preparation, or the resolution can eliminate the secondary interferogram and the baseline oscillation.

3.6 High antimony levels interfere with the 320 cm^{-1} boron absorption line. Antimony's strongest absorption line is 293 cm^{-1} , but a secondary absorption line occurs at 320 cm^{-1} .

4 Referenced Standards and Documents

4.1 SEMI Standards and Safety Guidelines

SEMI M59 — Terminology for the Silicon Technology

SEMI MF723 — Practice for Conversion Between Resistivity and Dopant Density for Boron-Doped, Phosphorus-Doped, and Arsenic-Doped Silicon

SEMI MF1391 — Test Method for Substitutional Atomic Carbon Content of Silicon by Infrared Absorption

SEMI MF1723 — Practice for Evaluation of Polycrystalline Silicon Rods by Float-Zone Crystal Growth and Spectroscopy

4.2 ASTM Standards²

ASTM E131 — Standard Terminology Relating to Molecular Spectroscopy

ASTM E168 — Standard Practices for General Techniques of Infrared Quantitative Analysis

ASTM E177 — Standard Practices for Use of the Terms Precision and Bias in ASTM Test Methods

ASTM E275 — Standard Practice for Describing and Measuring the Performance of Ultraviolet, Visible, and Near-Infrared Spectrophotometers

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

5 Terminology

5.1 General definitions for terms related to infrared absorption spectroscopy are found in ASTM E131.

5.2 Acronyms, terms, and symbols relating to silicon technology, including those appropriate to infrared spectroscopic analysis of impurities in silicon, are found in SEMI M59.

6 Summary of Test Method

6.1 A sample specimen of single crystal silicon is cooled to less than 15 K. Under these conditions the number of free carriers becomes negligibly small and the IR spectrum of the sample exhibits a series of absorption bands that are characteristic for each shallow impurity species.³

6.2 The sample specimen is illuminated with an incident white light source to flood the silicon with photons of greater energy than the silicon band gap to allow neutralization of compensated impurities.⁴

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>

³ Kolbesen, B. O. "Simultaneous Determination of the Total Content of Boron and Phosphorus in High-Resistivity Silicon by IR Spectroscopy at Low Temperature." *Appl. Phys. Lett.* 27 (1975): pp. 353–355.

⁴ Baber, S. C. "Net and Total Shallow Impurity Analysis of Silicon by Low Temperature Fourier Transform Infrared Spectroscopy." *Thin Solid Films* 72 (1980): pp. 201–210.

6.3 An infrared beam is directed through the sample specimen and a transmitted spectrum is collected. The spectrum is ratioed to the background spectrum and then converted to an absorbance spectrum.

6.4 Baselines are constructed at one of the characteristic absorption bands for each impurity/dopant to be measured.

6.5 The areas of the absorption bands are measured.

6.6 Concentrations of each impurity/dopant are calculated in accordance with Bouguer-Beer's Law with factors given in this Test Method.

7 Apparatus and Materials

7.1 *Cryostat* — To maintain the sample specimen temperature below 15 K. This cryostat may be liquid helium immersion, exchange gas, or closed cycle refrigeration.

7.2 *Sample Specimen Holder* — Constructed of high heat conductivity metal with an aperture(s) to block any of the infrared beam except that passing through the sample.

NOTE 1: The procedure of § 11 is based on the assumption that the cryostat can accommodate and utilizes a multisample holder.

7.3 *White-Light Source* — As shown in Figure 1.

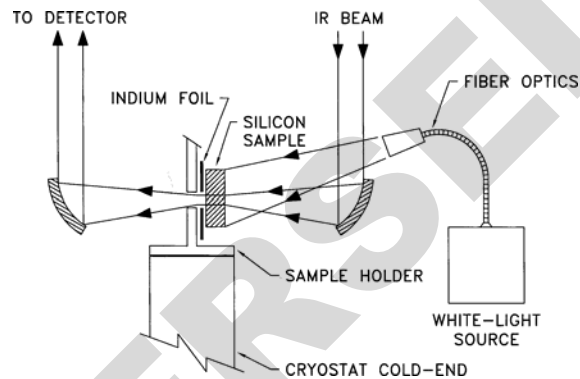


Figure 1
Sample Holder and Optics Suitable for Illumination with White Light via Fiber Optics

7.4 *Fourier Transform Infrared (FT-IR) Spectrometer* — Must be equipped with suitable optics and detector for use in the region from 250 cm^{-1} to 1300 cm^{-1} .

7.4.1 The spectrometer shall be capable of at least 1 cm^{-1} resolution. The resolution shall be sufficient so that after zero-filling, apodization, and Fourier transformation the phosphorus adsorption band at 315.9 cm^{-1} has a FWHM not to exceed 1.1 cm^{-1} .

7.4.2 The detector shall be sufficiently sensitive to provide a reasonable signal to noise response in the desired spectral region. A room temperature DTGS with a CsI window suffices for the higher concentrations of elements in this test method. However, a zinc-doped germanium Ge:Zn detector operated at 4.4 to 10 K is preferred to give a signal-to-noise ratio sufficient to properly determine the elements at the lower concentrations and for improved precision.

7.5 *Calcium Fluoride Crystal (CaF₂)* — Cut to nominal thickness of 5 mm.

8 Sample Preparation

8.1 If the samples are from polysilicon, they must first be converted to single crystal in accordance with SEMI MF1723 or other established means.

8.2 Sample specimen shall be cut and polished to fit the sample specimen holder. The surface may be mechanically or chemically polished. Each sample specimen shall have a thickness variation of less than 1% of overall thickness.