



Standard Test Method for Low Temperature FT-IR Analysis of Single Crystal Silicon for III-V Impurities¹

This standard is issued under the fixed designation F 1630; 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.

1. Scope

1.1 This test method covers the determination of electrically active boron, phosphorus, arsenic, aluminum, antimony, and gallium concentration in single crystal silicon.

1.2 This test method can be used for silicon in which the impurity/dopant concentrations are between 0.01 ppba and 5.0 ppba for each of the electrically active elements.

1.3 The concentration for each impurity/dopant can be obtained by application of Beer's Law. Calibration factors are given for each element.

1.4 *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:

- E 131 Terminology Relating to Molecular Spectroscopy²
- E 168 Practices for General Techniques of Infrared Quantitative Analysis²
- E 177 Practices for Use of the Terms Precision and Bias in ASTM Test Methods³
- E 275 Practice for Describing and Measuring the Performance of Ultraviolet, Visible, and Near-Infrared Spectrophotometers²
- F 723 Practice for Conversion Between Resistivity and Dopant Density for Boron-Doped and Phosphorus-Doped Silicon⁴
- F 1241 Terminology of Semiconductor Technology⁴
- F 1391 Test Method for Substitutional Atomic Carbon Content of Silicon by Infrared Absorption⁴
- F 1723 Practice for Evaluation of Polycrystalline Silicone Rods by Float-Zone Crystal Growth and Spectroscopy⁴

3. Terminology

3.1 Many of the terms associated with this test method can be found in Terminology E 131.

3.2 Definitions for terms related to silicon materials technology are found in Terminology F 1241.

3.3 Definitions:

3.3.1 *electrically active elements, n*—dopants or impurities in silicon that are members of either Group III (boron, aluminum, gallium, and indium) or Group V (phosphorus, arsenic, antimony and bismuth) of the periodic table.

3.4 Definitions of Terms Specific to This Standard:

3.4.1 *background spectrum*—a spectrum obtained without any sample specimen in the IR beam.

3.4.2 *baseline*—a straight line interpolation between points on either side of the absorption peak in the absorbance spectrum.

3.4.3 *FT-IR*—acronym for Fourier transform infrared (spectrometer).

3.4.4 *FWHM*—acronym for the full width of an absorption peak expressed in cm^{-1} at half its absorbance magnitude as measured from the baseline.

3.4.5 *LTFT-IR*—acronym for low temperature, Fourier transform infrared (spectrometer).

3.4.6 *sample spectrum*—the ratio of a spectrum obtained with the test specimen in the IR beam to a background spectrum.

4. Summary of Test Method

4.1 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 (1).⁵

4.2 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 (2).

4.3 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.

⁵ The boldface numbers in parentheses refer to the list of references at the end of this test method.

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

Current edition approved Dec. 10, 2000. Published January 2001. Originally published as F 1630-95. Last previous edition F 1630-95.

² *Annual Book of ASTM Standards*, Vol 03.06.

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

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

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

4.5 The areas of the absorption bands are measured.

4.6 Concentrations of each impurity/dopant are calculated in accordance with Bouguer-Beer's Law with factors given in this test method.

5. Significance and Use

5.1 LTFT-IR spectroscopy identifies and quantitates boron, phosphorus, aluminum, arsenic, indium, antimony, and gallium.

5.2 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 1.2.

5.3 The measurement of carbon in silicon at low temperature can be accomplished concurrently in accordance with Test Method F 1391. 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 FWHM of 5 to 6 cm^{-1} to a FWHM of 2.5 to 3.0 cm^{-1} at these temperatures.

5.4 Electronic grade polysilicon producers and users rely on LTFT-IR spectroscopy to evaluate polysilicon for quality assurance and research purposes.

6. Interferences

6.1 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 (3). 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.

6.2 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.

6.3 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.

6.4 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.

6.5 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.

6.6 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} .

7. Apparatus and Materials

7.1 *Cryostat*, which maintains the sample specimen temperature below 15 K is required. 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.

7.3 *White-light Source*, (see Fig. 1).

7.4 *Fourier Transform Infrared Spectrometer (FT-IR)*, 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 must be capable of at least 1.0 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} will have 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 will suffice for the higher concentrations of elements in this test method. However, a zinc-doped germanium Ge:Zn detector operated at 4.4 to 10.0 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 Practice F 1723 or other established means.

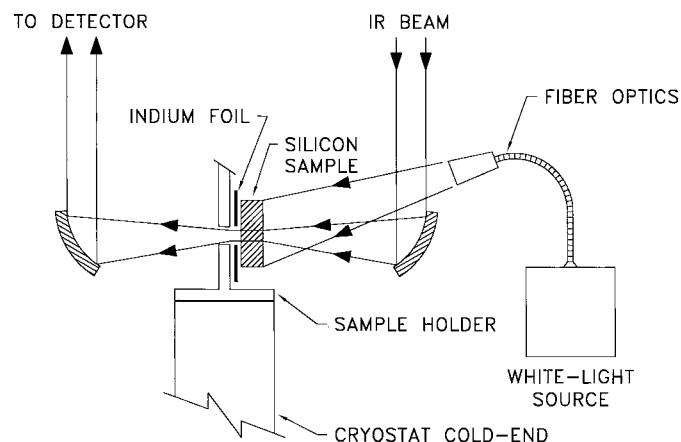


FIG. 1 Sample Holder and Optics Suitable for Illumination with White-light via Fiber-optics

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

8.3 For measurement of electrically active impurities, the sample specimens should be 3 to 5-mm thick with high purity silicon (>2000 Ω-cm) to allow for lower detection limits. Sample thicknesses between 5 and 20 mm may be used in cases where impurity levels to be measured are below 0.01 ppba. The sample specimens should be 1 to 2-mm thick for heavily doped silicon (<10 Ω-cm) to allow greater transmission of the infrared radiation.

9. Reference Specimens

9.1 One or more silicon samples that contains impurities in the range of the samples to be tested should be classified as reference specimens. These reference specimens should be analyzed repeatedly and periodically according to this test method. Compare the results obtained to previous data to establish that the measurement process is in control.

10. Testing of the Instrument

10.1 Establish FT-IR instrument stability by checking the 100 % *T* baseline.

10.1.1 Collect and store two background spectra sequentially through an open aperture of the cryostat specimen holder.

10.1.2 Ratio these two spectrum to obtain a transmittance spectrum.

10.1.3 Examine the spectrum from 1200 cm⁻¹ to 250 cm⁻¹. The spectrum should be 100 ± 0.5 % *T* over this range. Proceed only if this criterion is met, otherwise correct instrumental instability.

10.2 Check for detector linearity (4).

10.2.1 Examine one of the two single-beam (unratioed) spectrum obtained in 10.1.1 for nonzero response at wavenumbers where the detector is known to have zero response (below 200 cm⁻¹ for the zinc doped germanium detector with a CsI window). The observed response in this region should be less than 1.0 % of the maximum response over the 1200 to 250 cm⁻¹ region. If not, take corrective action before proceeding.

10.2.2 Alternately, collect a spectrum with a CaF₂ crystal wafer, 5 mm-thick, in the IR beam. Ratio this spectrum relative to one of the background spectrum obtained in 10.1.1 to obtain a transmittance spectrum. CaF₂ is totally opaque below 800 cm⁻¹. The spectrum must give 0.0 ± 0.5 % *T* from 800 to 250 cm⁻¹. If not, take corrective action before proceeding.

11. Procedure

11.1 This procedure assumes the cryostat can accommodate a multi-sample holder. Measure the thicknesses to ±0.02 mm and load all the sample specimen to be examined on to the sample specimen holder leaving one open slot. Mount them in the cryostat and cool the samples to less than 15 K.

11.2 Set instrumental parameter to give a resolution of 1.0 cm⁻¹ or better.

11.3 Collect 1000 scans of an empty sample chamber slot and use this as the background spectrum.

11.4 Move the first sample specimen into position.

11.5 Turn on the incident white-light source and ensure that

the sample specimen is fully illuminated with white light and properly aligned relative to the IR beam (see Fig. 1).

11.6 Collect a minimum of 300 scans of the sample. Zero-fill, apodize, and transform the interferogram into a spectrum and then ratio to the background spectrum. Covert to an absorbance spectrum and use as the sample specimen spectrum. Store this spectrum and subsequent ones for further manipulation and measurement of the peak areas.

11.7 Make sure that the first specimen is a reference specimen which serves as an audit to ensure that the entire instrument is performing correctly.

11.8 Repeat 11.4 through 11.6 for each sample specimen.

12. Data Reduction

12.1 This test procedure requires the measurement of the areas of the absorption bands before calculation of the concentration of each element. The absorption bands are very sharp, especially for the Group V elements, and therefore peak height measurements are difficult to reproduce from instrument to instrument. Use of peak areas greatly reduces this variability.

12.1.1 Establish baselines for each peak before measurement of the area. Only the area above the established baseline is used in the calculations. Several algorithms are available on various commercial FT-IR instruments to obtain the desired baseline corrected areas. The following is one suggested method:

12.1.1.1 Retrieve the sample absorbance spectrum from the computers storage disk. With the wavenumber expand commands available, zoom in on the region of the absorption band(s) of interest. Expand until this region is only slightly larger than the baseline limit regions given in Table 1.

12.1.1.2 Employ the interactive baseline correction routine to bring the spectral baseline to coincide with the 0.0 absorbance line. Refer to Table 1 for the upper and lower wavenumber regions for guidance in adjusting the baseline. Expand in the absorbance scale as necessary to improve the observation of the noise and fine features of the spectrum in order to provide the best placement of the baseline. Apply only linear corrections with the fit of the straight line through the points on both sides of the absorption peak(s). Note that the peaks for boron and phosphorus are very close together and thus only one baseline is obtained surrounding both peaks. Fig. 2 and Fig. 3 show spectrum before and after, respectively, baseline correction for boron and phosphorus spectral region.

TABLE 1 Peak Location, Baseline and Intergration Limits, and Calibration Factors

Element	Peak cm ⁻¹	Baseline Limits		Integr Limits		Factor ^A f(mm-cm)
		Upper	Lower	Upper	Lower	
Aluminum (Al)	473.2	479	467	475.2	471.2	32.7
Antimony (Sb)	293.6	296	289	295.1	292.1	10.6
Arsenic (As)	382.0	385	379	383.5	380.5	8.96
Boron (B)	319.6	323	313	321.5	318.0	9.02
Gallium (Ga)	548.0	552	544	549.5	546.5	42.4
Indium (In)	1175.9	1181	1169	1177.4	1174.4	244.0
Phosphorus (P)	316.0	323	313	317.5	314.5	4.93

^A The factors given here do not all have the same degree of certainty. The factors for boron, phosphorus, and arsenic are believed to be correct to < ±10 %. The other factors should be considered approximations and used for estimations only. A discussion of the origin of these factors is given in Appendix X1.