National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material 2551

Oxygen Concentration in Silicon Standard

SRM Set No.:

This Standard Reference Material (SRM) is intended for calibration of infrared spectrophotometers used to measure the 1107 cm^{-1} interstitial oxygen peak in silicon. Certified oxygen concentrations are given for low, medium, and high oxygen level Czochralski specimens. Each SRM unit is a set of four specimens comprising a float-zone specimen [with minimal oxygen concentration less than 0.1 parts per million atomic (ppma)], and the three Czochralski specimens which cover a range of roughly 8.5-17 mg/kg (15-30 ppma - (IOC-88)). [1-3] Each specimen has been individually measured and bears an SRM set number and a letter identification for each oxygen level (L, M, or H). Each specimen is nominally 25-mm square and 2-mm thick and has been polished on both sides. The specimen materials, which were obtained from Wacker Siltronic, Portland, OR, have resistivities greater than 3 ohm•cm.

CERTIFIED VALUES OF OXYGEN CONCENTRATION

Units	Low Level (L)	Medium Level (M)	High Level (H)
ppma	_____	_____	_____
mg/kg	_____	_____	_____
10^{17} atoms/cm^3	_____	_____	_____

UNCERTAINTY OF CERTIFICATION (ppma)*

Low Level (L)	Medium Level (M)	High Level (H)
0.029 (0.17 %)	0.030 (0.13 %)	0.031 (0.12 %)

NON-CERTIFIED THICKNESS VALUES (mm)

Float-Zone	Low Level	Medium Level	High Level
_____	_____	_____	_____

* The stated uncertainty is the 2σ precision with which the oxygen scale obtained from the eight-specimen calibration set is reproduced in each of the SRM sets. This does not include the uncertainty of the absolute values of oxygen for the calibration specimens. The certified portion of the SRM specimen is the central 6-mm diameter circle. Thickness values are not certified and are given as useful information only. To convert from ppma to mg/kg, multiply by 0.56967; to convert from ppma to atoms/cm^3, multiply by 0.49939×10^{17}.

Certification measurements were made by B.G. Rennex and sample preparation was done by J.M. Thomas, both of the NIST Semiconductor Electronics Division. The work was supported by the Materials Technology Group of this Division. Review of the statistical analyses was performed by J.J. Filliben of the NIST Statistical Engineering Division.

The preparation, certification, and issuance of this SRM were coordinated through the Standard Reference Materials Program by N.M. Trahey.

Gaithersburg, MD 20899
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Certification Apparatus: Power spectra were measured in the wavenumber vicinity of 1107 cm^{-1}, the location of the room temperature peak for interstitial oxygen, by a Fourier Transform Infrared (FTIR) spectrophotometer. The detector system comprised a gold-plated light-cone and a 2 mm-diameter, room temperature deuterated-triglycine-sulfate (DTGS) detector. The beam diameter at the specimen was 5 mm, and it was located at the specimen center to within $\pm$ 1 mm. The wavenumber resolution was 4 cm^{-1}. During the measurement, the sample chamber of the FTIR instrument was maintained at a temperature of 27.8 $\pm$ 0.5 °C. No detectable spurious blackbody radiation was found. [4]

Certification Measurement Protocol: In general, a certification measurement determination consisted of the following steps:

1a. Two SRM sets of four specimens each were mounted on a sample holder, along with a control specimen of known, medium oxygen concentration. After specimen loading, it was necessary to wait about an hour for transient thermal effects to reach steady state. Then, power spectra were measured in a test run in the following sequence: open beam; control specimen; first set (float-zone, low oxygen, medium oxygen, and high oxygen); open beam; control specimen; and second set (float-zone, low oxygen, medium oxygen, and high oxygen).

1b. Each power spectrum in the above test sequence was based on 90 scans, which took about five minutes, and at least four repeats of this sequence were made for each run. Thus, a certified oxygen value is computed using the average of four 5-min measurements spaced over a period of roughly 8 h.

2. The transmission spectrum for each specimen was calculated as the ratio of the specimen power spectrum over the open-beam power spectrum.

3. Absorption (coefficient) spectra were calculated for each test specimen and for each float-zone specimen. [1] The float-zone spectrum was then subtracted from the test specimen spectrum to arrive at the spectrum due to oxygen only.

4. The oxygen peak height was obtained as follows. A Gaussian curve fit to the absorption spectrum was made to determine the peak height and wavelength. A baseline was constructed, and the baseline value at the peak wavelength was subtracted from the peak height to calculate the net oxygen peak height.

5. Data on the control specimen were used to make a linear compensation for instrument drift over time; this improved instrument reproducibility by about a factor of three. Measurements were made on a separate four-specimen set (comprising a float-zone specimen and specimens at three oxygen levels) between each SRM run. These runs were made using the same procedure, including the use of a control specimen, as for the SRM runs, and they provided an estimate of the random uncertainty, or reproducibility, of the instrument over the entire period of SRM measurements.

Calibration of the NIST FTIR instrument was based on measurements of a subset of eight reference specimens from a larger set of specimens previously used in an international study called the Grand Round Robin (GRR). [2,3] The bias of the eight-specimen subset with respect to the complete GRR specimen set is -0.72%, as established by the GRR data. The measurements made to certify the SRM have been adjusted to eliminate this bias. These calibration measurements allowed a determination of an SRM conversion coefficient (from α to oxygen concentration) specific to the NIST FTIR instrument. The certified SRM oxygen concentration values are based on this SRM conversion coefficient, not on the GRR conversion coefficient. [4,5]

Also, a study was made to ascertain that no additional error was observed when repeated points were taken after a specimen had been removed from and replaced back into the sample holder. Initially, a significant offset occurred due to removal and replacement of a specimen, perhaps because of non-uniformities in the beam and detector at this level of precision. This error was eliminated when a light-cone was used in the detector assembly. [4]

Uncertainties: The SRM uncertainty is based on the precision of the NIST FTIR spectrophotometer and on uncertainties due to non-uniformity of thickness and oxygen concentration over the central 6-mm area of the SRM specimen sampled by the FTIR beam. Standard deviations were estimated for the various contributing factors (all of which are ISO Type A) and added in quadrature. [6] This sum was multiplied by a factor of two to get a 2σ value for the expanded uncertainty. The first contributing factor is instrument reproducibility, as estimated by the standard deviation for data taken on the NIST FTIR for the four-specimen set. The standard deviation of the reproducibility, as determined in a series of measurements independent of and concurrent with the certification measurements, is 0.0115 ppma for all three oxygen levels. The second contributing factor is variability of both thickness and oxygen concentration from one area to another over the specimen surface. The standard deviation for this factor is 0.0051 ppma for low oxygen, 0.0069 ppma for medium oxygen, and 0.0078 ppma for high oxygen specimens. The third contributing factor is variability of oxygen among the float-zone, or "zero-oxygen," SRM specimens. The standard deviation for this variation is 0.007 ppma, for all three oxygen levels.

Adding these three values of standard deviation in quadrature, and multiplying by two, gives the following 2σ estimates of total SRM precision: 0.029 ppma (0.17%) for low oxygen specimens, 0.030 ppma (0.13%) for medium oxygen specimens, and 0.031 ppma (0.12%) for the high oxygen specimens. These values of total SRM precision are intended to be of practical use for current IC industrial requirements. They are much smaller than the uncertainty values of an absolute measurement of oxygen concentration. They are also much smaller than the interlaboratory variability of 2.7% (1σ) from the GRR report, and this interlaboratory variability is an indication of the interlaboratory agreement expected without an SRM. [2,3]

The certified oxygen concentration values are independent of temperature and are internally consistent from any one SRM specimen or set to any other, to within the above-stated total SRM precision. And, if two distinct instruments calibrated by two different SRM sets were to have the same precision as the certifying spectrometer, the agreement between their values for identical specimens would be described by a precision equal to roughly twice the total SRM precision. That is, four separate σ values - one for each SRM and one for each instrument - would be added in quadrature to estimate the total comparison standard deviation.

RECOMMENDED CALIBRATION AND HANDLING INSTRUCTIONS FOR SRM 2551

Calibration Procedure: The detailed procedure for calibration of a user instrument will depend on the particular application. For guidance, a user should refer to standard test methods for measurement of oxygen in silicon. [1,7] More information is contained in the SRM certification report and in documents which explain the SRM experiment and the statistical methodology in greater detail. [4,5,8]

It is recommended that both the open beam and float-zone specimen be measured every time a calibration is made, unless a user can demonstrate that this is unnecessary. Such a demonstration would involve a statistical comparison of results with the open beam and float-zone spectra measured every time against results where this is not the case.

To obtain the best agreement with the certified SRM values, a user must use a 5-mm beam and must locate this beam at the center of the SRM specimen, to within 1 mm. Also, the user should make sure that the temperatures of the specimens to be measured are as close as possible to the temperatures of the SRM specimens. This is because the user calibration factor is temperature dependent even though the certified oxygen value is not. [7] That is, the measured absorption coefficient peak height varies with temperature in this range with a coefficient of 0.0016 K^{-1}, while the actual oxygen concentration remains constant. This means that the certified estimate of oxygen concentration can be used without adjustment even if a user's measurement temperature is different from the value used in the SRM 2551. However, the user must expect his own oxygen conversion coefficient to vary with temperature according to the just-quoted temperature coefficient.

The certified quantity is the interstitial oxygen concentration, OX_{srm}, for the low, medium, and high oxygen specimens. This oxygen concentration is proportional to the height of the 1107 cm^{-1} peak of the absorption coefficient spectrum, with the constant of proportionality being the conversion coefficient. Without an SRM, a user calculates an oxygen value, OX_u, as a product of a measured absorption coefficient peak height and the internationally accepted conversion coefficient, C. [2,3] With the SRM, the instrument conversion coefficient must be adjusted by a calibration factor determined from the calibration. This calibration factor is equal to the ratio, R_u, of (OX_{srm}/OX_u), where OX_{srm} is the certified oxygen value for an SRM specimen, and OX_u is the measured oxygen value for that same SRM specimen using the international value of C.

The subscript j = l, m, or h, identifies each of the three SRM specimens. R_{uj} refers to the three calibration factor values obtained by the user, u, with the three SRM specimens. For the three SRM specimens, the ratios, $R_{uj} = (OX_{srmj}/OX_{uj})$ are the calibration factors for the user instrument, and the products, R_{uj} x C, are the conversion coefficients for the user instrument. These three conversion coefficients may now be used to calculate oxygen values for unknown specimens.

In general, a user should evaluate the three calibration factors for the low, medium, and high level oxygen SRM specimens, but then must choose which value to use in a particular measurement. If the three values are close (e.g. within the reproducibility of the user instrument), the average of all three values should be used. If there are larger differences in the three calibration factors, R_{uj}, the user may use the calibration factor of the SRM specimen with the closest value to that of the unknown specimen. Alternatively, a user can use an interpolation, an example of which is given below. This example is for an unknown specimen with an oxygen value between those of the low and medium level SRM specimens.

Let OX_{ul}, OX_{um}, and OX_x be the user-measured, peak-height values for the low and medium SRM specimens, and for the unknown specimen, respectively. And, let R_{ul} and R_{um} be the previously determined calibration factors for the same SRM specimens. The interpolated value of the calibration factor, R_x, is then:

$$R_x = R_{ul} + (OX_x - OX_{ul})\,(R_{um} - R_{ul}) / (OX_{um} - OX_{ul})$$

The measured value, OX, (for the unknown specimen) of interstitial oxygen concentration, traceable to the SRM, is now:

$$OX = R_x \times OX_x$$

An interpolation in the range between the mid-oxygen specimen and the high-oxygen specimen can be made in an equivalent manner.

Handling Procedures: The SRM specimens are mounted on aluminum templates. Do not touch the polished surfaces of the SRM specimens with the fingers or with any hard or abrasive material. Handle the specimens by holding the aluminum templates. If it should be necessary to remove specimens from these templates, please follow the instructions below:

1. Gradually warm the template to approximately 70 °C or until the mounting wax begins to flow. Carefully remove the specimen with non-metallic tweezers or with a vacuum wand, taking care not to scratch the specimen surface.

2. While the specimen is still warm, flush it with tepid methyl alcohol, or an alternative solvent, until all wax is removed. Clean cotton may be used with the alcohol.

3. After all traces of wax have been removed with the alcohol, wash with a warm solution of liquid detergent and de-ionized water to ensure that all wax residue has been removed. Then, rinse with de-ionized water to remove all traces of detergent.

4. Make a final rinse with methyl alcohol and blow dry with nitrogen to avoid spotting.

5. To replace a specimen into the aluminum templates, put four dabs of mounting wax on the four inside corners of the template. Slowly heat the template until the wax begins to flow. Place the specimen (at room temperature) squarely into the recesses of the template and continue to press it against the template with a cotton swab until the wax begins to flow again. Finally, allow the template to cool.

REFERENCES

[1] ASTM Standard F1188, Standard Test Method for Interstitial Atomic Oxygen Content of Silicon by Infrared Absorption," Annual Book of ASTM Standards, Vol. 10.05, ASTM, Philadelphia, PA (1991).

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[3] Baghdadi, A., Scace, R.I., and Walters, E.J., Semiconductor Measurement Technology: "Database for and Statistical Analysis of the Interlaboratory Determination of the Conversion Coefficient for the Measurement of the Interstitial Oxygen Content of Silicon by Infrared Absorption," NIST Special Publication 400-82 (1989).

[4] Rennex, B.G., NIST Special Publication 260-119, Standard Reference Materials: "The certification of a Standard Reference Material for the Determination of Interstitial Oxygen Concentration in Semiconductor Silicon by Infra-Red Spectrophotometry" (in prep).

[5] Rennex, B.G. and Ehrstein, J.R., "Methodology for the Utilization of High-Precision/Reduced-Absolute-Accuracy Measurements in Standard Reference Materials" (to be published in the NIST J. of Res., 1994).

[6] "Guide to the Expression of Uncertainty in Measurement," ISO, Geneva Switzerland, 1993. Available from Bureau International des Poids et Mesures, Pavilon de Breteuil, F-92312 Sevres Cedex, France.

[7] DIN Standard 50 438/1, "Determination of Impurity Content in Semiconductors by Infrared Absorption; Oxygen in Silicon," Beuth Verlag, Berlin (1993) [in German. An English translation is published in the Annual Book of ASTM Standards, Vol. 10.05, ASTM, Philadelphia, PA (1993).]

[8] Rennex, B.G., "Experimental Techniques for Precise Quantitative Measurements on a Spectrometer for Quality Control" (to be published in 1994).