JSNM

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JSNM-SI-002

Test method for determination of low carbon impurity concentration in single crystal silicon by photoluminescence spectroscopy

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List of committee member for JSNM-SI-001-02

This document is a translation of JSNM standard in Japanese.

In the event of any doubt arising, the original standard in Japanese is to be evidenced.

JSNM standard
JSNM-SI-002

Test method for determination of low carbon impurity concentration in single crystal silicon by photoluminescence spectroscopy

1. Scope

This standard specifies a method for measuring the carbon impurity concentration in single crystal silicon by photoluminescence. The materials to which this standard is applicable should have an interstitial oxygen concentration of approximately 1×10^{17} to 2×10^{17} atoms/cm^3, a resistivity of approximately 50 Ω·cm or more for n-type materials and 1k Ω·cm or more for p-type materials. The measurable range is 1×10^{14} to 3×10^{15} atoms/cm^3 (2 to 60 ppba).

Remark 1: The following are the reference standards for this standard.

JIS H 0615 Test method for determination of impurity concentrations in silicon crystal by photoluminescence spectroscopy.

SEMI MF1389-0704 Test methods for photoluminescence analysis of single crystal silicon for III-V impurities

JIS K 8541 Nitric acid (reagent)

JIS K 8819 Fluoric acid (reagent)

JEITA EM-3503 Standard test method for substitutional atomic carbon content of silicon by infrared absorption

SEMI MF1391-1107 Test method for substitutional atomic carbon content of silicon by infrared absorption

SEMI MF1188-1107 Test method for interstitial oxygen content of silicon by infrared absorption with short baseline

Remark 2: The interstitial oxygen concentration is obtained by the infrared absorption method according to the SEMI MF1188-1107, with a conversion coefficient of 3.14×10^{17} atoms/cm^2 (IOC-88).

2. Definition of terms

The main terms used in this standard are defined as follows.

(1) Photoluminescence (PL): Light emitted from a material as a result of their luminescent recombination when excess electrons and holes are generated in the material by light irradiation.

Remark: The analysis of photoluminescence of a semiconductor crystal allow us to evaluate the band structure of the crystal and impurities and defects in the crystal.

(2) Exciton: A state in which a free electron and a free hole in a semiconductor crystal are coupled by coulomb force.

Remark: There are two types of excitons: free exciton (FE), which moves around freely in the crystal, and bound exciton (BE), which is trapped by the electronic levels created by impurities or defects. Under strong excitation conditions, a bound multiple exciton complex (BMEC) in which multiple excitons are trapped by the electronic level is generated. BMEC with (n + 1) bound excitons is written as "bn".

(3) Phonon: The energy quantum of the lattice vibration in the crystal.

Remark: Since silicon is an indirect-transition-type semiconductor, emission lines with phonon emissions for momentum conservation are observed during the emission process, and are called phonon sidebands. Types of phonons include, transverse acoustic (TA) phonons, longitudinal acoustic (LA) phonons, transverse optical (TO) phonons, longitudinal optical (LO) phonons. In emission processes involving impurities or defects, the selection rule is relaxed by the interaction with impurities or defects, and emission line without phonons (no phonon; NP) can also be observed.

(4) Luminescence activation: When impurities contained in the crystal do not act as luminescent recombination centers and, as a result, cannot be detected by photoluminescence, light emission centers composed of the same impurities can be formed by irradiating high energy particles. The luminescence activation is the process of forming the light emission centers so that they can be detected by photoluminescence.

(5) G-line: Luminescent line originated from the complex of interstitial and substitution carbon atoms (G-center) formed when silicon crystal is irradiated with high energy particles such as electrons. It shows a sharp peak at 0.969 eV.

Remark 1: Since this defect is generated from carbon impurities in the crystal, G-line intensity is used as an index of carbon impurity concentration.

Remark 2: When silicon is irradiated with high energy particles such as electrons, interstitial oxygen and interstitial carbon complex (C-center) is also generated and has a sharp peak at 0.789 eV, called C-line. The C-line intensity is also correlated with the carbon concentration, but it is strongly affected by the oxygen concentration because it contains oxygen impurities as a component.

3. Samples

3.1 Silicon crystal

Samples should be treated basically to fulfil the JIS H 0615 requirement.

(1) In the case of a polished wafer for semiconductor device fabrication, a pellet of about 5×10 mm is cut out from the wafer and used as a sample. After the activation by electron beam irradiation, PL measurement is performed as it is.

(2) If the material to be measured is not a polished wafer, a pellet of about 5×5 mm or more and a thickness of about 1 mm is cut out and used as a sample. The sample should be rinsed with pure water and etched to get

mirror-like surface. For etchant, nitric acid (HNO_3) specified in JIS K 8541 and hydrofluoric acid (HF) specified in JIS K 8819 are mixed in volume ratio HNO_3 : HF = 5 : 3. The samples are dipped for 1 to 2 minutes. After rinsing with pure water, drying, and activation of carbon impurities by electron beam irradiation, PL measurement is performed on the samples.

3.2 Luminescence activation

The pellet is irradiated with 1 MeV electrons with a fluence of 1×10^{15} electrons/cm^2 at room temperature in order to form G-center which is luminescent center including carbon impurities as compositional elements. During this process, the sample should be cooled so that the temperature does not exceed 100 ° C.

4. Measuring equipment

The equipment consists of a laser light source, a cryostat, an optical system, and a spectrometer with the same performance as specified in JIS H 0615. Each of these devices has the following specification.

(1) Laser light source

A continuous-wave laser should be used which has an oscillation wavelength in the range of 450-650 nm and an output with 50 mW or more on the sample surface.

(2) Cryostat

In order to perform PL measurement at the temperature of 4.2 K, liquid-helium-immersion-type cryostat should be used. The cryostat has a window (windows) through which the sample is irradiated with the laser light and the PL light is extracted from the sample. When the sample is mounted on the sample holder in the cryostat, the sample should not be excessively stressed: For example, one end of the sample is pressed gently with a phosphor bronze spring.

(3) Optical system

The system should consist of an infrared cut filter that removes infrared light contained in the laser light source, optical path changing flat mirrors, condensing lens or mirrors that guide PL light to the spectrometer, and long-pass filter to brock laser light and higher-order light from diffraction grating. The condensing lens or mirrors should be optically aligned with the spectrometer and photodetector so that PL light can reach the photodetector with as low loss as possible.

(4) Spectrometer

The applicable spectrometer is as follows.

(a) The spectrometer consists of a dispersive monochromator, a photodetector, and a signal processing system. The measurement wavelength ranges are from 1270 nm (0.976 eV) to 1290 nm (0.961 eV) for G-line measurement and from 1076 nm (1.152 eV) to 1142 nm (1.086 eV) for near-band-edge emission measurement specified in JIS H 0615. The wavelength resolution of 0.25 nm is required in these regions.

Note: The spectral position shall be indicated by the wavelength λ (nm) and the photon energy E (eV), and both are expressed by the following formula.

$$E = 1240 / \lambda$$

(b) The recommended dispersive spectroscope has a focal length of about 0.3 to 1 m and a 600 grooves/mm grating blazed at 1000 to 1200 nm.

(c) For the photodetector, a photomultiplier tube should be used which has high sensitivity in near infrared region in the case of a wavelength-scanning type spectrometer. In the case of a multichannel spectrometer, a cooled InGaAs diode array is recommendable.

(d) For the signal processing system, the phase-locked detection (lock-in) method is suitable for weak light amplification in the case of a wavelength-scanning type spectrometer. Laser beam is passed through an optical chopper with a duty cycle of 50% and irradiated on the sample. Signal from photodetector is amplified by a lock-in amplifier and the optical output signal for each wavelength is recorded on the recorder or is plotted out by computer. If a multichannel spectrometer is used, output of the signal processor which is built in the photodetector should be directly linked with a personal computer.

Remark: Fourier transform spectrometer can be used as a spectrometer. In this case, the equipment parameters are not specified in this standard.

5. Measurement method

5.1 Overview of measurement method

The sample is mounted on the sample holder and immersed in liquid helium in the cryostat. Under the measurement environment of **5.2**, the sample is irradiated with the laser beam of the intensity shown in **5.3**. PL light from the sample is measured over a wavelength range of **5.5** with a wavelength resolution of **5.4**.

5.2 Measurement environment

The measuring system should be installed in a dark room with low electromagnetic noise. The environmental temperature should be from 15 to 25 °C, the fluctuation during measurement should be within ± 1 °C, and the relative humidity should be 60 % or less.

5.3 Excitation light intensity

The excitation laser beam has an intensity of 50 mW on the sample surface and a beam diameter of 2.5 mm.

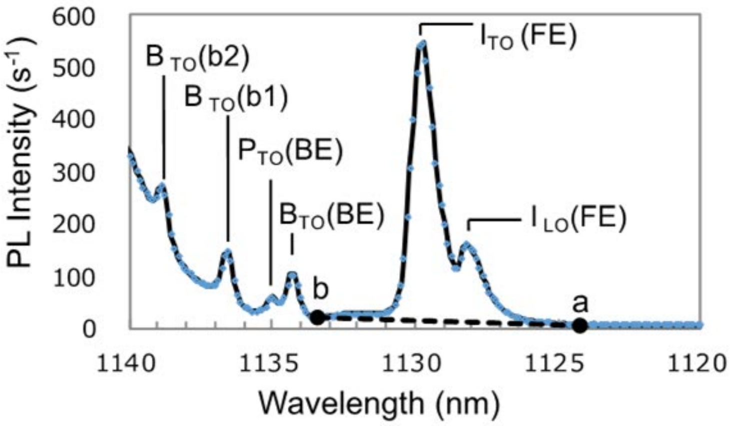


Fig. 1: PL spectrum of near-band-edge emission at 4.2K.

Remark: The sample is a p-type, high resistivity silicon crystal (carbon concentration: 6.3×10^{15} atoms /cm^3, oxygen concentration: 1.6×10^{17} atoms/cm^3). The baseline drawing is shown (dashed line a b).

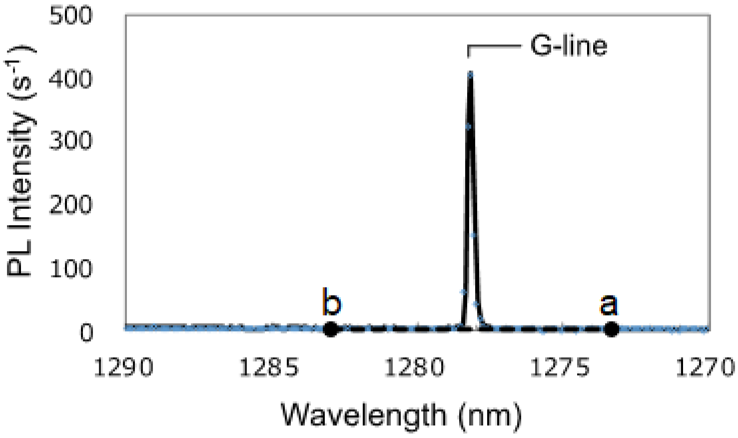


Fig. 2: PL spectrum of G-line at 4.2K.

Remark: The sample is a p-type, high resistivity silicon crystal (carbon concentration: 6.3×10^{15} atoms/cm^3, oxygen concentration: 1.6×10^{17} atoms/cm^3). The baseline drawing is shown (dashed line a b).

5.4 Wavelength resolution

The wavelength resolution is 0.25 nm in the wavelength region of I_{TO} (FE) line and G-line.

5.5 Wavelength range

The wavelength range is as follows.

TO phonon sideband of band-edge emission (I_{TO}): 1140-1120 nm (1.088-1.107 eV)

G-line: 1270-1290 nm (0.976-0.961 eV)

6. Data analysis

6.1 Identification of spectral line

Figures 1 and 2 show examples of the PL spectra of the near-band-edge emission and the G-line, respectively, measured according to **5**. The origin of the spectral components in the near-band-edge emission is identified from their positions.

Remark: The emission lines in the spectrum are denoted by X_{TO} (BE). The first symbol X indicates the type of impurity (B: boron, P: phosphorus, Al: aluminum, and As: arsenic). The subscript indicates the type of phonon involved. The type of exciton is shown in parentheses. The symbol I indicates the intrinsic emission of silicon.

6.2 Measurement of peak intensity

Baselines are necessary to measure the peak intensities of I_{TO}(FE) line and G-line. The method of baseline drawing for the I_{TO} (FE) line conforms to JIS H 0615 standard: The baseline is the straight-line **a b** connecting the spectral point **a** at 1126 nm (1.101 eV) and valley **b** between I_{TO} (FE) line and B_{LO} (BE) line, as shown in Fig. 1. The baseline for the G-line is a straight line over the range of ± 5 nm on both sides of the line, as shown in Fig. 2. The peak intensities of the I_{TO}(FE) and G-line measured by using the baselines described above are represented by $I_{TO}(FE)$ and G. The intensity ratio of the G-line with respect to the I_{TO} (FE) line, G / I_{TO}, is used as an index of the carbon impurity concentration.

6.3 Concentration calculation

The carbon impurity concentration is calculated using the relationship between the G-line intensity ratio G/ I_{TO} and the carbon impurity concentration as the calibration curve (Fig. 3).

Remark 1: Relationship in Fig. 3 was obtained from the round-robin test of the PL measurement following the method of **5** by 7 organizations (#1 to #7) after luminescence activation by the method described in **3.2**. The round-robin test was performed on the 4 samples (E8, E9, EA, EB) with n-type conductivity and a resistivity of approximately 50 Ω·cm or more, and 3 samples (G1, G3, G5) with p-type conductivity and a resistivity of approximately 1 kΩ·cm or more, as shown in Table 1. Intensity ratio G/ I_{TO} was calculated by the method described in **6.2**, normalized by the intensity ratio of G1 whose carbon concentration was median value, and plotted against carbon concentration measured by SIMS. (For detail, referred to Commentary **6.3**.)

Remark 2: The approximation formula of the calibration curve shown in Fig. 3 is as follows.

$$G / I_{TO} = 2.520\times10^{-30}\times N_C^2 \qquad (G / I_{TO} \leqq 1) \qquad (1),$$

$$G / I_{TO} = -1.457\times10^{-32}\times N_C^2 + 2.825\times10^{-15}\times N_C - 7.7384\times10^{-1} \qquad (G / I_{TO} > 1) \qquad (2),$$

where N_C is the carbon impurity concentration in atoms/cm^3.

6.4 Detection limit

The detection limit is determined by the noise level in the near-band-edge emission region and G-line region in calculating the intensity ratio G/ I_{TO} (the carbon concentration index). For the silicon single crystals to which this standard is applied, the noise level in the G-line emission region is dominant and governs the detection limit. If the detection limit is defined as the concentration corresponding to the G-line intensity twice as high as the noise level around the G-line, the limit is determined to be 8×10^{13} atoms/cm^3 from the calibration curve in Fig. 3.

Remark: The detection limit has been verified to be reduced to about 4×10^{13} atoms/cm^3 with increasing the integration time of the detector from about 60 seconds in the round robin test to 1 hour. (Y. Satake, M. Tajima, S. Asahara, and A. Ogura: "Detection limit of carbon concentration measurement in Si for photoluminescence method after electron irradiation," Jpn. J. Appl. Phys. 59, 126501 (2020).)

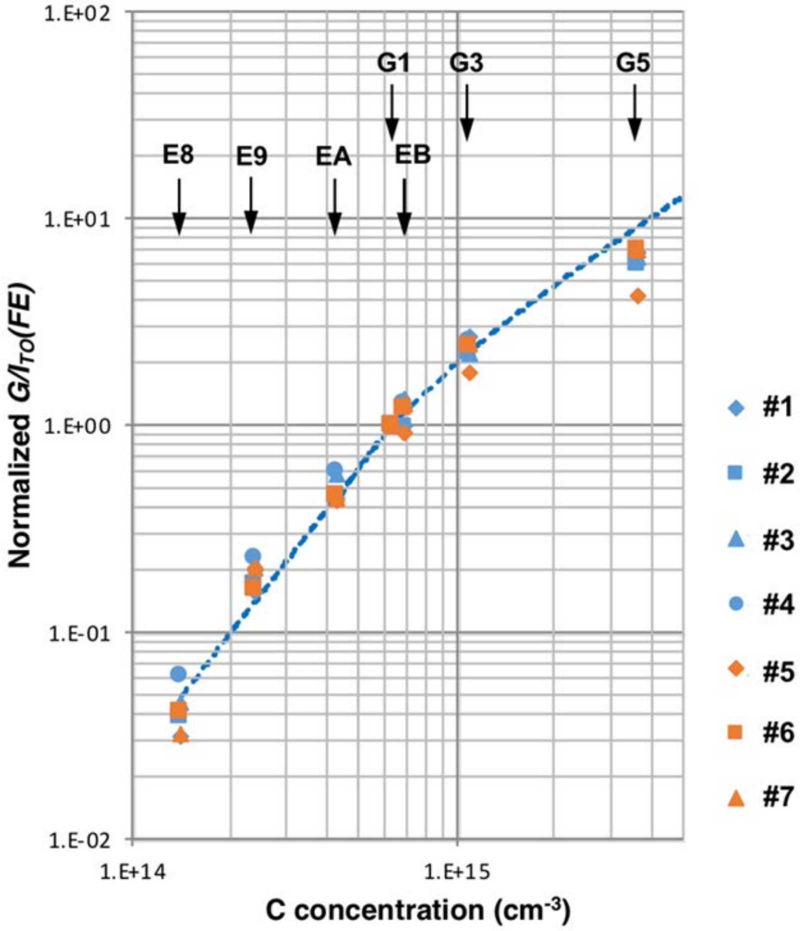


Fig. 3: Calibration curve for carbon impurities in silicon crystals.

Remark: The PL intensity ratio G/I_{TO} is plotted against the carbon impurity concentration obtained by SIMS. The regions of $G/I_{TO} \leq 1$ and $G/I_{TO} > 1$ are approximated by the quadratic exponentiation formula (1) and quadratic polynomial formula (2), respectively.

7. Calibration

Although the conditions for the PL measurement are specified in **5**, the conditions cannot be exactly the same due to the difference in measuring instruments. Therefore, the calibration curve has to be corrected according to the measurement conditions of each measuring equipment using standard samples whose carbon concentration has been determined by other method like infrared absorption spectroscopy (JEITA EM-3503, SEMI MF1391-1107) or secondary ion mass spectrometry (SIMS). The following is the correction method of the calibration curve using standard samples, where it is recommendable to use the samples with the carbon concentration of 4 levels or higher.

(1) Measure the PL spectrum of each standard sample according to the measurement conditions in **5**.

(2) Calculate the intensity ratio according to the method specified in **6**.

(3) Plot the intensity ratio of the standard sample on the calibration curve (Fig. 3).

(4) Shift the calibration curve on the both logarithmic axes vertically so that the difference from the intensity ratios of the standard samples becomes the smallest.

(5) Corresponding to the vertical shift in (4), the coefficients in formula (1) and (2) are changed.

Remark: Minimizing the difference from the measured intensity ratios by shifting the calibration curve in the vertical direction in (4) is equivalent to minimizing the difference from the calibration curve by multiplying the measured intensity ratios by a coefficient. If the intensity ratio multiplied by this coefficient is used, there is no need to change the coefficients in formula (1) and (2).

Table 1: Characteristics of silicon samples used in round-robin test

Sample No.	E8	E9	EA	EB	G1	G3	G5
Conductivity type	*n*-type				*p*-type		
Resistivity (Ω·cm)	50-70				5300	5200	1410
Oxygen conc. ($\times 10^{17}$ atoms/cm^3)	1-2				1.6	1.5	2.1
Carbon conc. ($\times 10^{14}$ atoms/cm^3)	1.4	2.4	4.3	6.9	6.3	11	36

Remark: These silicon single crystal samples were grown by the magnetic-field-applied Czochralski method.

8. Accuracy and reliability

The accuracy and reliability of the measurement method specified in this standard are determined based on the results of round-robin tests conducted by 7 organizations on samples with the carbon concentration of 7 levels shown in Table 1.

8.1 Error in intensity ratio

The error in obtaining the intensity ratio G / I_{TO}, which is an index of carbon concentration, is determined by the noise level on the baseline with respect to the G-line intensity for samples with characteristics within the applicable range covered by this standard. The noise level is defined as one-half of the difference between the maximum and minimum background levels in the range of 5 nm close to the G-line. The error of the intensity ratio G/ I_{TO} is obtained by dividing the noise level by the G-line intensity.

Figure 4 summarizes the results for the 7 samples: within 20 % or less for the sample with the lowest carbon concentration (1.4×10^{14} atoms/cm^3) and within 5 % or less for the samples with the carbon concentration of 6×10^{14} atoms/cm^3 or more.

8.2 Accuracy

The errors which are the differences of the concentrations determined by each organization using the calibration curve for the 7 standard samples in Table 1 from the C concentrations determined by SIMS are shown in Fig. 5. The error tends to increase as the carbon concentration decreases. The error of the carbon concentration value in all samples is within 30 % or less, as in JIS H 0615 standard for dopant impurity quantification. Note that the data for sample G5 is excluded in Fig. 5, since its oxygen concentration of 2.1×10^{17} atoms/cm^3 exceeds slightly the upper limit of 2×10^{17} atoms/cm^3 in this standard. The oxygen concentration outside the range causes an error.

8.3 Reproducibility

Reproducibility of the G-line intensity ratio G / I_{TO} was tested by five organizations for sample G1 with approximately median carbon concentration in Table 1. The measurement was repeated three times inconsecutively with optical alignment of sample and spectrometer in each time. Figure 4 shows the deviation of the G-line intensity ratio from the 3 times average for 5 organizations. This indicates that the measurement error in reproducibility of the intensity ratio is within 10 % or less.

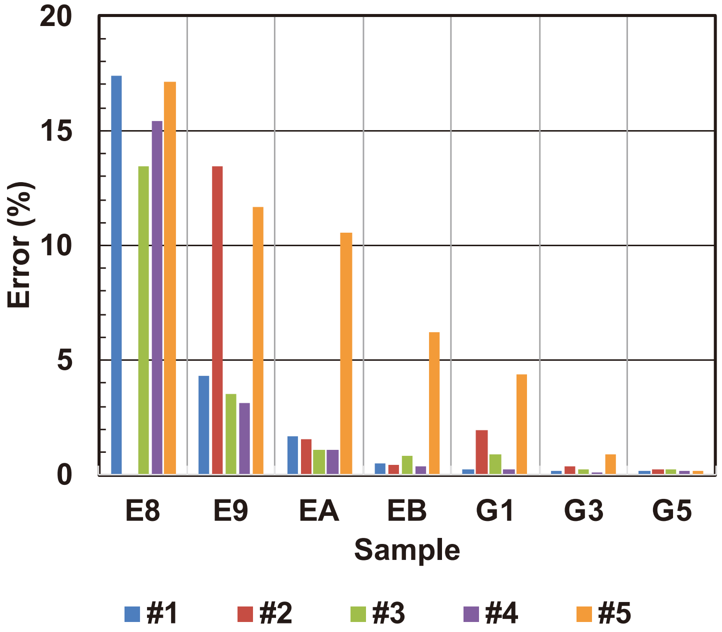


Fig. 4: Error in intensity ratio G / I_{TO}

Remark: The figure shows the error induced by noise on the baseline near the G-line when organizations #1 - #5 determined the intensity ratio G / I_{TO} of each sample.

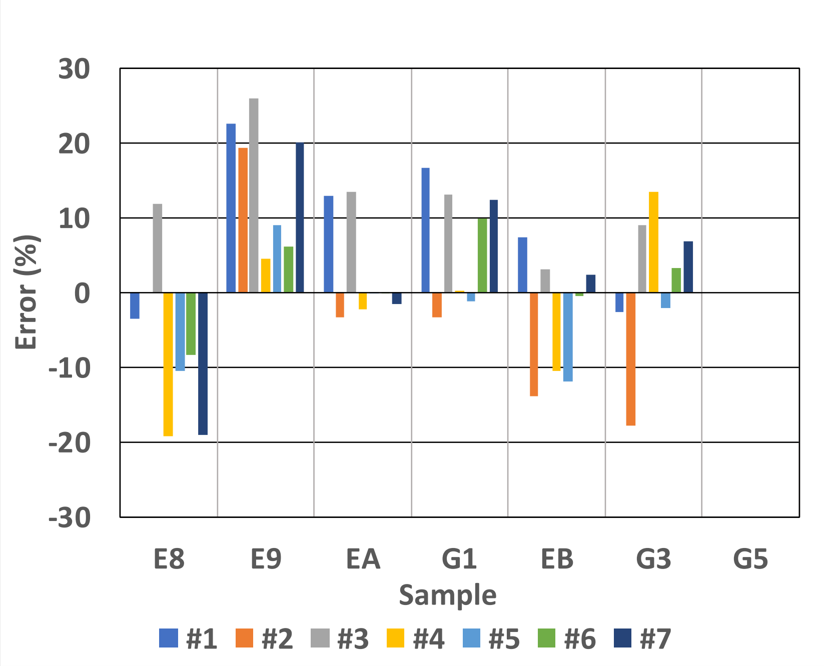


Fig. 5: Error in carbon concentration obtained from calibration curve

Remark: The figure shows the differences of the concentrations determined by organization #1-#7 using the calibration curve for the 7 standard samples from those determined by SIMS. Sample G5 was excluded, because its oxygen concentration exceeded the upper limit of this standard and error became large.

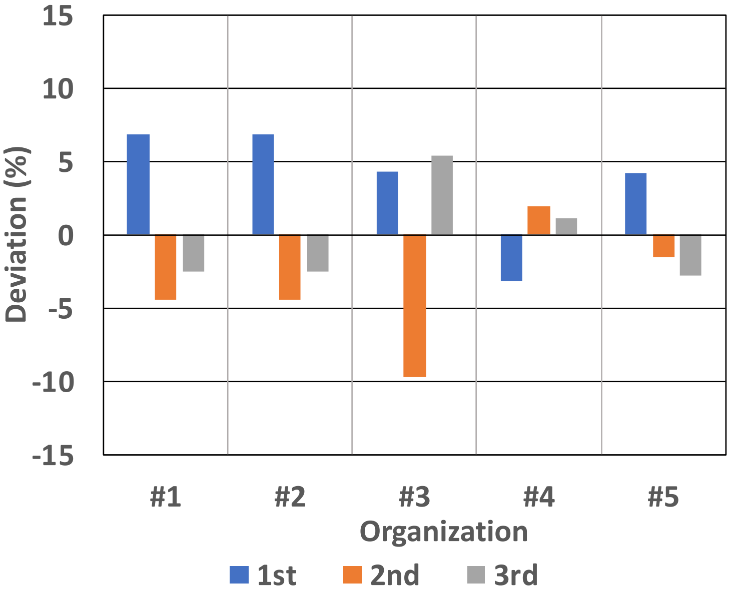


Fig. 6: Reproducibility of intensity ratio G / I_{TO} in 3 times repeated measurement by 5 organizations

Remark: Deviations from the average of three times measurements (1st, 2nd, 3rd) of intensity ratio G/ I_{TO} for sample G1 by organizations #1 - #5.

JSNM-SI-002

Test method for determination of low carbon impurity concentration in single crystal silicon by photoluminescence spectroscopy

Commentary

This commentary is an explanation of the main body and related matters, and is not the part of this standard.

I. Purpose of establishment

Silicon power devices are important for realization of low carbon society. Because remaining carbon impurities in single crystal silicon with the low concentration even less than 5×10^{14} atoms/cm^3 affect device characteristics of the state-of-the-art silicon power device like IGBT (Insulated Gate Bipolar Transistor), precise control of the carbon impurities in silicon is needed. Under these circumstances, the standard of the measurement method of low carbon concentration in silicon, which is interface between crystal makers and device makers, is eagerly sought. The Fourier transform infrared spectroscopy (FT-IR) method has been standardized and is widely used for the measurement of the carbon concentration in silicon. However, the sensitivity is not high enough for the current requirement, because the detection limit of the FT-IR method is approximately 2×10^{15} atoms/cm^3. Based on this situation, this standard specifies a method for measuring the carbon concentration with the range of the order of 10^{14} atoms/cm^3 in a silicon single crystal by photoluminescence (PL).

II. Background of establishment

The activity of standardization of the PL method began at January in 2017 as the 1st preparatory meeting for the PL method under Material Standards Study Group for Semiconductor Supply-Chain (M4S) in Japan Society of Newer Metals (JSNM). This preparatory meeting continued till the 5th meeting in March 2018. This activity continued as one of entrusted projects of Ministry of Economy, Trade and Industry, “Acquisition and Promotion of International Standards for Energy Saving in 2018”. The 1st meeting of National Working Group of the PL method (PL-NWG) was held in June 2018 and continued till the 15th meeting in February 2018. Based on these results, the new JSNM standard of PL method was standardized by Standardization Committee in February 2021, through discussion and deliberation in Silicon Standardization Promotion Committee and Photoluminescence Standardization Working Group.

III. Principle

Carbon is introduced in silicon crystal as a contaminant during crystal growth or as an impurity in starting poly crystalline silicon. The carbon atom occupies the lattice site (C_s) in an as-grown crystal and is electrically inactive. In the case that high energy particles like electrons are irradiated on silicon crystals, Si atoms at the lattice site are displaced to the interstitial sites and interstitial Si (Si_i) atoms are formed. Si_i displaces C_s to the interstitial site and interstitial carbon (C_i) is formed. C_i is not stable and is trapped by interstitial oxygen (O_i) or C_s, forming complex like C_i-O_i or C_i-C_s, which generates the electronic level called C-center or G-center, respectively. Luminescence lines from the radiative transition through these levels are termed C-line, G-line respectively1). Based on the fact that these complexes contain carbon, principle of this method is to estimate the carbon concentration from the intensity of these luminescence lines2-6).

When the impurity concentration is estimated from the PL intensity, it is necessary to reduce the effects of other radiative and non-radiative transitions than the radiative transition of the target impurity, because the emission occurs as a result of the competition of all the recombination processes. In the case of the PL method for the determination of the donor and acceptor impurity concentrations in silicon crystals standardized by JIS and SEMI, the intensity ratio between the bound exciton and free exciton lines is used to remove these effects, because the differences in the defects and the surface condition are reflected in the free exciton intensity7). The intensity ratio between C-line and the free exciton line and that between G-line and the free exciton line are also effective for the carbon quantification, however, this procedure is not enough. Major luminescence is only impurity-bound exciton and free exciton in the case of the donor and acceptor impurity quantification, while C-line and G-line are added to the luminescence process in the case of the carbon impurity quantification. Moreover, C-line and G-line are strongly affected by the oxygen concentration3,5), because oxygen participates in the formation of the C-center and G-center. Therefore, the concentrations of donor, acceptor and oxygen impurities are restricted in a certain range in this method. In practice, scope of this standard limits the applicable materials to single crystals having the interstitial oxygen concentration of about 1×10^{17} to 2×10^{17} atoms/cm^3, the resistivity of about 50 Ω·cm or more for n-type conductivity and that of about 1 kΩ·cm or more for p-type conductivity.

IV. Explanation of standard items

Main items of the main body of this standard are explained in detail.

3. Samples

3.1 Silicon crystal

Sample preparation basically follows JIS H 0615, and the same care is necessary. Moreover, samples should not be placed in thermal ambient higher than 100 °C before the PL measurement, because G-line disappears by thermal treatment higher than 250 °C and defects introduced by the irradiation are not stable in thermal treatment between 150 °C and 450 °C. It should be noted that G-line is not affected by high-intensity laser illumination during PL measurement.

3.2 Luminescence activation

Electron irradiation for luminescence activation of carbon in silicon crystals can be done at several outsourcing facilities like public facilities such as Japan Atomic Energy Agency and commercial establishments where electron irradiation is performed for sterilization or material reforming. The electron irradiation condition in this standard, “acceleration energy of 1 MeV and fluence of 1×10^{15} electrons/cm^2”, is determined by referring the conditions written in technical papers[1,3-6] already published and by considering convenience of the irradiation. In the process for the determination of the calibration curve, a sample set with the irradiation condition of 2 MeV acceleration energy and fluence of 1×10^{15} electrons/cm^2 was also prepared, and the PL measurement was performed on the samples by 2 organizations. An index of the carbon impurity concentration, G/I_{TO}, is supposed to increase in 2 MeV electron irradiation from the fact that the amount of radiation-induced defects is larger in 2 MeV than in 1 MeV, from the previous experimental results. However, the effect was within the experimental error and did not exceed “the error in the intensity ratio of G/I_{TO} is within 20 % or less”, shown in **8.1** in the main body. From the results mentioned above, the calibration curve can be determined by the method shown in **7** under the different irradiation condition, if the difference in the condition is not large.

Because electrons with energy of both 1 MeV and 2 MeV can penetrate silicon crystal with thickness less than 2 mm, there is no difference between the results of PL measurement from the irradiation side and those from the back side.

4. Measuring equipment

(1) Laser light source

DPSS (Diode Pumped Solid State) laser widely used in scientific experiment with wavelength of 532 nm is recommendable as the light source.

(2) Cryostat

Although the measurement at 4.2 K with a sample being immersed in liquid He is defined in this standard by reference to JIS H 0615, the measurement temperature can be raised up to liquid nitrogen temperature described in **6.3** in this commentary. In that case, immersion-type and conductive-type cryostats using liquid nitrogen as a coolant and a conductive-type He gas closed cycle cryostat can be used. However, they were not included in this standard, because the accuracy of the quantification at higher temperatures was not verified.

(4) Spectrometer

Recently multichannel spectrometer using an InGaAs diode array with high sensitivity and high measurement speed is used generally. Because PL intensity from indirect-bandgap silicon crystals is not strong, a high sensitive InGaAs diode array is suitable for the detector. It should be noted that the correction of the spectral response of the spectrometer is not defined. The error caused by the difference in the spectral response can be corrected by the method described in **7** in the main body as written in **6.3** in this commentary.

5. Measuring method

5.3 Excitation light intensity

In JIS H 0615, the excitation light intensity on a sample surface is defined as 50 mW with a beam diameter of 2.5 mm, where the incident light is chopped with a duty ratio of 50 %. The intensity equivalent to JIS H 0615 is 100 mW for a multichannel spectrometer using continuous light excitation in this standard. However, the excitation light intensity is defined as 50 mW in this standard because of the following reasons: (1) The difference in the excitation light intensity can be corrected by the correction of the calibration curve by the measurement of standard samples described in **6.3** in this commentary and in commentary **IV 5.3** in JIS H 0615, and (2) error in I_{TO}(FE) line intensity increases in the 100 mW excitation, since electron-hole-droplet emission becomes dominant.

In the round-robin test, some organizations could not change beam diameter from tens of micrometers and the intensity per unit area increased by hundreds of times over this standard. Nonetheless, there was no large difference in the correlation between the intensity ratio and the carbon concentration shown in Fig. 1 (a).

5.4 Wavelength resolution

For measurement of G-line, high wavelength resolution less than 0.02 nm is needed to measure the precise spectral shape, because G-line used in this standard is very sharp with a half width of about 0.06 nm. In such a case, a spectrometer with a high wavelength dispersion is needed and the measurement becomes difficult because of the reduction of the signal intensity. Therefore, the wavelength resolution in this standard is defined as 0.25 nm of almost the same value as JIS H 0615 so that the measurement can be performed at general organizations. For this reason, a slight variation of the wavelength resolution affects the intensity of G-line. This can be corrected by the method in **7** in the body, as described in **6.3** in this commentary. In any case, however, all measurements should be performed under the same wavelength resolution.

6. Data analysis

6.3 Concentration calculation

The process of creating the calibration curve in Fig. 3 is explained as follows[8)]. After luminescence activation for 42 silicon crystals made by 7 organizations, preliminary measurements were performed by 2 organizations, and 21 samples for round-robin test were selected based on the carbon concentrations reported from each organization. Ten organizations joined round-robin test of the PL measurement. Three of them measured at the temperatures of 15 K and 77 K. As shown in Table 1, 7 samples with almost the same oxygen concentrations, which were grown by the magnetic-field-applied Czochralski (MCZ) method, were selected and their carbon concentrations were measured by SIMS. Four samples (E8, E9, EA, EB) in the 7 samples were of n-type conductivity with the resistivity of 50 Ω·cm and 3 samples (G1, G3, G5) were of p-type conductivity with the resistivity of more than 1 kΩ·cm.

From the measurement results of the 7 samples, the intensity ratio G/I_{TO} was calculated by the method shown in **6.2** and plotted on a double logarithmic graph against the carbon concentration measured by SIMS, as shown in Fig. C1 (a). Although the variations of G/I_{TO} of respective samples among organizations are not small, the relations between G/I_{TO} and the carbon concentration for all the samples show a positive correlation for all the organizations and the shapes of all the correlation curves are quite similar. In order to clarify the similarity, the intensity ratio G/I_{TO} were normalized by the ratio for sample G1, whose carbon concentration is approximately the median of the 7 samples, and this normalized intensity ratio $[G/I_{TO}]_N$ were plotted on a double logarithmic graph against the carbon concentration measured by SIMS, as shown in Fig. C1 (b). In Fig. C1 (b), it is shown that all the data points are located very near one correlation curve, and that this correlation can be used as the calibration curve. Although the deviation of the data points at 15 K and 77 K were large before the normalization, these points got closer to the correlation curve after the normalization. However, only 4.2 K data was used in this standard, because the deviation of 4.2 K data was smaller than that of 15 K and 77 K data, resulting in the high precision for the measurement at 4.2 K.

The cause of the above-mentioned variation in the intensity ratio G/I_{TO} among the organizations is that the measurement conditions were not always the same. The differences of the measurement conditions are as follows. (1) Because the spectral response of optical measurement systems such as spectrometers and photodetectors differs depending on the respective apparatuses, there is a difference in the intensity ratio between I_{TO}(FE) line and G-line with different wavelength positions. (2) As described in **IV 5.4** in this commentary, the intensity decrease of G-line occurs by slightly lowering the wavelength resolution because of its sharp line shape, while the intensity decrease of I_{TO}(FE) line does not occur because of its broad line shape. (3) Excitation-intensity dependences of I_{TO}(FE) line and G-line are not the same. These variations of the intensity ratio do not occur in measurements in one organization, where the spectral response of optical measurement systems, the wavelength resolution and the excitation light intensity are fixed. In this standard, not intensity but intensity ratio is used as an index of the concentration. Furthermore, the ratio is normalized by the ratio for G1 sample, as expressed by $[G/I_{TO}]_N$. These procedures remove the variations in the intensity ratio caused by the differences of the measurement conditions.

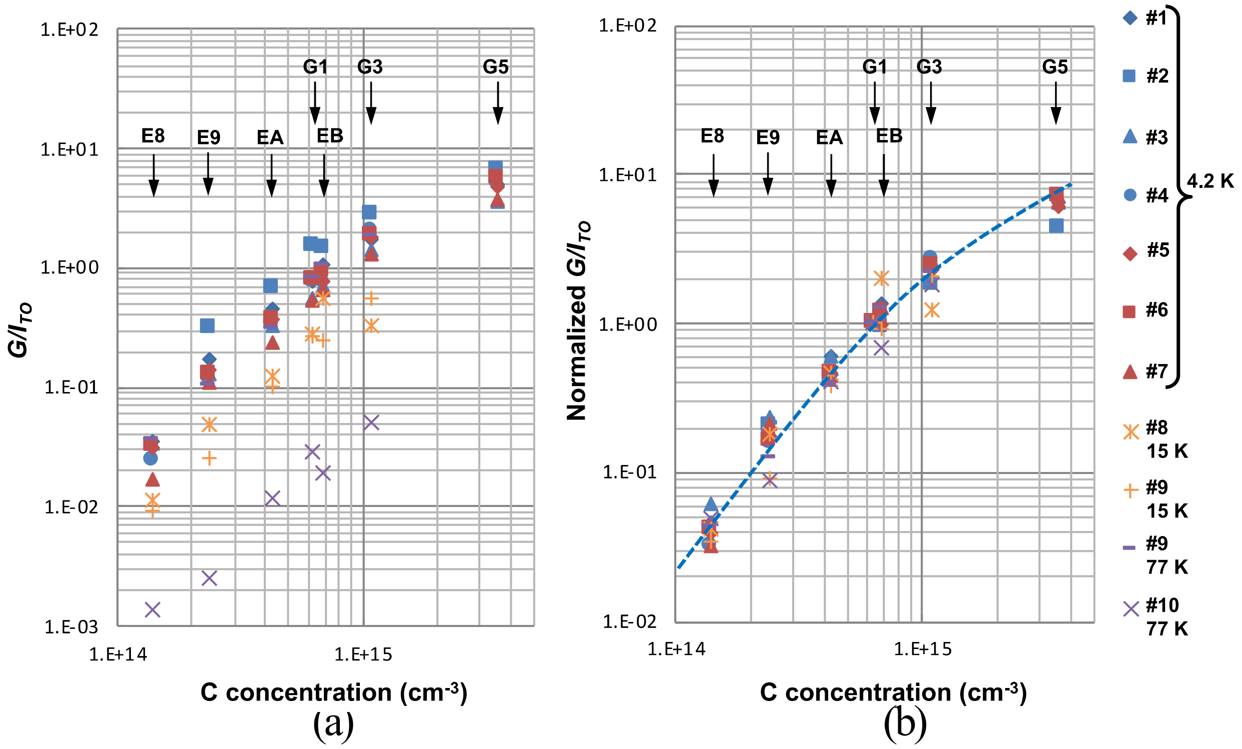
Based on the above results, the calibration curve shown in Fig. 3 of the main body is made by approximating the relationship between the carbon concentration and the average value of the normalized intensity ratio of each sample at 4.2 K in Fig. C1 (b) in this commentary. The reason why the intensity ratios in Fig. C1 (a) were not averaged simply is that the correlation curve for the organization having large intensity ratios is emphasized by the simple average. Similarity of the correlation curve is equally reflected on a logarithmic axis by averaging after the normalization of the intensity ratio in Fig. C1 (b).

As described in **8.2** in the main body, the error in the data point for sample G5 is large, because the oxygen concentration of sample G5 (2.1×10^{17} atoms/cm^3) exceeds a little the upper limit of this standard (2×10^{17} atoms/cm^3). The correction method of the calibration curve for the oxygen concentration difference has already been studied and has been reported in Ref. 10 in detail. The calibration curve in Fig. 3 in the main body was determined considering the above correction and slightly differs from the calibration curve in Fig. C1 (b) in the high carbon concentration range ($>1\times10^{15}$ atoms/cm^3). In Ref. 10, the calibration curve in Fig. C1 (b) is denoted “old calibration curve”, and is distinguished from “revised calibration curve” in Fig. 3.

The detection limit has been verified to be reduced to approximately 4×10^{13} atoms/cm^3 with increasing the integration time of the detector from about 60 seconds in the round robin test to 1 hour.9).

7. Calibration

The correction of the calibration curve in this standard is basically the same as JIS H 0615. In JIS H 0615, the donor and acceptor concentrations can be determined from the calibration curves without the correction in many cases, because the difference of the intensity ratio among organizations is small. However, the correction is necessary in this standard, because the difference of the intensity ratio G/I_{TO} among organizations is large, as described in **IV 6.3** in this commentary. Since the intensity ratio is used as an index of the carbon concentration and its correlation with the carbon concentration is given on the logarithmic scale, the calibration can be performed by shifting the calibration curve in Fig. 3, as written in the main body.



(a) (b)

Fig. C1: Dependence of (a) intensity ratio and (b) normalized intensity ratio of G-line on carbon concentration

Remark: Dependence of (a) intensity ratio G/I_{TO} and (b) normalized intensity ratio $[G/I_{TO}]_N$ on carbon concentration for samples used in round-robin test in Table 1. (Organizations #1 to #7 measured at 4.2 K and organizations #8 to #10 measured at 15 K or 77 K.)

8. Accuracy and reliability

Carbon concentration is determined by SIMS to obtain the calibration curve in this standard. Therefore, the error in SIMS measurement directly leads to the error of this method.

V. Standard samples

Samples in Table 1 used in round-robin test are the basis for the creation of the calibration curve in this standard. They are most suitable for the standard samples for the calibration. Japan Society of Newer Metals defined these samples used in round-robin test as the primary standard samples. The Society prepared about 15 sets of the secondary standard samples and distributed them to related organizations. Lending of standard samples is also available from this society.

VI. References

1) G. Davies and R. C. Newman: “Carbon in monocrystalline silicon,” *Handbook of Semiconductors,* eds. T. S. Moss and S. Mahajan, Ch.21, p. 1557 (Elsevier, Amsterdam, 1994).
2) J. Weber and M. Singh: “New method to determine the carbon concentration in silicon,” Appl. Phys. Lett. **49**, 1617 (1986).
3) M. Nakamura, E. Kitamura, Y. Misawa, T. Suzuki, S. Nagai, and H. Sunaga: “Photoluminescence measurement of carbon in silicon crystals irradiated with high energy electrons,” J. Electrochem. Soc. **141**, 3576 (1994).
4) S. Nakagawa, K. Hirose, and M. Tajima: “Quantitative photoluminescence analysis of ultra-low concentration of impurities in silicon wafers,” Proc. Science and Technology of Silicon Materials 2007, p. 227 (2007).
5) S. Nakagawa: “Magnetic field-applied Czochralski silicon wafers for power devices,” Oyo Buturi, **84**, 976 (2015) [in Japanese].
6) M. Tajima, A. Ogura: “Quantification of carbon in Si crystals by photoluminescence at liquid-nitrogen and room temperatures,” Oyo Buturi, **87**, 655 (2018) [in Japanese].
7) M. Tajima: “Determination of boron and phosphorous concentration in silicon by photoluminescence analysis,” Appl. Phys. Lett. **32**, 719 (1978).
8) M. Tajima, S. Samata, S. Nakagawa, J. Oriyama and N. Ishihara: “Round-robin test of photoluminescence method after electron irradiation for quantifying low-level carbon in silicon,” Jpn. J. Appl. Phys. **59**, SGGK05 (2020).
9) Y. Satake, M. Tajima, S. Asahara, and A. Ogura: “Detection limit of carbon concentration measurement in Si for photoluminescence method after electron irradiation,” Jpn. J. Appl. Phys. **59**, 126501 (2020).
10) M. Tajima, S. Samata, S. Nakagawa, Y. Shinozuka, J. Oriyama and N. Ishihara: “Calibration curve for the photoluminescence method after electron irradiation for quantifying low-level carbon in silicon,” Jpn. J. Appl. Phys. **60**, 026501 (2021).

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