(19) DANMARK

(10) **DK/EP 3671817 T3**

Patent- og Varemærkestyrelsen

(12) Oversættelse af europæisk patentskrift

(51) Int.Cl.: ***H 01 L 21/66 (2006.01)*** ***C 30 B 29/06 (2006.01)*** ***G 01 N 21/64 (2006.01)*** *C 30 B 13/00 (2006.01)* *C 30 B 15/00 (2006.01)* *G 01 N 21/27 (2006.01)*

(45) Oversættelsen bekendtgjort den: **2022-08-01**

(80) Dato for Den Europæiske Patentmyndigheds bekendtgørelse om meddelelse af patentet: **2022-05-04**

(86) Europæisk ansøgning nr.: **18846613.0**

(86) Europæisk indleveringsdag: **2018-07-30**

(87) Den europæiske ansøgnings publiceringsdag: **2020-06-24**

(86) International ansøgning nr.: **JP2018028362**

(87) Internationalt publikationsnr.: **WO2019035343**

(30) Prioritet: **2017-08-18 JP 2017157924**

(84) Designerede stater: **AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR**

(73) Patenthaver: **Shin-Etsu Handotai Co., Ltd., 2-1, Ohtemachi 2-chome , Chiyoda-ku, Tokyo 100-0004, Japan**

(72) Opfinder: **KIMURA Akihiro, c/o Shirakawa R&D Center, Shin-Etsu Handotai Co., Ltd., 150 Aza Ohira, Oaza Odakura, Nishigo-mura, Nishishirakawa-gun, Fukushima 961-8061, Japan**

(74) Fuldmægtig i Danmark: **Plougmann Vingtoft A/S, Strandvejen 70, 2900 Hellerup, Danmark**

(54) Benævnelse: **FREMGANGSMÅDE TIL MÅLING AF CARBONKONCENTRATION**

(56) Fremdragne publikationer:

EP-A1- 2 952 883
JP-A- H04 344 443
JP-A- 2012 102 009
JP-A- 2013 152 977
JP-A- 2015 101 529

DESCRIPTION

TECHNICAL FIELD

[0001] The present invention relates to a method for measuring carbon concentration in a semiconductor sample, especially a silicon wafer, and more particularly to a method for measuring carbon concentration in an FZ silicon single crystal (which will be referred to as an FZ single crystal) manufactured by a floating zone (FZ) method.

BACKGROUND ART

[0002] In semiconductor wafers each of which is used as a CIS (CMOS image sensor) or a power device substrate, realization of a high lifetime has been demanded, and a decrease of carbon has been requested to avoid a reduction in lifetime, and accurately measuring low carbon concentration is very important. Measuring the carbon concentration by an FT-IR method (Fourier transformation infrared spectroscopy) has been possible heretofore, but the sensitivity is poorer than a recent request level. Compared to this, a low-temperature photoluminescence (PL) method has high sensitivity.

[0003] According to the PL method, light having energy larger than a bandgap is used as an excitation source, and excited electron-hole pairs are formed when a silicon wafer is irradiated with excitation light. This is a method for detecting light emission (luminescence) at the time of recombination of these pairs through a metastable state, and evaluating/quantifying defects and impurities which are present in the silicon wafer.

[0004] A method for irradiating a silicon single crystal with an electron beam and measuring carbon impurity concentration in the silicon single crystal from peak intensity of photoluminescence caused by carbon-oxygen composite defects produced in this single crystal is disclosed in Patent Document 1, and dependence of the peak intensity of such photoluminescence on both carbon concentration and oxygen concentration in a silicon single crystal is disclosed in Patent Document 2.

[0005] According to the measuring method in Patent Document 1, carbon concentration in the silicon single crystal and a ratio (an intensity ratio) of peak (G line) intensity caused by interstitial carbon-substitutional carbon composite defects in a spectrum based on the PL method to silicon peak (which is referred to as a TO line in Patent Document 1, and will be referred to as a free excitation luminescence (FE: Free Excitation) line hereinafter) intensity are acquired in accordance with each of a plurality of silicon single crystals having different carbon concentrations, and a correlation between the carbon concentration and the intensity ratio is derived in advance. Then, according to the method, the carbon concentration in a measurement silicon single crystal is measured based on the correlation and the intensity ratio of the peak acquired from the silicon single crystal (the measurement silicon single crystal) whose carbon concentration is unknown. However, oxygen concentrations in the silicon single crystals are not taken into consideration here, and the carbon concentrations can be measured in the silicon single crystals having the same oxygen concentration only (Patent Document 2).

[0006] Thus, Patent Document 3 discloses a carbon concentration evaluating method by which a correlation between a ratio of carbon concentration and oxygen concentration ([Cs]/[Oi]) in a silicon single crystal and a peak intensity ratio (G/C) of a G line after irradiation of an electron beam and a peak (a C line) caused by interstitial carbon-interstitial oxygen composite defects is obtained in advance and unknown carbon concentration is obtained from oxygen concentration in a measurement silicon single crystal and a result of the peak intensity ratio based on the correlation.

[0007] Further, paragraph [0065] in Patent Document 4 has a description that it is preferable for respective oxygen concentrations in first samples to be equal to further accurately obtain a correlation between G line intensity and an ion implantation amount of impurities since a balance between C line intensity and the G line intensity changes depending on the oxygen concentration in a silicon semiconductor.

CITATION LIST

PATENT LITERATURE

[0008]

Patent Document 1: Japanese Unexamined Patent Application Publication No. 2013-152977

Patent Document 2: Japanese Unexamined Patent Application Publication No. H4-344443

Patent Document 3: Japanese Unexamined Patent Application Publication No. 2015-101529

Patent Document 4: Japanese Unexamined Patent Application Publication No. 2015-222801

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0009] As described above, in the carbon concentration measurement based on the PL method, since the peak caused by the composite defects of the carbon and the oxygen is used, many studies on correction of the oxygen concentration have been conducted. However, an extent of the oxygen concentration which requires use of a different calibration curve has been unrevealed. In case of the FZ single crystal in particular, its oxygen concentration is extremely lower than that of a CZ single crystal (a single crystal manufactured by a Czochralski (CZ) method), and it has been conventionally considered that the carbon concentration can be uneventfully quantified by one calibration curve.

[0010] However, the present inventor has found a problem that, in the event of using a polycrystalline silicon ingot (which will be referred to as pure-poly) and a CZ crystal silicon ingot (which will be referred to as a CZ single crystal), when the carbon concentration is obtained with the use of one calibration curve based on the PL method like conventional examples, a deviation between the carbon concentration obtained by the FT-IR method and the carbon concentration obtained by the PL method becomes large in an FZ single crystal using the pure-poly as a starting material in case of low concentration but, on the contrary, a deviation between the carbon concentration obtained by the FT-IR method and the carbon concentration obtained by the PL method becomes large in an FZ silicon single crystal using the CZ single crystal as a starting material in case of high concentration, and quantifying the accurate carbon concentration is difficult.

[0011] In view of the above-described problems, it is an object of the present invention to provide a method for measuring carbon concentration which enables the accurate carbon concentration measurement even if a type of a starting material differs in a semiconductor sample made of an FZ single crystal in particular in the carbon concentration measurement using the PL method.

SOLUTION TO PROBLEM

[0012] To achieve the object, the present invention provides a method for measuring carbon concentration which obtains the carbon concentration in a measurement semiconductor sample made of an FZ silicon single crystal manufactured by a floating zone (FZ) method from measurement values measured by a photoluminescence (PL) method, the method including:

previously preparing respective FZ silicon single crystals manufactured by the FZ method from a plurality of types of starting materials which have different contained oxygen concentrations due to a difference in manufacturing methods, and creating and preparing calibration curves each indicating a relationship between a measurement value based on the photoluminescence (PL) method and the carbon concentration from standard samples made of the respective FZ silicon single crystals in accordance with the respective types of starting materials of the FZ silicon single crystals;

selecting a calibration curve of the same type of starting material as a starting material of the measurement semiconductor sample from the plurality of prepared calibration curves; and obtaining the carbon concentration of the measurement semiconductor sample from the measurement value of the measurement semiconductor sample based on the photoluminescence method with the use of the selected calibration curve.

[0013] In this manner, since the oxygen concentration in the FZ single crystal is determined in dependence upon contained oxygen concentration of the starting material, preparing the calibration curve in accordance with each of types of the starting materials having different oxygen concentrations enables accurately quantifying the carbon concentration.

[0014] It is preferable that the plurality of calibration curves prepared in accordance with the respective types of starting materials are prepared in accordance with the standard sample whose starting material type is a polycrystalline silicon ingot (pure-poly) and the standard sample whose starting material type is a silicon single crystal ingot (CZ single crystal) pulled up by a Czochralski (CZ) method.

[0015] In this manner, the contained oxygen concentration of the pure poly is low and, on the other hand, the counterpart of the CZ single crystal is high. Thus, preparing the calibration curve in accordance with each of types of the starting materials enables the accurate carbon concentration measurement.

[0016] At this time, it is preferable that each calibration curve indicative of the relationship between the measurement values based on the PL method and the carbon concentrations is created by making reference to measurement values of carbon concentrations measured by a measuring method other than the PL method regarding the standard samples configured to obtain the calibration curves.

[0017] Further, a carbon concentration domain of the calibration curve measured by a measuring method other than the PL method can be set to 1×10^{14} atoms/cm^3 or more.

[0018] That is, since the carbon can be detected with high sensitivity by the PL method, the lower carbon concentration can be measured as compared with any other measuring method than the PL method. Thus, in a high carbon concentration domain (e.g., a domain of 1×10^{14} atoms/cm^3 or more) which can be quantified by a conventional method (a measuring method other than the PL method), when the calibration curve is created with the use of the carbon concentrations quantified by the conventional method and PL measurement values, the highly reliable calibration curve can be created.

[0019] Furthermore, in this case, it is preferable that as the calibration curve, one provided by extrapolating the calibration curve created by making reference to the carbon concentrations measured by the measuring method other than the PL method is prepared.

[0020] When the calibration curve provided by extrapolating the calibration curve created by making reference to the carbon concentrations measured by a measuring method other than the PL method is used, the low carbon concentration which is, e.g., approximately 1×10^{13} atoms/cm^3 can be quantified.

[0021] Further, in a case where the carbon concentration in the measurement semiconductor sample has been measured as 1×10^{14} atoms/cm^3 or more, it is preferable to verify whether the measured carbon concentration coincides with the carbon concentration measured by the measuring method other than the PL method and correct the calibration curve when they do not coincide with each other.

[0022] When the calibration curve is corrected in this manner, the further reliable calibration curve can be obtained, and the more accurate measurement can be carried out.

ADVANTAGEOUS DEFFECTS OF INVENTION

[0023] According to the present invention, it is possible to provide the method for measuring carbon concentration which enables the accurate carbon concentration measurement even if semiconductor samples or especially semiconductor samples made of FZ single crystals have different types of starting materials and different contained oxygen concentrations.

BRIEF DESCRIPTION OF DRAWINGS

[0024]

FIG. 1 shows a conventional calibration curve in a relationship between G line intensity/FE line intensity based on a PL method and carbon concentrations based on an FT-IR method;

FIG. 2 shows a correlation between the carbon concentrations based on the FT-IR method and carbon concentrations obtained with the use of a conventional calibration curve by the PL method;

FIG. 3 shows starting material type-specific calibration curves in the relationship between the G line intensity/FE line intensity based on the PL method and the carbon concentration based on the FT-IR method; and

FIG. 4 shows a correlation between the carbon concentration based on the FT-IR method and carbon concentration obtained with the use of a calibration curve based on a method of the present invention by the PL method.

DESCRIPTION OF EMBODIMENT

[0025] An embodiment of the present invention will now be described hereinafter, but the present invention is not restricted thereto.

[0026] Since FZ single crystals contain low oxygen, it has been conventionally considered that measurement values are not affected by the oxygen, and carbon concentration has been obtained with the use of one calibration curve by the PL method. However, it has been found out that, when starting materials whose contained oxygen concentrations are different due to a difference in manufacturing method are used, values measured by the FT-IR method greatly deviate from values obtained by the PL method. Thus, the present inventor has turned his thought to creating a calibration curve in accordance with each of the starting materials having different contained oxygen concentrations, thereby bringing the present invention to completion.

[0027] That is, the present invention is a method for measuring carbon concentration which obtains the carbon concentration in a measurement semiconductor sample made of an FZ single crystal from measurement values measured by a photoluminescence (PL) method, the method including:

previously preparing respective FZ single crystals manufactured by the FZ method from a plurality of types of starting materials which have different contained oxygen concentrations due to a difference in manufacturing methods, and creating and preparing calibration curves each indicating a relationship between a measurement value based on the photoluminescence (PL) method and the carbon concentration from standard samples made of the respective FZ single crystals in accordance with the respective types of starting materials of the FZ single crystals;

selecting a calibration curve of the same type of starting material as a starting material of the measurement semiconductor sample from the plurality of prepared calibration curves; and

obtaining the carbon concentration of the measurement semiconductor sample from the measurement value of the measurement semiconductor sample based on the photoluminescence method with the use of the selected calibration curve.

[0028] In the method for measuring carbon concentration according to the present invention, it is preferable to measure carbon concentration of a semiconductor standard sample by a measuring method other than the PL method, make reference to the measured carbon concentration of the semiconductor standard sample, create a calibration curve indicative of a relationship between a measurement value obtained by the PL method and the carbon concentration obtained by the measuring method other than the PL method, then obtain a "measurement value based on the PL method" of a measurement semiconductor sample, and obtain carbon concentration of the measurement semiconductor sample from the calibration curve.

[0029] As the method for measuring the carbon concentration of the semiconductor standard sample other than the PL method, there is, for example, a well-known FT-IR method or a SIMS method (secondary ion mass spectrometry). A carbon concentration domain to be measured by the measuring method (the FT-IR method in particular) other than the PL method can be set to 1×10^{14} atoms/cm^3 or more, and its upper limit may be set to 5×10^{17} atoms/cm^3 at which dislocation of the silicon single crystal does not occur.

[0030] After measuring the carbon concentration by the carbon concentration measuring method other than the PL method, a "measurement value based on the PL method" of the semiconductor standard sample is obtained. The carbon concentration measurement based on the PL method can be carried out in accordance with a conventional method. That is, the sample is irradiated with an electron beam to substitute a carbon atom (Cs) at a site of substitution with a counterpart at an interstitial site (Ci), and a carbon-oxygen composite defect which is called a G line (Ci-Cs) or a C line (Ci-Oi) is produced. The PL measurement is performed while cooling this defect with a liquid He, and each peak intensity including that of an FE line which is luminescence resulting from silicon is obtained. Further, as PL measurement values, it is possible to use G line intensity, C line intensity, G line intensity/FE line intensity or C line intensity/FE line intensity standardized with the use of the FE line intensity, and G line intensity/B (boron concentration), C line intensity/B (boron concentration), G line intensity/P (phosphorous concentration), or C line intensity/P (phosphorous concentration) standardized with the use of dopant concentration, and others.

[0031] At this time, in the present invention, a plurality of calibration curves of the carbon concentrations in the FZ single crystals are prepared in accordance with respective types of starting materials having different contained oxygen concentrations in the FZ single crystals.

[0032] Thus, to prepare the plurality of calibration curves of the carbon concentrations in the FZ single crystals in accordance with the respective types of the starting materials of the FZ single crystals in advance, phosphorous-doped FZ single crystals having a diameter of 150 mm and a resistivity of 150 Ωcm were pulled up as standard samples. The number of the FZ single crystals using a polycrystalline silicon ingot as a starting material is four, and the number of the FZ single crystals using a CZ single crystal ingot is five (the former may be referred to as pure-poly FZ and the latter may be referred to as CZ-FZ hereinafter).

[0033] Here, carbon concentration measurement values based on the FT-IR method were compared with carbon concentrations obtained from measurement values based on the PL method.

[0034] It is to be noted that low carbon concentrations can be measured by the PL method, but the crystals were daringly manufactured so that high carbon concentration which can be detected by the FT-IR method can be provided for the purpose of confirming reliability of the measurement results of the PL method by the FT-IR method.

[0035] The carbon concentration measurement based on the FT-IR method is standardized by JEITA (JEITA EM-3503), and its detection lower limit is 2×10^{15} atoms/cm^3. A recent academic meeting has reported that 1×10^{14} atoms/cm^3 was measured (The 76th Japan Society of Applied Physics Autumn Meeting, 13p-1E-1, 2015).

[0036] After growing the FZ single crystals which are the standard samples, a sample was sliced off from a crystal tail portion (a position which is 100 cm from a shoulder portion) of each crystal.

[0037] First, in a state where no electron beam is applied, the carbon concentration of each sample was measured by the FT-IR method. Then, after applying the electron beam with 2 MeV and 400 kGy, the PL measurement was performed. FIG. 1 shows a relationship (a calibration curve) between each carbon concentration quantified by the FT-IR method and the G line intensity/FE line intensity obtained by the PL measurement after the electron beam application.

[0038] Here, all the four pure-poly FZ had the oxygen concentration of 5.0×10^{15} atoms/cm^3 at the crystal tail portion (the position which is 100 cm from the shoulder portion) of each crystal. On the other hand, the CZ-FZ had 1.3 to 2.3×10^{16} atoms/cm^3. In this manner, there is no significant difference in oxygen concentration between the pure-poly FZ and the CZ-FZ in the FZ single crystals, the concentrations have sufficiently small values, the relationship (the calibration curve) in FIG. 1 can be regarded as one line, and hence it has been conventionally considered that no problem occurs even if the carbon concentrations are quantified with the use of one calibration curve.

[0039] Thus, as measurement samples, 10 pure-poly FZ and 10 CZ-FZ were further pulled up, and a sample was sliced off from each crystal tail portion (the position which is 100 cm from the shoulder portion). First, in a state where no electron beam is applied, the carbon concentration of each sample was measured by the FT-IR method. Then, after applying the electron beam with 2 MeV and 400 kGy, the PL measurement was performed, and the carbon concentrations were obtained in accordance with the relationship (the calibration curve) in FIG. 1.

[0040] FIG. 2 shows a relationship between the carbon concentrations obtained by the FT-IR method and the carbon concentrations obtained by the PL method with the use of the calibration curve of the conventional method in FIG. 1. In this manner, in case of the pure-poly FZ, a deviation between both types of the concentrations is considerable when the concentrations are low, and values of both the types of the concentrations are close to each other when the concentrations are high. On the other hand, in case of the CZ-FZ, it has been found out that values of both the types of the concentrations substantially coincide with each other when the concentrations are low, but a deviation between them are considerable when the concentrations are high.

[0041] It is supposed that this is caused by the use of the same calibration curve without discriminating the calibration curves depending on the pure-poly FZ and the CZ-FZ. Thus, to confirm this supposition, the present inventor has decided to obtain the calibration curve in FIG. 1 in accordance with each of types of starting materials of the FZ single crystals. This is shown in FIG. 3. It has been found out from FIG. 3 that the calibration curve of the pure-poly FZ is different from that of the CZ-FZ.

[0042] This means that it has been conventionally considered that both the pure-poly FZ and the CZ-FZ have sufficiently small oxygen concentrations, there is almost no difference between the oxygen concentrations, and one calibration curve can suffice without discriminating both the materials, but a difference in oxygen concentration between them is actually significant, and the calibration curves must be discriminated for them. That is, in FIG. 3, the CZ-FZ have smaller G/FE values than those of the pure-poly FZ to the carbon concentrations on the same level. That is, since the CZ-FZ has the higher oxygen concentrations, a C line (Ci-Oi) is prone to be formed as compared with the pure-poly FZ and, in other words, a G line (Ci-Cs) is hard to be formed, and G/FE values are small. Moreover, in case of the low oxygen concentrations like those of the pure-poly FZ or the CZ-FZ, when the carbon is present at high concentration (e.g., 2×10^{15} atoms/cm^3 or more (analogy from FIG. 3)), sufficiently high G line intensity is formed, and an influence of the oxygen concentration is hard to see.

[0043] As described above, it has been found out that, as the accurate carbon concentration measuring method for the FZ single crystals, the calibration curves must be created in accordance with the respective starting material types of the FZ single crystals in the low carbon concentration domain which is a target of the low-temperature PL method in particular.

[0044] The calibration curves for the respective starting material types of the FZ single crystals were applied to the 20 FZ single crystals in accordance with the starting material types. FIG. 4 shows a relationship between the carbon concentrations obtained by the FT-IR method and the carbon concentrations obtained by the PL method based on this method using calibration curves of the pure-poly FZ and the CZ-FZ. Both the concentrations excellently coincide with each other. In this manner, it has been confirmed that the calibration curves must be prepared in accordance with the respective starting material types in case of the FZ silicon single crystals.

[0045] It is to be noted that, in case of the CZ-FZ, an influence of the contained oxygen concentration in the CZ crystal as a starting material has been confirmed.

[0046] The five CZ-FZ used for drawing of FIG. 1 or FIG. 3 and the 10 CZ-FZ used for drawing of FIG. 2 or FIG. 4 had the oxygen concentrations which range from 4.0×10^{17} atoms/cm^3 to 1.2×10^{18} atoms/cm^3 in a tail portion (a position which is 100 cm from a shoulder portion) of each CZ crystal as a starting material.

[0047] The oxygen concentrations in the FZ single crystals fabricated with the use of such a

CZ starting material were 1.3 to 2.3×10^{16} atoms/cm^3 likewise in each crystal tail portion (a position which is 100 cm from the shoulder portion). In this manner, it has been confirmed that since almost all of the oxygen in the CZ crystal ingots scatters in an FZ process and the oxygen concentration remaining in the FZ crystals become constant to some extent, the calibration curve of the CZ-FZ does not have to be prepared in accordance with each oxygen concentration, and one calibration curve can suffice.

[0048] That is, to quantify the carbon concentrations in the FZ single crystals, it is necessary and sufficient to prepare the calibration curves in accordance with the respective starting material types of the FZ single crystals irrespective of the oxygen concentration in the CZ crystal as the starting material.

[0049] Additionally, as to the low concentration domain which cannot be quantified by the conventional method, preparing a calibration curve obtained by extrapolating the calibration curve obtained here enables quantification and, specifically, the lower carbon concentration than 1×10^{14} atoms/cm^3, e.g., the low carbon concentration which is approximately 1×10^{13} atoms/cm^3 can be quantified when applied to the extrapolated calibration curve.

[0050] It is to be noted that, when the measured carbon concentration in a measurement semiconductor sample is high carbon concentration which is 1×10^{14} atoms/cm^3 or more, verifying whether the measured carbon concentration coincides with carbon concentration measured by a measuring method other than the PL method enables verifying the reliability of the calibration curve. When both the concentrations do not coincide with each other, correcting the calibration curve can obtain the further reliable calibration curve.

EXAMLE

[0051] Although the present invention will now be more specifically described hereinafter with reference to an example and a comparative example of the present invention, the present invention is not restricted to these examples.

(Example)

[0052] As described above, calibration curves were discriminated in accordance with respective starting material types of the pure-poly FZ and the CZ-FZ in advance to obtain the calibration curves in FIG. 3.

[0053] Then, as measurement samples, each phosphorous-doped FZ single crystal which has a diameter of 150 mm and a resistivity of 150 Ωcm and uses a pure-poly or CZ single crystal as a starting material was newly grown (the former is a crystal A and the latter is a crystal B).

According to the PL method, low carbon concentration can be measured, but each crystal was manufactured daringly so that high carbon concentration which can be detected by the FT-IR method can be provided to confirm the reliability of a measurement result of the PL method by the FT-IR method. A sample was sliced off from each crystal tail portion (a position which is 100 cm from a shoulder portion), a part of the sample was irradiated with an electron beam with 2 MeV and 400 kGy, and then the PL measurement was performed.

[0054] Consequently, G line intensity/FE line intensity of 88.5 was obtained in the crystal A, and the counterpart of 35.1 was obtained in the crystal B. Further, as Example, when a calibration curve of the pure-poly FZ was applied in the crystal A and a calibration curve of the CZ-FZ was applied in the crystal B in accordance with the respective starting materials to obtain carbon concentrations, the carbon concentrations in the respective samples were 4.2×10^{14} atoms/cm^3 in the crystal A and 4.6×10^{14} atoms/cm^3 in the crystal B.

[0055] On the other hand, remaining samples sliced off from the respective crystal tail portions were directly measured by the FT-IR to obtain carbon concentrations. As a result, both the crystals A and B had 4.4×10^{14} atoms/cm^3, and it has been confirmed that they excellently coincide with the carbon concentration obtained by the PL method.

[0056] Subsequently, as a measurement sample, a phosphorous-doped FZ crystal which has a diameter of 150 mm and a resistivity of 150 Ωcm and uses a CZ single crystal as a starting material was prepared. At this time, the crystal was manufactured so that low carbon concentration can be provided (a crystal C). A sample was sliced off from a crystal tail portion (a position which is 100 cm from a shoulder portion), a part of the sample was irradiated with an electron beam with 2 MeV and 400 kGy, and then the PL measurement was performed.

[0057] Consequently, G/FE was 2.8. As Example, when a calibration curve of the CZ-FZ was used in accordance with a type of the starting material and it was extrapolated to a low concentration side, the carbon concentration of 3.4×10^{13} atoms/cm^3 was obtained.

(Comparative Example)

[0058] As Comparative Example, the PL measurement values (the G line intensity/FE line intensity) of the crystals A and B obtained in Example were applied to the conventional calibration curve in FIG. 1 to obtain carbon concentrations. Consequently, the crystal A had 7.7×10^{14} atoms/cm^3 whilst the crystal B had 3.7×10^{19} atoms/cm^3, and the carbon concentration of the crystal A (the pure-poly FZ) was largely different from the value obtained in Example or the value obtained by the FT-IR. That is because, as can be understood from a comparison between the calibration curve in FIG. 1 and those in FIG. 3, a deviation between the carbon concentrations based on the FT-IR method and the PL method in the vicinity of 4×10^{14} atoms/cm^3 is small in the CZ-FZ but large in the pure-poly FZ.

[0059] Furthermore, when a remaining sample sliced off from the crystal tail portion of the crystal C in Example was subjected to the FT-IR method, the quantification was impossible due to a detection lower limit value or a smaller value. On the other hand, according to the method of Example, it has been confirmed that extrapolating the starting material type-specific calibration curve enables the quantification as described above.

REFERENCES CITED IN THE DESCRIPTION

Cited references

Patent documents cited in the description

- JP2013152977A [0008]
- JPH4344443A [0008]
- JP2015101529A [0008]
- JP2015222801A [0008]

Patentkrav

1. Fremgangsmåde til måling af carbonkoncentration som bestemmer carbonkoncentration i en målehalvlederprøve fremstillet af en FZ-siliciumenkrystal fremstillet ved en floating-zone- (FZ) metode fra måleværdier målt med en fotoluminescens- (PL) metode, hvilken fremgangsmåde omfatter:

tidligere fremstilling af respektive FZ-siliciumenkrystaller fremstillet ved FZ-metoden fra en flerhed af typer af udgangsmaterialer, som har forskellige indeholdte oxygenkoncentrationer på grund af en forskel af fremstillingsfremgangsmåder, og etablering og forberedelse af kalibreringskurver, som hver indikerer et forhold mellem en måleværdi baseret på fotoluminescens- (PL) metoden og carbonkoncentrationen fra standardprøver fremstillet af de respektive FZ-siliciumenkrystaller i henhold til de respektive typer af udgangsmaterialer af FZ-siliciumenkrystallerne;

udvælgelse af en kalibreringskurve af den samme type af udgangsmateriale som et udgangsmateriale af målehalvlederprøven fra flerheden af de forberedte kalibreringskurver; og

bestemmelse af carbonkoncentrationen af målehalvlederprøven fra måleværdien af målehalvlederprøven baseret fotoluminescensmetoden under anvendelse af den valgte kalibreringskurve.

2. Fremgangsmåden til måling af carbonkoncentration ifølge krav 1, hvor flerheden af kalibreringskurver fremstillet i henhold til de respektive typer af udgangsmaterialer fremstilles i overensstemmelse med standardprøven, hvis type af udgangsmateriale er en polykrystallinsk siliciumingot, og standardprøven, hvis type af udgangsmateriale er siliciumenkrystalingot fremstillet ved en Czochralski-metode.

3. Fremgangsmåden til måling af carbonkoncentration ifølge krav 1 eller 2, hvor hver kalibreringskurve, som indikerer forholdet mellem måleværdierne baseret på PL-metoden og carbonkoncentrationerne, dannes med reference til måleværdier af carbonkoncentrationer målt med en målemetode anden end PL-metoden med hensyn til standardprøverne konfigureret til at bestemme kalibreringskurverne.

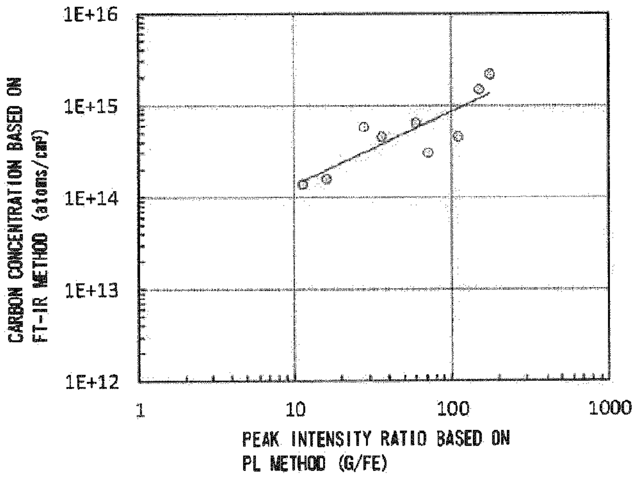
4. Fremgangsmåden til måling af carbonkoncentration ifølge krav 3, hvor et carbonkoncentrationsdomæne af kalibreringskurven målt med en målemetode anden end PL-metoden er 1×10^{14} atomer/cm^3 eller mere.

5. Fremgangsmåden til måling af carbonkoncentration ifølge krav 3 eller 4, hvor som kalibreringskurven forberedes en kurve, som tilvejebringes ved ekstrapolering af kalibreringskurven, som forberedes med reference til carbonkoncentrationerne målt med målemetoden anden end PL-metoden.

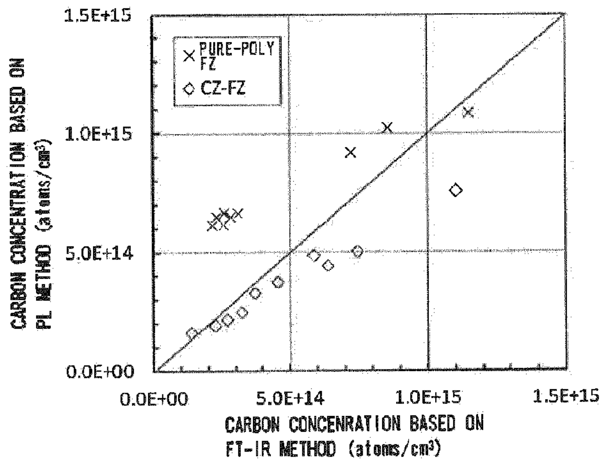
6. Fremgangsmåden til måling af carbonkoncentration ifølge et hvilket som helst af kravene 1 til 5, hvor i et tilfælde, hvor carbonkoncentrationen i målehalvleder-prøven er blevet målt som 1×10^{14} atomer/cm^3 eller mere, om den målte carbonkoncentration stemmer overens med carbonkoncentrationen målt med målemetoden anden end PL-metoden, verificeres, og kalibreringskurven korrigeres, når de ikke stemmer overens med hinanden.

DRAWINGS

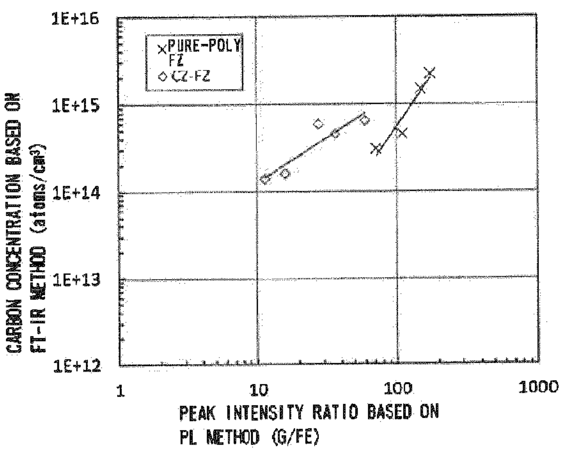
[FIG. 1]



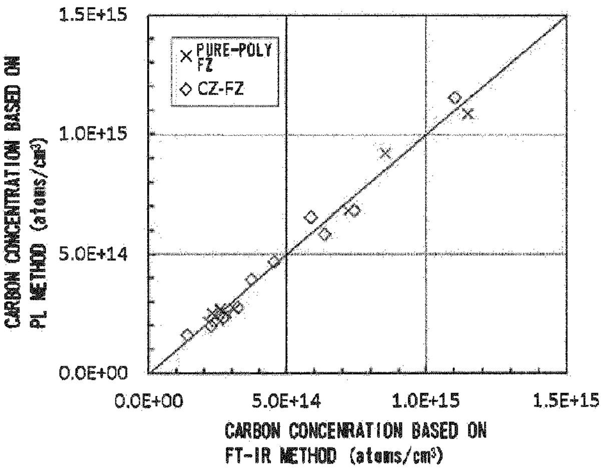
[FIG. 2]



[FIG. 3]



[FIG. 4]


1.5E+15
1.0E+15
5.0E+14
0.0E+00
0.0E+00
5.0E+14
1.0E+15
1.5E+15
PURE-POLY FZ
CZ-FZ
CARBON CONCENTRATION BASED ON PL METHOD (atoms/cm³)
CARBON CONCENRATION BASED ON FT-IR METHOD (atoms/cm³)