

METHOD OF INSPECTING SILICON SINGLE CRYSTAL AND METHOD OF MANUFACTURING SILICON SINGLE CRYSTAL

FIELD OF THE INVENTION

[0001] The present invention relates to a method of inspecting a silicon single crystal grown by the Czochralski process. More particularly, it relates to a method of inspecting a silicon single crystal that permits the detection with high sensitivity of an L/D region and a B-band region in the silicon single crystal with low oxygen concentration that has been grown by the Czochralski process.

The present invention further relates to a method of manufacturing a silicon single crystal that provides a silicon single crystal without an L/D region and without a B-band region by employing the inspection result of the above inspection method.

DISCUSSION OF THE BACKGROUND

[0002] The Czochralski process (also referred to as the "CZ process", hereinafter) of growing silicon single crystals while pulling them from a starting material melt is widely employed as a method of growing silicon single crystals for manufacturing semiconductor wafers.

[0003] In the CZ process, the types and distribution of defects incorporated into the crystal during the growth of a silicon single crystal are known to depend on the pulling rate V of the crystal and the temperature gradient G at the solid-liquid boundary. Fig. 6 is a drawing showing the normal relation between V/G and the types and distribution of defects. As shown in Fig. 6, when V/G exceeds a certain value, excessive vacancies form and void defects where atomic vacancies agglomerate, known as crystal-originated particles (COPs), occur. Additionally, when V/G is small, there are excess interstitial silicon atoms, and dislocation clusters called large dislocations (L/Ds), which are aggregates of interstitial silicon, form.

[0004] Further, between the region in which COPs form and the region in which L/Ds form (the L/D region), there are multiple regions that behave differently when heat treated. As shown in Fig. 6, between the region in which COPs form and the region in which L/Ds form, there are three regions in the form of the OSF region, P_v region, and P_i region, in order of descending V/G . The OSF region is a region containing platelike oxygen precipitates (OSF: oxidation-induced stacking faults) in an as-grown state (a state in which no heat treatment is conducted following crystal growth), in which OSFs form when hot oxidized at

elevated temperature (generally at about 1,000°C to 1,200°C). The Pv region is a region that contains oxygen precipitation nuclei in an as-grown state, in which oxygen precipitates tend to form when subjected to a two-stage heat treatment at a low temperature and a high temperature (for example, about 800°C and about 1,000°C). The Pi region is a region that contains almost no oxygen precipitation nuclei in an as-grown state, in which oxygen precipitates tend not to form even when subjected to a heat treatment. As V/G is lowered, the B-band, a region that tends to form oxygen precipitates despite being part of the Pi region, appears adjacent to the L/D region.

[0005] The above COPs and L/Ds greatly impact device characteristics when integrated circuits are formed on the outer layer portion of a silicon single crystal wafer. Thus, it is desirable to grow silicon single crystals under conditions in which such defects do not occur. To that end, it is important to inspect silicon single crystals that are grown, correctly determine the distribution of the various regions, and provide necessary feedback to crystal growth. For example, if an OSF region is forming, the growing conditions can be modified by decreasing the pulling rate V. If a B-band is forming, modifying the growing conditions by increasing the pulling rate V makes it possible to stably produce silicon single crystals that are free of crystalline defects at good yield.

[0006] Currently, the copper decoration method is widely employed as a method for determining various regions in single silicon crystals (for example, see Japanese Unexamined Patent Publication (KOKAI) No. 2001-81000 and Luciano Mule'Stagno, *A Technique for Delineating Defects in Silicon*, Solid State Phenomena, Vols. 82-84 (2002), pp. 753-758). In the copper decoration method, copper that has adhered to the surface of a sample is heat treated to diffuse it into the interior of the sample, after which the sample is rapidly cooled to render defects in the crystal surface apparent. When needed, selective etching is conducted to detect minute defects.

[0007] Conventionally, it has been highly desirable to provide wafers with good gettering capability in which oxygen precipitates are formed to a high density. However, oxygen precipitates are a type of crystal defect. When oxygen precipitates are present on the surface of a wafer on which a device is being formed, they contribute to device defects. In recent years, as device cleaning has advanced, the danger of impurity contamination has been greatly reduced. In terms of the quality demanded of wafers, gettering capability aside, it is anticipated that in the next generation of wafers, not just wafers with fewer COPs

and L/Ds, but wafers with even fewer oxygen precipitates, which are a type of crystal defect, will be in demand.

[0008] Generally, the oxygen precipitates in wafers can be reduced by diminishing the concentration of oxygen in the crystal. However, based on research, the present inventor found that in silicon single crystal samples of low oxygen concentration, it is difficult to identify the L/D region and B-band region by the conventional copper decoration method.

SUMMARY OF THE INVENTION

[0009] Accordingly, it is an object of the present invention to provide a means capable of detecting with high sensitivity the L/D region and B-band region in silicon single crystals of low oxygen concentration.

[0010] The present inventor conducted extensive research into achieving the above object, resulting in the following discoveries:

(1) Conducting copper decoration at low temperatures at which oxygen precipitates did not form in the B-band made it possible to avoid the formation of oxygen precipitates in the B-band region, and by rapidly cooling so that copper, which has a rapid diffusion rate, does not diffuse beyond L/D regions, it was possible to selectively render apparent just L/Ds. That made it possible to detect the L/D region with high sensitivity in silicon single crystals of low oxygen density.

(2) By conducting a prescribed pretreatment (heat treatment) before the copper decoration of (1), it was possible to render the B-band region and L/D region apparent. By subtracting the L/D region detected in (1) above from the region rendered apparent here, it was possible to detect the B-band region in silicon single crystals of low oxygen concentration, which has conventionally been difficult.

The present invention was devised on the basis of the above discoveries.

[0011] An aspect of the present invention relates to a method of inspecting a silicon single crystal, which comprises:

decorating with copper a surface of a sample cut out of a silicon single crystal ingot with an interstitial oxygen concentration, according to old American Society for Testing and Materials (old ASTM), of less than 12×10^{17} atoms/cm³ that has been grown by the Czochralski process;

subjecting the decorated sample to a heating and cooling treatment comprising heating the sample for equal to or more than five minutes at a

temperature region of equal to or higher than 700°C but less than 800°C followed by rapidly cooling the sample from the temperature region at a cooling rate exceeding 2.5°C/minute;

selectively etching the surface of the sample following the heating and cooling treatment; and

specifying an L/D region based on a localized state of pits on the surface of the sample following the selective etching.

[0012] A further aspect of the present invention relates to a method of inspecting a silicon single crystal, which comprises:

subjecting one of two samples, that have been cut out of a silicon single crystal ingot with an interstitial oxygen concentration, according to old American Society for Testing and Materials (old ASTM), of less than 12×10^{17} atoms/cm³ that has been grown by the Czochralski process as well as have approximately the same crystal region distribution each other, to a pretreatment comprising heating within a temperature region of 750°C to 900°C and then heating within a temperature region of 1,000°C to 1,150°C;

decorating surfaces of the two samples with copper;

subjecting the decorated samples to a heating and cooling treatment comprising heating the samples for equal to or more than five minutes at a temperature region of equal to or higher than 700°C but less than 800°C followed by rapidly cooling the samples from the temperature region at a cooling rate exceeding 2.5°C/minute;

selectively etching the surfaces of the samples following the heating and cooling treatment; and

specifying a B-band region based on a result of comparing a localized state of pits on the surface of the sample subjected to the pretreatment and that of the sample not subjected to the pretreatment following the selective etching.

[0013] In the above aspects, the selective etching may be carried out by Wright etching.

[0014] In the above aspects, the copper decoration may be carried out by immersing the sample in a copper-containing solution with a copper concentration of equal to or greater than 3×10^{20} atoms/cm³.

[0015] A still further aspect of the present invention relates to a method of manufacturing a silicon single crystal, which comprises:

growing a silicon single crystal to be inspected by the Czochralski process;

inspecting the silicon single crystal to be inspected by the method of inspecting according to any of the above aspects;

determining a condition of pulling a silicon single crystal based on a result of the inspection; and

growing a silicon single crystal by the Czochralski process under the determined pulling condition to obtain a silicon single crystal that contains neither an L/D region nor a B-band region.

[0016] The present invention makes it possible to detect the L/D region and B-band region with high sensitivity in silicon single crystals of low oxygen concentration that are grown by the CZ process. By feeding the results obtained back into the crystal growth conditions when employing the CZ process, it is possible to stably mass produce high-quality silicon single crystals.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] The present invention will be described in the following text by the exemplary, non-limiting embodiments shown in the figure, wherein:

Fig. 1 is a descriptive drawing of the configuration of the silicon single crystal pulling device employed in Examples.

Fig. 2 shows the results of observation of the state of localized pits in Example 1.

Fig. 3 shows the results of observation of the state of localized pits in Example 2.

Fig. 4 shows (left) the results of lifetime measurement in Example 2 and (right) the results of lifetime measurement in a sample subjected to a different pretreatment.

Fig. 5 shows the results of observation of the state of localized pits in Example 3.

Fig. 6 is a descriptive drawing showing the relation between the types and distribution of regions formed in a silicon single crystal ingot and the crystal growth conditions in the CZ process.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0018] The present invention relates to a method of inspecting a silicon single crystal (referred to as "Method 1", hereinafter), which comprises:

decorating with copper a surface of a sample cut out of a silicon single crystal ingot with an interstitial oxygen concentration, according to old American Society for Testing and Materials (old ASTM), of less than 12×10^{17} atoms/cm³ that has been grown by the Czochralski process;

subjecting the decorated sample to a heating and cooling treatment comprising heating the sample for equal to or more than five minutes at a temperature region of equal to or higher than 700°C but less than 800°C followed by rapidly cooling the sample from the temperature region at a cooling rate exceeding 2.5°C/minute;

selectively etching the surface of the sample following the heating and cooling treatment; and

specifying an L/D region based on a localized state of pits on the surface of the sample following the selective etching; and also relates to a method of inspecting a silicon single crystal (referred to as "Method 1", hereinafter), which comprises:

subjecting one of two samples, that have been cut out of a silicon single crystal ingot with an interstitial oxygen concentration, according to old American Society for Testing and Materials (old ASTM), of less than 12×10^{17} atoms/cm³ that has been grown by the Czochralski process as well as have approximately the same crystal region distribution each other, to a pretreatment comprising heating within a temperature region of 750°C to 900°C and then heating within a temperature region of 1,000°C to 1,150°C;

decorating surfaces of the two samples with copper;

subjecting the decorated samples to a heating and cooling treatment comprising heating the samples for equal to or more than five minutes at a temperature region of equal to or higher than 700°C but less than 800°C followed by rapidly cooling the samples from the temperature region at a cooling rate exceeding 2.5°C/minute;

selectively etching the surfaces of the samples following the heating and cooling treatment; and

specifying a B-band region based on a result of comparing a localized state of pits on the surface of the sample subjected to the pretreatment and that of the sample not subjected to the pretreatment following the selective etching.

[0019] In the method of inspecting a silicon single crystal of the present invention, the silicon single crystal that is subjected to inspection is grown by the Czochralski process and has an interstitial oxygen concentration, according to old American Society for Testing and Materials (old ASTM), of less than 12×10^{17} atoms/cm³. It is difficult to identify the L/D region and B-band region by the conventional copper decoration method in such silicon single crystals of low oxygen concentration. Thus, there are problems in that the L/D region ends up

being detected as a smaller size than the actual size and detection of the B-band region becomes difficult.

By contrast, the present invention permits the highly sensitive detection of the L/D region by Method 1, and the detection with high sensitivity of both the L/D region and B-band region by Method 2. That is because copper decoration, comprising heating the sample to a relatively low temperature and rapidly cooling it, permits selective copper decoration of the L/D region, and conducting a heat treatment comprised of the two states of low temperature and high temperature as a pretreatment before copper decoration permits copper decoration of the L/D region and even the adjacent B-band region.

The method of inspecting a silicon single crystal of the present invention will be described more specifically below.

[0020] The sample that is subjected to copper decoration can be a lengthwise-sliced sample that has been obtained by vertically slicing in an axial direction a silicon single crystal ingot grown by the CZ process, or a wafer sample that has been sliced in a crosswise direction with a wire saw or the like. The interstitial oxygen concentration, as set forth above, is less than 12×10^{17} atoms/cm³ by old ASTM conversion. At equal to or more than 12×10^{17} atoms/cm², regions in which oxygen precipitates other than the L/D region tend to be formed also end up being copper decorated in copper decoration in the present invention, precluding the highly sensitive detection of the L/D region. That is, the inspection method of the present invention is for use on silicon single crystals of low oxygen concentration. A lower limit of the interstitial oxygen concentration (old ASTM) of the silicon single crystal that is inspected of, for example, about 10×10^{17} atoms/cm³ is desirable for clearly distinguishing the L/D region from regions adjacent to the L/D region.

[0021] In Method 2, two samples having approximately the same crystal region distribution each other are employed. That is because, as set forth further below, specifying the B-band region by comparing the L/D region specified in one of the samples with the region in which pits have formed in the other sample requires that the samples have roughly identical crystal region distributions. The two samples of roughly identical crystal region distributions can be the two equal halves of an ingot that has been split lengthwise along its central axis, or a wafer sample that has been divided into two or four parts through its geometric center.

[0022] Since Method 2 comprises steps that are shared by Method 1, Method 1 will be primarily described first below, followed by Method 2.

[0023] As set forth above, Method 1 comprises "copper decoration," "a heating and cooling treatment," "selective etching," and "specification of an L/D region." Each of these steps will be sequentially described below.

[0024] Copper decoration can be conducted in the same manner as common copper decoration. Specifically, for example, the sample is immersed in a copper-containing solution, removed from the solution, and dried by allowing it to naturally dry for a prescribed period. The copper-containing solution can be in the form of a copper nitrate aqueous solution or a mixed solution of copper nitrate and hydrofluoric acid (HF). From the perspective of uniform decoration of the L/D region (in Method 2, L/D region + B-band region), the copper concentration in the solution is desirably equal to or greater than 3×10^{20} atoms/cm³. The higher the concentration of copper in the copper-containing solution the better from the perspective of uniform decoration. For example, it is also possible to employ a solution containing copper up to the upper limit of solubility. The solubility of copper depends on temperature. For example, it is about 4.4×10^{20} atoms/cm³ at 0°C.

[0025] Next, the decorated sample is subjected to a heating and cooling treatment. The heating and cooling treatment can be conducted using any of the various heat treatment furnaces such as the benchtop electric furnaces and horizontal oxidation furnaces that are commonly employed in the heat treatment of silicon wafers. Unless specifically stated otherwise, the temperature and rate of heat treating the sample that are stated in the present invention refer to the temperature and rate for the atmosphere to which the sample is exposed (for example, the atmosphere within the oven used for the heat treatment). Unless specifically stated otherwise, the atmosphere to which the sample is exposed is not specifically limited, and can be any atmosphere, such as air.

[0026] The heat treatment following copper decoration can thermally diffuse the copper into the sample. The temperature to which the sample is heated following the above decoration in the present invention is equal to or higher than 700°C but less than 800°C. At a heating temperature of equal to or higher than 800°C, an oxygen precipitate ends up forming in the B-band region due to heating, making it difficult to selectively copper decorate the L/D region. At a heating temperature of less than 700°C, copper decoration in the L/D region becomes inadequate. At a heat treatment time of less than 5 minutes at the above heating temperature, it is difficult to render the boundary with the L/D region clearly apparent, so the heat treatment time is set to equal to or more than

5 minutes. No great change in effect is achieved by lengthening the heat treatment beyond 5 minutes, so the upper limit is not specifically limited. For example, the heat treatment can be conducted for 10 minutes or so. However, 5 minutes is optimal for conducting a rapid inspection. It is not necessary to keep the temperature constant during heating. The temperature can be varied within the range of equal to or higher than 700°C but less than 800°C. The heating furnace can be heated to the heating temperature before introducing the sample, or the temperature can be raised to the above heating temperature after introducing the sample. When the temperature is raised after introducing the sample, employing a rate of temperature increase of about 2°C to about 7°C per minute is desirable from the perspective of precipitating copper compounds during the subsequent rapid cooling.

[0027] In the present invention, rapidly cooling the sample following heating can cause copper compounds to precipitate in the L/Ds (dislocation clusters). In common copper decoration, for example, as described in above-cited Japanese Unexamined Patent Publication (KOKAI) No. 2001-81000, the sample is removed from the heating furnace and allowed to stand and cool to room temperature. By contrast, in the present invention, the cooling rate is controlled so as to exceed 2.5°C/minute. Desirably, the cooling rate exceeds 2.5°C/minute in the course of lowering the temperature from the heating temperature region (equal to or higher than 700°C but less than 800°C) to a temperature of 50 °C to 100°C lower than the above heating temperature region. When the cooling rate during cooling from the above heat temperature region is 2.5°C/minute or lower, the rapidly diffusing copper diffuses beyond the L/D region and copper decoration of the L/D region becomes inadequate. As a result, the boundaries with adjacent regions become unclear, and it becomes difficult to identify the L/D region. The cooling rate can be controlled by setting the heat treatment furnace.

[0028] A rapid cooling rate is desirable to inhibit the diffusion of copper. For example, the cooling rate of equal to or more than 100°C/min, equal to or more than 200°C/min, and in particular, equal to or more than 300°C/min can be employed. When the performance of common heat treatment furnaces is taken into account, equal to or less than about 500°C/minute may be the upper limit of the cooling rate. However, since the faster the decrease, the better it is for inhibiting the diffusion of copper as set forth above, the upper limit is not specifically limited. The sample that has been cooled to a prescribed temperature can be removed from the heat treatment furnace and left standing

at room temperature.

[0029] When the surface of the sample that has been subjected to copper decoration and a heating and cooling treatment is selectively etched, copper compounds that have precipitated into L/Ds by copper decoration are removed from the surface of the sample. That makes it possible to detect the L/Ds as pits. Accordingly, in the present invention, the L/D region is specified based on the localized state of pits in the sample surface following selective etching. For example, the sample surface can be examined under converging lamps following selective etching and the region in which pits are localized can be specified as the L/D region. When specifying regions in the present invention, it is possible to additionally employ lifetime map (recombination lifetime distribution) measurement. Lifetime map measurement can identify regions within crystals; the procedure is known (for example, see the specification of Japanese Patent No. 4,200,845). It affords the advantage of rendering the boundaries between regions clearly apparent. However, a relative determination is made regarding the magnitude of the lifetime value. Thus, by lifetime measurement alone, it is difficult to reliably specify the L/D region and the B-band region. By contrast, in the present invention as set forth above, the L/D region and B-band region can be detected with high sensitivity in a silicon single crystal of low oxygen concentration that has been grown by the CZ process, a feat not readily accomplished in the past. When used in combination with lifetime map measurement, the boundaries between the L/D region and the B-band region with other regions can be clearly confirmed.

[0030] The above selective etching can be conducted with Secco solution (Secco etching: for example, a combination of HF = 100 cc and $K_2Cr_2O_7$ = 50 g (0.15 mol/L)); Wright solution (Wright etching: for example, a combination of HF = 60 cc, HNO_3 = 30 cc, Cr_2O_3 = 30 cc (5 mol/L), $Cu(NO_3)_2$ = 2.2 g, H_2O = 60 cc, CH_3COOH = 60 cc). From the perspective of the stability of the etching solution, Wright etching is desirably conducted. The pits can be observed visually or under a microscope.

[0031] Usually, the size of the L/D region decreases near the boundary with the B-band region on the outer perimeter portion. Thus, if heavy etching is employed, the pits derived from the L/D region on the outer perimeter portion are removed, sometimes specifying the L/D region as a smaller size than the actual size. Accordingly, to increase the detection sensitivity in the L/D region, an etching depth of equal to or less than 5 μm is desirable.

[0032] In Method 1 as set forth above, the L/D region is specified based on the localized state of pits on the sample surface following selective etching. Method 1 includes embodiments that determine that no L/D region is contained in the sample when no localized pits are observed.

[0033] In Method 2, two samples that are cut from the same silicon single crystal ingot are subjected to different treatments. One of the samples is subjected to the same treatment as in Method 1 above. That makes it possible to specify the L/D region in the sample. The other sample is subjected to a pretreatment to render the B-band region apparent in addition to the L/D region by copper decoration prior to conducting the same treatment as for the sample used to specify the L/D region. In the pretreatment, the sample, before being decorated with copper, is heated to within a temperature region of 750°C to 900°C (referred to as "low temperature heating", hereinafter) and then heated to within a temperature region of 1,000°C to 1,150°C (referred to as "high temperature heating", hereinafter). Conducting two-stage heating in the above two temperature regions can cause oxygen precipitates to form in the B-band region, making it possible to copper decorate the oxygen precipitates along with L/Ds in the subsequent copper decoration and heating and cooling processing. As a result, since both the copper compounds that have precipitated in L/Ds and the copper compounds that have precipitated in the oxygen precipitates in the B-band region are removed by selective etching, pits are locally present in the "L/D region + B-band region." The surface of the sample in which the "L/D region + B-band region" have been rendered apparent can be compared to the other sample in which just the L/D region has been rendered apparent, and the region in which pits other than the L/D region are locally present can be specified as the B-band region. This makes it possible to detect with high sensitivity the L/D region and the B-band region in silicon single crystals of low oxygen content, which was difficult in the past. By contrast, in single stage heating and in heating to a temperature outside the above temperature region, it is impossible to generate oxygen precipitates in the B-band region and specification of the B-band region becomes difficult. In the course of specifying the B-band region, as set forth above, it is possible to combine the use of lifetime map measurement. This combined use makes it possible to more clearly determine the boundaries of the regions.

[0034] The low temperature heating in the above pretreatment is desirably conducted for a period that is adequate to grow precipitation nuclei of critical size.

A period of about three hours is suitable. It can be conducted for a period exceeding three hours, but the density of the precipitation nuclei changes little. Thus, a period of about three hours is adequate. The high temperature heating is desirably conducted for a period that is adequate to grow the precipitation nuclei formed by low temperature heating into precipitates. A period of about 16 hours is suitable. It can be conducted for a period exceeding 16 hours, but the density of the precipitates changes little. Thus, a period of about 16 hours is adequate. When transitioning from the low temperature heating to the high temperature heating, the rate of temperature increase can be about 1°C/min to about 10°C/min, for example. From the perspective of smoothly advancing the growth of the precipitates, the pretreatment is desirably conducted in an atmosphere containing oxygen (an oxidizing atmosphere). The oxygen concentration in the oxidizing atmosphere is, for example, 10 volume percent to 100 volume percent. It is desirable to conduct the pretreatment by dry oxidation to smoothly advance the growth of the precipitates.

[0035] In the course of transitioning from the pretreatment to copper decoration, it is possible to remove the sample from the heat treatment furnace immediately following the pretreatment, but it is desirable to control the cooling rate to prevent the formation of slips due to rapid cooling. From this perspective, following cooling at a cooling rate of about 1°C/min to about 10°C/min to 900°C to 950°C in the heat treatment furnace following the high temperature heating, for example, it is desirable to remove the sample from the heat treatment furnace and allow it to stand at room temperature.

[0036] In Method 2, the "L/D region + B-band region" is rendered apparent in one of two samples having roughly the same crystal region distribution. In the other sample, the L/D region alone is rendered apparent, thereby permitting both detection of the L/D region and the B-band region. The following embodiments are also included:

(1) Rendering apparent the region in which pits are locally present in just the sample that has been subjected to the pretreatment, and when no pits are locally apparent in the other sample, determining that the region in which the pits are locally present is the B-band region, and that no L/D region is present in the samples.

(2) The reverse of (1) above, that is, determining that an L/D region is present in the samples but that no B-band region is present.

(3) When no localized pits are found in either of the two samples, determining

that neither an L/D region nor a B-band region is present in the samples.

As set forth above, Method 2 makes it possible to determine the presence or absence of an L/D region and a B-band region.

[0037] Before and after the above steps, pretreatments and posttreatments such as mirror etching with a mixed acid (containing HF and HNO₃), washing with pure water, washing with HF, and SC-1 washing can be conducted as desired. For example, prior to the heat treatment, the sample can be washed or etched to remove naturally forming oxide films. Prior to selective etching, the sample can be washed or etched to remove the copper remaining on the surface.

[0038] The inspection result of the inspection method of the present invention can be used to optimize the pulling conditions during the growth of silicon single crystals by the CZ process. If neither an L/D region or B-band region is detected, the same pulling conditions (specifically, the V/G) can be determined to be the optimal conditions for growing silicon single crystals that do not contain those regions. Additionally, when an L/D region and/or a B-band region is detected, for example, the pulling rate can be increased to adjust the pulling conditions so as to increase the V/G, thereby making it possible to grow silicon single crystals with neither an L/D region or a B-band region.

That is, the present invention also provides a method of manufacturing a silicon single crystal, comprising growing a silicon single crystal to be inspected by the Czochralski process; inspecting the silicon single crystal to be inspected by the inspection method of the present invention; determining a condition of pulling a silicon single crystal based on a result of the inspection; and growing a silicon single crystal by the Czochralski process under the determined pulling condition to obtain a silicon single crystal that contains neither an L/D region nor a B-band region. With the exception that the pulling condition in the CZ process is determined as set forth above, the method of manufacturing a silicon single crystal of the present invention makes it possible to manufacture silicon single crystals by known manufacturing steps based on the CZ process. In the present invention, it is also possible to determine the pulling condition in combination with a known inspection method that is capable of detecting a COP region, OSF region, Pv region, or Pi region. Thus, it is possible to provide high-quality silicon single crystals free of crystal defects and oxygen precipitates in a more reliable fashion.

EXAMPLES

[0039] The present invention will be described in detail below based on examples. However, the present invention is not limited to the examples.

[0040] Example 1: Detecting an L/D region and a B-band region in a wafer sample

(1) Growing a silicon single crystal by the CZ process

Using the silicon single crystal pulling device shown in Fig. 1, a silicon single crystal ingot (single crystal diameter: 300 mm, crystal orientation: $\langle 100 \rangle$, polarity: p-type (boron-doped), length of single crystal core: 2,000 mm) with an interstitial oxygen concentration of 11.8×10^{17} atoms/cm³ (old ASTM) was grown. The silicon single crystal pulling device shown in Fig. 1 will be described in detail below.

The silicon single crystal pulling device 10 shown in Fig. 1 was equipped with a chamber 11, a rotating support shaft 12 positioned to run vertically through the center of the bottom of chamber 11, a graphite susceptor 13 secured to the upper end of rotating support shaft 12, a quartz crucible 14 housed within graphite susceptor 13, a heater 15 positioned around graphite susceptor 13, a support shaft driving mechanism 16 for raising, lowering, and turning rotating support shaft 12, a seed chuck 17 supporting a seed crystal, a pulling wire 18 from which seed chuck 17 was suspended, a wire winding mechanism 19 for winding wire 18, a heat shielding member 22 for inhibiting temperature variation in the silicon melt 21 and to prevent heating of silicon single crystal ingot 20 by radiant heat from heater 15 and quartz crucible 14, and a control device 23 controlling the various components.

In the top portion of chamber 11 was provided a gas inlet 24 for introducing Ar gas into chamber 11. The Ar gas was introduced into chamber 11 via a gas tube 25 and a gas inlet 24. The quantity introduced was controlled by a conductance valve 26.

In the bottom of chamber 11 was provided a gas outlet 27 for discharging Ar gas from within chamber 11. The Ar gas that was sealed in chamber 11 passed through gas outlet 27, discharge gas tube 28, and was discharged to the exterior. Part way along discharge gas tube 28 were provided a conductance valve 29 and a vacuum pump 30. Vacuum pump 30 aspirated the Ar gas within chamber 11 while controlling its flow with conductance valve 29, thereby maintaining a state of reduced pressure within chamber 11.

Further, a magnetic field generating device 31 for applying a magnetic field to silicon melt 21 was provided outside chamber 11. The magnetic field

generated by magnetic field generating device 31 could be a horizontal magnetic field or a cusp magnetic field.

[0041] (2) Fabricating samples to be inspected

The silicon single crystal ingot grown in (1) above was sliced in a crosswise direction with a wire saw to obtain wafer samples. The samples obtained were divided into four equal fan-shaped samples, one of which was used in (3) below and another of which was treated in (4) below.

[0042] (3) Heating and cooling treatment to detect an L/D region

One of the samples (referred to as "Sample 1", hereinafter) fabricated in (2) above was treated as follows.

(i) After cleaning the sample with pure water and ultrasound, it was mirror etched for 5 minutes with an $\text{HNO}_3\text{:HF} = 5\text{:}1$ (volumetric ratio) etching solution and then rinsed with water for 10 minutes.

(ii) A copper-containing solution for copper decoration was prepared in the form of a copper nitrate aqueous solution by dissolving 30 g of copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) in five liters of water. The sample treated in (i) above was immersed for five minutes in the copper nitrate aqueous solution thus prepared, withdrawn, and naturally dried.

(iii) The sample that had been treated in (ii) above was loaded into a benchtop electric furnace (internal furnace temperature: 660°C ; internal furnace atmosphere: air). The temperature was raised at a rate of $5^\circ\text{C}/\text{min}$, and maintained for five minutes at 750°C . Subsequently, cooling was conducted to 660°C at a rate of $5^\circ\text{C}/\text{min}$, and the sample was unloaded from the benchtop electric furnace.

(iv) The surface of the sample that had been treated in (iii) above was etched for five minutes with an etching solution of $\text{HNO}_3\text{:HF} = 5\text{:}1$ (volumetric ratio), and thoroughly rinsed with water for 10 minutes to remove the copper precipitate from the surface.

[0043] (4) Pretreatment and heating and cooling treatment to detect L/D region + B-band region

One of the samples fabricated in (2) above (referred to as "Sample 2", hereinafter) was treated as follows.

(i) After cleaning the sample with pure water and ultrasound, it was mirror etched for 5 minutes with an $\text{HNO}_3\text{:HF} = 5\text{:}1$ (volumetric ratio) etching solution and then rinsed with water for 10 minutes.

(ii) The sample that had been treated in (i) above was loaded into a heat

treatment furnace and maintained for three hours at 780°C in an oxidizing atmosphere (dry O₂ (= 100 percent dry oxygen)), the temperature was raised by 5°C/min to 1,000°C, and the sample was maintained for 16 hours at that temperature. Subsequently, the temperature was lowered by 2°C/min to 950°C, and the sample was unloaded from the heat treatment furnace and cooled to room temperature.

(iii) The sample that had been treated in (ii) above was etched for three minutes with an etching solution of H₂O:HF = 1:1 (volumetric ratio) to remove the oxide film from the surface.

(iv) The sample treated in (iii) above was etched for five minutes in an etching solution of HNO₃:HF = 5:1 (volumetric ratio) and then rinsed with water for 10 minutes. Subsequently, the sample was subjected to the treatment of (ii) to (iv) in (3) above.

[0044] (5) Forming pits by selective etching

Following the treatment of (3) and (4) above, selective etching was conducted by etching the wafer surface to a depth of 5 μm with Wright solution. Following etching, the surface was observed under converging lamps; photographs taken of it are shown in Fig. 2. In the photographs of Fig. 2, the photo on the left shows the observation result of the wafer surface subjected to the treatment of (3) above, and the photo on the right shows the observation result of the wafer surface subjected to the treatment of (4) above.

[0045] As shown in Fig. 2, the localized presence of pits in an L/D region was confirmed in the wafer surface subjected to the treatment of (3) above, and the localized presence of pits in an "L/D region + B-band region" was confirmed in the wafer surface subjected to the treatment of (4). A B-band region was specified by subtracting the localized region of pits in the wafer surface subjected to the treatment of (3) above from the localized region of pits in the wafer surface subjected to the treatment of (4) above.

The above results indicated that the present invention permitted the specification of an L/D region and a B-band region in a silicon single crystal of low oxygen concentration.

In the photo on the right in Fig. 2, the presence of pits was also confirmed in a Pv region. That was because the oxygen precipitates that had been formed in the Pv region by the pretreatment had been decorated with copper. Since the positions and shapes of the Pv region, L/D region, and B-band region that formed differed, as was known, they could be readily distinguished.

In the photo on the right in Fig. 2, the region in which no pits were found that was present between the B-band region and Pv region was a Pi region, a region that inhibits precipitation. Thus, the present invention permits the detection of Pv regions and Pi regions in addition to L/D regions and B-band regions.

[0046] Example 2: Determination and detection of L/D regions and B-band regions in wafer samples

With the exception that a sample obtained from a silicon single crystal ingot grown under the different condition from Example 1 was employed, the same treatments were conducted as in Example 1. The treated wafer surface was selectively etched by etching to a depth of 5 μm with Wright solution. The surface following etching was examined under converging lamps; photographs taken of it are shown in Fig. 3. In the photographs of Fig. 3, the photo on the left shows the observation result of the wafer surface subjected to the treatment of (3) above (heating and cooling treatment to detect an L/D region), and the photo on the right shows the observation result of the wafer surface subjected to the treatment of (4) above (pretreatment and heating and cooling treatment to detect L/D region + B-band region).

In the photo on the left in Fig. 3, no localized pits were observed in the wafer subjected to the treatment of (3) above, so the evaluated sample was determined not to contain an L/D region. By contrast, based on the state of the localized pits in the photo on the right in Fig. 3, a B-band region and Pv region were determined to be present in the evaluated sample. In addition, based on the photo on the right in Fig. 3, a region in which no pits were found that was present between the B-band region and Pv region was determined to be a Pi region.

[0047] Lifetime map measurement

A lifetime measuring apparatus WT-2000 from Semilab was employed. Recombination lifetime measurement of the sample treated in (4) above (pretreatment and heating and cooling treatment to determine L/D region + B-band treatment) and in (5) above in Example 2 was conducted to obtain lifetime maps. The result is shown on the left in Fig. 4. Separately, lifetime maps were obtained for the sample that had been treated in the same manner as in (4) and (5) above with the exception that the heat treatment was conducted for 10 hours at 1,000°C instead of the pretreatment of (4)(ii). The result is shown on the right in Fig. 4.

In the photo on the right in Fig. 4, the B-band region was not detected.

By contrast, in the photo on the left in Fig. 4, a region distribution identical to that in the photo on the right in Fig. 3, which also contained a B-band, was confirmed. By combining the result of lifetime map measurement in this manner, the boundaries between regions could be more clearly identified.

[0048] Example 3: Detecting an L/D region and a B-band region in samples sliced lengthwise

A silicon single crystal ingot grown by the same method as in Example 1 was sliced axially along the center axis of the ingot to obtain samples sliced lengthwise. The samples obtained were equally divided in two along the center axis of the ingot. One of the samples was subjected to the treatment of (3) in Example 1, and the other sample was subjected to the treatment of (4) in Example 1. Subsequently, the selective etching of (5) in Example 1 was conducted. The surface following selective etching was observed under a converging lamp; photographs taken of it are shown in Fig. 5. In Fig. 5, "CE" means the center axis direction of the ingot, and "ED" means the outer perimeter surface direction of the ingot.

The photo on the upper left in Fig. 5 shows the observation result of the sample surface subjected to the treatment of (3). The photo on the upper right in Fig. 5 shows the observation result of the sample surface treated in (4). The lower photo in Fig. 5 shows the result of superposing the region specifying results of the upper left photo and the upper right photo. By superposing the results in this manner, it was possible to specify the B-band as indicated in the lower photo in Fig. 5.

[0049] The present invention is useful in the field of manufacturing silicon single crystal wafers.

CLAIMS

1. A method of inspecting a silicon single crystal, which comprises:
 - decorating with copper a surface of a sample cut out of a silicon single crystal ingot with an interstitial oxygen concentration, according to old American Society for Testing and Materials (old ASTM), of less than 12×10^{17} atoms/cm³ that has been grown by the Czochralski process;
 - subjecting the decorated sample to a heating and cooling treatment comprising heating the sample for equal to or more than five minutes at a temperature region of equal to or higher than 700°C but less than 800°C followed by rapidly cooling the sample from the temperature region at a cooling rate exceeding 2.5°C/minute;
 - selectively etching the surface of the sample following the heating and cooling treatment; and
 - specifying an L/D region based on a localized state of pits on the surface of the sample following the selective etching.
2. A method of inspecting a silicon single crystal, which comprises:
 - subjecting one of two samples, that have been cut out of a silicon single crystal ingot with an interstitial oxygen concentration, according to old American Society for Testing and Materials (old ASTM), of less than 12×10^{17} atoms/cm³ that has been grown by the Czochralski process as well as have approximately the same crystal region distribution each other, to a pretreatment comprising heating within a temperature region of 750°C to 900°C and then heating within a temperature region of 1,000°C to 1,150°C;
 - decorating surfaces of the two samples with copper;
 - subjecting the decorated samples to a heating and cooling treatment comprising heating the samples for equal to or more than five minutes at a temperature region of equal to or higher than 700°C but less than 800°C followed by rapidly cooling the samples from the temperature region at a cooling rate exceeding 2.5°C/minute;
 - selectively etching the surfaces of the samples following the heating and cooling treatment; and
 - specifying a B-band region based on a result of comparing a localized state of pits on the surface of the sample subjected to the pretreatment and that of the sample not subjected to the pretreatment following the selective etching.
3. The method of inspecting a silicon single crystal according to claim 1 or

2, wherein the selective etching is carried out by Wright etching.

4. The method of inspecting a silicon single crystal according to any of claims 1 to 3, wherein the copper decoration is carried out by immersing the sample in a copper-containing solution with a copper concentration of equal to or greater than 3×10^{20} atoms/cm³.

5. A method of manufacturing a silicon single crystal, which comprises:

growing a silicon single crystal to be inspected by the Czochralski process;

inspecting the silicon single crystal to be inspected by the method of inspecting according to any of claims 1 to 4;

determining a condition of pulling a silicon single crystal based on a result of the inspection; and

growing a silicon single crystal by the Czochralski process under the determined pulling condition to obtain a silicon single crystal that contains neither an L/D region nor a B-band region.