[Title]

Annealed Wafer and Manufacturing Method of Annealed wafer

[Field of the Invention]

[0001]

The present invention relates to an annealed wafer and a manufacturing method of the annealed wafer.

[BACKGROUND OF THE INVENTION]

[0002]

Semiconductor substrates, particularly, silicon single crystal wafers (hereinafter, also simply referred to as "substrates") are used as substrates for fabricating highly-integrated MOS devices. Many of the silicon single crystal wafers are substrates which are obtained by slicing a silicon single crystal ingot manufactured by the Czochralski (CZ) method.

[0003]

In such a silicon single crystal wafer, oxygen introduced during single crystal production is present in a supersaturated concentration. The oxygen is precipitated in later device processing, and oxygen precipitates are formed in the substrate. When a sufficient amount of the oxygen precipitates are present in the substrate, the precipitates getter heavy metals, which are introduced during the device processing, in the substrate and have an effect of maintaining the substrate surface which

is a device active layer clean.

[0004]

A technique to which such effect is applied is called intrinsic gettering (IG) and used for preventing characteristics deterioration due to heavy metal contamination. Therefore, an appropriate degree of oxygen precipitation is required to occur during device processing in a silicon single crystal substrate.

[0005]

In order to ensure gettering ability, oxygen precipitates of a predetermined density or more have to be present in the center in the thickness of a silicon single crystal wafer. As a result of past tests, it is known that when 5×10^{8} or more oxygen precipitates per cm^{3} are ensured in the center in the thickness of a silicon single crystal wafer, gettering ability for heavy metals such as Fe, Ni, and Cu is provided even in heat treatment in a low-temperature device processing wherein the highest temperature is equal to or less than 1100°C.

[0006]

Meanwhile, silicon semiconductor substrates obtained by high-temperature heat treatment (hereinafter, referred to as "annealing") of silicon single crystal wafers (hereinafter, referred to as "annealed wafers") are widely used in fabrication of high-density highly integrated devices.

[0007]

Herein, silicon single crystal wafers which have not undergone annealing before delivery are referred to as "mirror wafers", and substrates before undergoing annealing are referred to as "substrates" so as to distinguish them from each other.

[0008]

It is known that the annealed wafers do not have grown-in defects such as COP (Crystal Originated Particles) on the substrate surfaces and are good in device characteristics, for example, in GOI(gate oxide integrity) characteristics. This is for the reason that the grown-in defects present bear the substrate surfaces shrink or vanish through high-temperature annealing, and, as a result, defect-free layers are formed in the regions within several micrometers from the surfaces.

[0009]

However, the annealed wafers are also known to have inferior gettering characteristics compared with the thus-described mirror wafers without epitaxial deposition. A conceivable reason for that is that, generally, oxygen precipitation nuclei serving as nuclei of oxygen precipitation vanish due to annealing of 1100°C or more, and therefore oxygen precipitation does not occur in the device processing thereafter.

[0010]

As methods which compensate for insufficient oxygen

precipitation in the annealed wafers, for example, manufacturing methods of annealed wafers using nitrogen-doped substrates as substrates have been proposed (see Patent Documents 1 and 2 below).

[0011]

This is for the reason that, when nitrogen is doped, thermally stable oxygen precipitation nuclei are formed during crystal growth, and they do not shrink or vanish even during an annealing step; thus, oxygen precipitates are generated based on such oxygen precipitation nuclei in device heat treatment after annealing. When such substrates are used as substrates, oxygen precipitation after annealing can be ensured.

[0012]

However, as the diameter of recent annealed wafers is increased from 200 mm to 300 mm, a new requirement about oxygen precipitation characteristics has emerged. The requirement is to control the oxygen precipitate density to be uniform in a substrate plane. The reason for that is that, if there is a location where the oxygen precipitate density is low in the substrate plane, gettering ability at that part becomes weak, which leads to deterioration in device yield. In order to manufacture an annealed wafer in which the oxygen precipitate density is uniform in the plane, growth conditions of nitrogen doped crystals have to be precisely controlled. In

conventional techniques, the growth conditions of the nitrogen doped crystals are not taken into consideration. Therefore, annealed wafers manufactured by such techniques cannot solve this problem since locations where oxygen precipitation densities are low are generated in the substrate plane therein (see Patent Documents 3 and 4 below).

[0013]

Also, manufacturing methods of annealed wafers in which the oxygen precipitation densities are uniform in the plane (Patent Documents 5 and 6 below). Japanese Patent Application Laid-Open (*kokai*) No. 2003-59932 discloses a method in which V/G which is one of crystal pulling parameters is adjusted to within a certain range so that the entire substrate becomes a special region called an OSF region. Also, Japanese Patent Application Laid-Open (*kokai*) No. 2003-243404 discloses a manufacturing method in which the crystal pulling parameter V/G is suppressed to be in a range which is 0.175 or more and 0.225 or less. However, in such methods, since the crystal pulling parameter V/G is limited to an extremely narrow range, control of crystal pulling becomes difficult, which is a factor of lowered yield. Particularly, there are problems that, since the uppermost limit of the crystal pulling speed is regulated, the pulling speed cannot be sufficiently increased, and productivity is lowered.

[0014]

As described above, it has been difficult to manufacture an annealed wafer in which the oxygen precipitate density is high and oxygen precipitates are uniformly distributed in the substrate plane.

[Patent Document 1]

Japanese Patent Application Laid-Open (*kokai*) No. 2000-26196

[Patent Document 2]

Japanese Patent Application Laid-Open (*kokai*) No. 10-98047

[Patent Document 3]

Japanese Patent Application Laid-Open (*kokai*) No. 2000-26196

[Patent Document 4]

Japanese Patent Application Laid-Open (*kokai*) No. 10-98047

[Patent Document 5]

Japanese Patent Application Laid-Open (*kokai*) No. 2003-59932

[Patent Document 6]

Japanese Patent Application Laid-Open (*kokai*) No. 2003-243404

[DISCLOSURE OF THE INVENTION]

[PROBLEM]

[0015]

It is an object of the present invention to provide an annealed wafer in which oxygen precipitation after annealing is sufficiently high and radial distribution of oxygen precipitate density is uniform and a manufacturing method of the annealed wafer.

[MEANS FOR SOLVING THE PROBLEM]

[0016]

The present inventors have carried out extensive studies for the manufacturing method of the annealed wafer which is free from the above described problems of conventional techniques, wherein oxygen precipitation after annealing is sufficiently high and the radial distribution of oxygen precipitate density is uniform. As a result, in view of the fact that the radial distribution of oxygen precipitates is closely related to defect regions of the substrate wherein growth conditions of a nitrogen-doped crystal are to be controlled, the present inventors have found out that the radial distribution of oxygen precipitates can be made uniform by optimally controlling crystal growth conditions such as V/G upon growth of the nitrogen-doped crystal and accomplished the present invention.

[0017]

Specifically, the present invention relates to

(1) an annealed wafer having a surface defect-free layer and excellent gettering ability in the entire wafer surface, wherein a minimum value of an oxygen precipitate density in the annealed wafer plane is $5\times10^{8}/cm^{3}$ or more, and an oxygen precipitate density radial distribution variation is 0.5 or less.

[0018]

The present invention also relates to

(2) a method for manufacturing an annealed wafer, comprising annealing a silicon single crystal substrate which does not include a V region (region in which volume density of voids having a size of 50 nm or more is $1\times10^5/cm^3$ or more) and an I region (region in which density of dislocation pits having a size of 1 μm or more is $10/cm^2$ or more) as defect regions, and does not include a region in which the size of voids is 50 nm to 150 nm and the density of the voids is $10^4/cm^3$ or more and $10^5/cm^3$ or less.

[0019]

Furthermore, the present invention relates to

(3) the method for manufacturing an annealed wafer described in (2), wherein a silicon single crystal is grown in the following range as crystal growth conditions at manufacturing a silicon single crystal by the Czochralski method:

a V/G upper limit value ($mm^2/°C$ min) is $1.6 \times \exp(1.0 \times 10^{-15} \times$ nitrogen concentration ($atoms/cm^3$)) $\times$ (V/G)crit and

a V/G lower limit value ($mm^2/°C$ min) is $\exp(-7.1 \times 10^{-16} \times$ nitrogen concentration ($atoms/cm^3$)) $\times$ (V/G)crit

(wherein, V is a pulling speed (mm/min), G is a mean temperature gradient (°C/mm) in a crystal growth axial direction from a melting point to 1350°C, (V/G)crit is a lower limit value of V/G which does not include the I region as a defective region in the silicon single crystal to which nitrogen is not doped, wherein the I region is a region to which excessive interstitial

atoms are introduced from solid-liquid interface during crystal growth and a dislocation pit is generated);

a substrate is sliced from the nitrogen-doped grown silicon single crystal in which the nitrogen concentration is 1×10^{14} atoms/cm^3 or more and 5×10^{15} atoms/cm^3 or less and serves as a substrate; and

the substrate is subjected to heat treatment at 1150°C or more and 1250°C or less for 10 minutes or more and two hours or less in a rare gas having an impurity of 5 ppm or less or in a non-oxidizing atmosphere in which an oxide film thickness after the heat treatment is suppressed to 2 nm or less.

[0020]

The present invention also relates to

(4) the method for manufacturing an annealed wafer described in (3), wherein as the crystal growth conditions at manufacturing the silicon single crystal by the Czochralski method, a cooling rate of 1100 to 1000°C is 4°C/minute or more.

[EFFECT OF THE INVENTION]

[0021]

According to the manufacturing method of the present invention, conventional silicon single crystal manufacturing apparatuses according to the CZ method can be used without modification, and complex manufacturing processes are not performed; therefore, high-quality silicon semiconductor substrates can be stably supplied without largely increasing

the cost.

[0022]

In addition, according to the present invention, the annealed wafer which has no ununiformity of oxygen precipitates and is excellent in device property can be provided. In addition, the annealed wafer is an optimal substrate for manufacturing a substrate for MOS device which requires high degree of integration and high reliability.

[BEST EMBODIMENTS FOR CARRYING OUT THE INVENTION]

[0023]

Hereinafter, best modes for carrying out the invention will be described.

[0024]

At first, a crystal manufacturing method for achieving oxygen precipitates radial uniformity will be described.

[0025]

The oxygen precipitate density of an annealed wafer using a nitrogen-doped substrate depends on the nitrogen concentration; and the higher the nitrogen concentration, the higher the oxygen precipitate density. This is for the reason that, when nitrogen is doped, oxygen precipitation nuclei which are stable even at a high temperature are formed in the substrate, and they do not vanish and remain also after annealing. In the annealed wafer in which oxygen precipitation nuclei remain, oxygen precipitates are formed in the heat treatment of the

following device step. The number of the oxygen precipitation nuclei which are stable even at a high temperature is dependent on the nitrogen concentration. Therefore, when the nitrogen concentration is increased, the oxygen precipitate density is also increased. When the nitrogen concentration is 5×10^{14} atoms/cm^3 or more, the oxygen precipitate density becomes $5\times10^{8}/cm^3$. Therefore, gettering ability for heavy metals such as Fe, Ni, and Cu is ensured even in low-temperature device processing heat treatment wherein the highest temperature is 1100°C or less.

[0026]

As a result of detailed research, the following index was obtained for radial distribution of oxygen precipitates. Specifically, when the oxygen precipitate density is measured in the radial direction of an annealed wafer, and when an oxygen precipitate density radial distribution variation expressed by the following expression is more than 0.5, decrease in device yield due to insufficient gettering becomes notable. The oxygen precipitate density radial distribution variation can be obtained by the following expression.

[0027]

Oxygen precipitate density radial distribution variation = (oxygen precipitate density maximum value - oxygen precipitate density minimum value)/oxygen precipitate density maximum value

When the oxygen precipitate radial distribution after heat treatment of an annealed wafer, wherein a nitrogen-doped substrate is used as a substrate, was researched in detail, it was found out that locations where the oxygen precipitate density is lower than surrounding areas were present. When looking at an oxygen precipitate density profile, that part is depressed like a valley. Therefore, hereinafter, such region where the oxygen precipitate density is low will be referred to as a precipitation valley region. When the precipitation valley region is present, the oxygen precipitate radial variation degree becomes 0.5 or more.

[0028]

It was found out that, in the case of an annealed wafer using nitrogen-doped crystal, the precipitation valley region is closely corresponding to a defect region. This means that when the crystal diameter is increased to 300 mm, controlling defect regions in the crystal plane becomes difficult, and the radial distribution of the oxygen precipitate density also becomes uneven since the cooling rate during crystal growth is different outside and inside of the crystal.

[0029]

Hereinafter, after describing the relation between the nitrogen concentration and V/G and defective regions in a substrate, how the precipitate valley region of the annealed wafer is related to the defect region of the substrate will be

described.

[0030]

Figs. 1(a) and 1(b) are explanatory drawings for explaining the relation between defect regions and a nitrogen concentration in a silicon ingot which is pulled in accordance with the Czochralski (CZ) method. Fig. 1(a) is a graph showing the relation between the defect regions which are present in a substrate used as a substrate before annealing and nitrogen concentration, and Fig. 1(b) is a schematic drawing showing the defect regions and nitrogen concentration distribution in the silicon crystal ingot 200 during pulling.

[0031]

In the CZ method, as is publicly known, the single crystal ingot 200 is grown while it is gradually pulled up from molten silicon 201. Then, in a substrate obtained by slicing the ingot 200, as shown in Fig. 1(a), three types of defect regions (V region, OSF region, and I region) are present.

[0032]

The V region is a region to which excessive vacancies are introduced from a solid-liquid interface during crystal growth, and voids formed by aggregations of the atomic vacancies are present therein.

[0033]

The OSF region is a region in which OSF is generated when a silicon single crystal wafer is subjected to oxidation heat

treatment. Herein, the OSF is disk-like stacking fault having a diameter of about several μm wherein oxygen precipitates (OSF nuclei) are present at the center thereof. The OSF is formed when interstitial atoms, which are generated from an oxide film/silicon interface when oxidation heat treatment is carried out, aggregate around the OSF nuclei. The OSF nuclei are, among oxygen precipitates, particular oxygen precipitates that have property of collecting interstitial atoms, and it is conceivable that they are already present in the substrate at the point immediately after crystal growth. Since the size of the OSF nuclei is small (conceivably, 10 nm or less), they are not detected by existing evaluation methods such as foreign matter measurement and infrared tomography. Therefore, the presence of the OSF can be confirmed for the first time when oxidation heat treatment is carried out.

[0034]

The I region is a region to which excessive interstitial atoms are introduced from the solid-liquid interface during crystal growth, and dislocation loops formed by gathering of the interstitial atoms are present therein. In the I region, oxygen precipitation do not readily occur; therefore, in an annealed wafer using a substrate containing an I region, a region where the oxygen precipitate density is low is generated.

[0035]

According to conventional knowledge, defective regions

of a substrate is determined by the nitrogen concentration and crystal growth conditions of V/G (wherein, V: pulling speed (mm/min), G: mean temperature gradient in crystal growth axis direction from a melting point to 1350°C (°C/mm)) (V. V. Voronkov, K. Crystal Growth, 59 (1982) 625, and M. Iida, W. Kusaki, M. Tamatsuka, E. Iino, M. Kimura and S. Muraoka, Defect in Silicon, ed. T. Abe, W. M. Bullisetal (ECS., Pennington N. J., 1999) 499).

[0036]

In the case of a substrate sliced from single silicon crystal to which nitrogen is not doped, when V/G is larger than a particular value, atomic vacancies are excessively introduced, and the V region or the OSF region is formed in the substrate. When V/G is smaller than a particular value, interstitial atoms are excessively introduced, and the I region is formed in the substrate. Meanwhile, nitrogen affects the amount of the atomic vacancies and interstitial atoms introduced from a solid-liquid interface. Therefore, the defective regions of a substrate sliced from nitrogen-doped silicon single crystal can be shown in a two-dimensional defective region map wherein the nitrogen concentration and V/G are serving as two axes as shown in Fig.1(a).

[0037]

As shown in Fig. 1(a), one nitrogen-doped-crystal ingot has a certain width in the nitrogen concentration and V/G and shown by a rectangular region (referred to as "growth condition

region") in the nitrogen concentration-V/G diagram. This is for the reason that, as shown in Fig. 1(b), the lower the part in the ingot 200 of the nitrogen-doped crystal, the higher the nitrogen concentration, and V/G is low in the crystal outer periphery portion compared with the center portion.

[0038]

Nitrogen addition to a CZ-silicon single crystal is carried out by use of a nitrogen-doped melt; however, it is known that the percentage (segregation coefficient) of the nitrogen concentration incorporated from the melt to the crystal upon solidification is very small. Therefore, most of the nitrogen in the melt remains in the melt, and the nitrogen concentration in the melt is increased as crystal growth progresses. As a result, the nitrogen concentration becomes high in the lower portion of the crystal. Meanwhile, the mean temperature gradient G (°C/mm) in the crystal growth axis direction from the melting point to 1350°C depends on crystal cooling power; however, G is larger in the crystal outer peripheral portion since the crystal outer peripheral portion is generally readily cooled. As a result, V/G is lower in the crystal outer peripheral portion.

[0039]

When the range of growth conditions of one nitrogen-doped crystal ingot is overlapped with the two-dimensional defective region map wherein the nitrogen concentration and V/G are

serving as two axes, the defective regions of the crystal can be described. For example, in a crystal of growth conditions range shown in Fig. 1(a), the V region is present in the crystal center side, and the OSF region is present in the crystal outer peripheral portion. When the nitrogen concentration range is fixed, and V/G is increased, the void region is spread over the entire substrate surface. When V/G is reduced, the void region shrinks to the substrate center, and the I region is spread over the entire substrate surface. When V/G is fixed, and the nitrogen concentration is increased, the OSF region is generated from an outer peripheral portion and spread to the entire substrate surface.

[0040]

The relation between precipitation valley regions in an annealed wafer and defect regions in a substrate were researched; and, as a result, it was found out that, as shown in Fig. 2(a) and 2(b), the precipitation valley region has a close relation with the defect regions in the substrate. Specifically, a precipitation valley region of the annealed wafer is generated in the location corresponding to the V region boundary of the substrate, and the region is slightly expanded to the V region side and the OSF region side.

[0042]

Fig. 2(a) is a graph showing the relation between the nitrogen concentration and V/G. In the graph, in a growth

condition region 1, the nitrogen concentration is 5×10^{13} to 1×10^{14} atoms/cm^3 and V/G (relative value) is 1.3 to 2.1; in a grow condition region 2, the nitrogen concentration is 1×10^{14} to 5×10^{14} atoms/cm^3 and V/G (relative value) is 1.3 to 2.1; in a growth condition region 3, the nitrogen concentration is 1×10^{15} to 5×10^{15} atoms/cm^3 and the V/G (relative value) is 1.3 to 2.1;and, in a growth condition region 4, the nitrogen concentration is 1×10^{15} to 5×10^{15} atoms/cm^3 and V/G (relative value) is 1.0 to 0.6.

[0042]

Fig. 2(b) is a chart showing oxygen precipitate radial distribution in substrate plane, whether the oxygen precipitate density is equal to or more than 5×10^{8}/cm^3 or not ("○" means it is equal to or more than 5×10^{8}/cm^3 and "×" means it is less than 5×10^{8}/cm^3 (hereinafter, same in similar drawings)), and whether the oxygen precipitate density radial distribution variation is equal to or less than 0.5 or not ("○" means it is equal to or less than 0.5, and "×" means it is larger than 0.5 (hereinafter, same in similar drawings)). As shown in the chart, when the growth condition region includes the precipitate valley region, the oxygen precipitate density radial distribution variation exceeds 0.5.

[0043]

In the case of the growth condition region 4 in Fig. 2(a), since the precipitation valley region is not included in

substrates, the oxygen precipitate density radial distribution variation of 0.5 or less can be achieved. However, in order to satisfy these conditions, V/G has to be reduced, in other words, the crystal pulling speed V has to be reduced. Reducing the crystal pulling speed V is not preferred in terms of manufacturing since productivity is reduced.

[0044]

As described above, in conventional manufacturing conditions, the V/G range which can achieve precipitate density radial uniformity was extremely narrow, which was inconvenient in practice. Therefore, in order to find manufacturing conditions which can expand the V/G range which can achieve precipitate density radial uniformity, research focused on crystal growth parameters other than the nitrogen concentration and V/G was carried out. As a result, it was found out that setting the cooling rate of the crystal which is 1100°C to 1000°C during crystal growth to 4°C/minute or more affects the oxygen precipitate radial distribution.

[0045]

Figs. 3(a) and 3(b) are explanatory drawings for explaining conditions for manufacturing annealed wafers in which oxygen precipitates are uniform. Fig. 3(a) is a graph showing the relation between the nitrogen concentration and V/G, and Fig. 3(b) is a chart showing defect distribution, whether the oxygen precipitate density is equal to or more than 5 x

$10^8/cm^3$ or not, and whether the oxygen precipitate density radial variation is equal to or less than 0.5 or not. In a shown growth condition region 5, the nitrogen concentration is 1×10^{14} to 5×10^{14} atoms/cm^3 and V/G (relative value) is 1.3 to 1.5. Herein, an NF region in Fig. 3(a) is a new defective region found between a V region boundary and an OSF region boundary. This region is found for the first time when the cooling rate of the crystal which is at 1100 to 1000°C during crystal growth is 4°C/minute or more, and it is a region in which OSF and voids are not present.

[0046]

As is clear from comparison between Fig. 2 and Fig. 3, when the cooling rate of a crystal at 1100 to 1000°C is 4°C/minute or more, while the boundary positions of the OSF region does not change, the boundary of the V region is shifted to the lower-nitrogen and high-V/G side. Accordingly, the precipitate valley region is also shifted to the low-nitrogen and high-V/G side. As a result, it was found out that the range of the nitrogen concentration and V/G to be employed in order to uniform the oxygen precipitate radial distribution is enlarged to the low-nitrogen and high-V/G side.

[0047]

In the growth condition regions 3 and 5 of Fig. 3(a), although the part out of the OSF region is present, the radial distribution of oxygen precipitates is uniform since the

precipitation valley region is not included therein. In other words, the oxygen precipitate radial distribution is not related to the distribution of the OSF region. In the case of the growth condition region 5, precipitate radial uniformity can be achieved by a substrate not including the OSF region.

[0048]

According to conventional knowledge, for example, in Japanese Patent Application Laid-Open (*kokai*) No. 2003-59932, the relation between the defect region and oxygen precipitate density distribution was discussed merely in relation with the OSF region. Therefore, there has been merely the idea that the OSF region has to be controlled for oxygen precipitate radial distribution control. However, as a result of this research, it has been found out as new knowledge that what is truly important for controlling the radial distribution of oxygen precipitates is not the OSF region, but control of the precipitate valley region associated with the V region distribution.

[0049]

As a result of expansion of the nitrogen concentration range to the low-nitrogen side, the nitrogen concentration range is expanded. Consequently, the oxygen precipitate density can be widely controlled in accordance with requirements from device users. As a result of expansion of V/G to the high-V/G side, productivity of silicon single crystal

can be improved since the pulling speed V can be further increased.

[0050]

The range of V/G where the oxygen precipitate density radial distribution variation is equal to or less than 0.5 is between the lower boundary of the precipitate valley region and the I region boundary as shown in Fig. 3(a). When various experimental results are put together, the above described V/G range can be expressed as a function of the nitrogen concentration. Specifically, the V/G upper limit value (mm^2/°C min) is $1.6 \times \exp(1.0 \times 10^{-15} \times$ nitrogen concentration (atoms/cm^3)) $\times$ (V/G)crit, and the V/G lower limit value (mm^2/°C min) is $\exp(-7.1 \times 10^{-16} \times$ nitrogen concentration (atoms/cm^3)) $\times$ (V/G)crit, (wherein (V/G)crit is the V/G value of the part corresponding to the boundary of the V region and the I region in a silicon single crystal to which nitrogen is not added.)

[0051]

The oxygen precipitation radial distribution of a substrate and void radial distribution of a substrate are in the following relation. Figs. 4(a) and 4(b) are graphs explaining radial distribution of voids and radial distribution of oxygen precipitates. Fig. 4(a) is a graph showing the relation between the nitrogen concentration and V/G, and Fig. 4(b) includes graphs showing results of densities of voids, which have a size of 50 to 150 nm in respective regions of A,

B, and C, measured in the substrate radial direction.

[0052]

In the A region in Fig. 4(a), the nitrogen concentration is 1×10^{14} atoms/cm^3 and V/G (relative value) is 1.3 to 2.1; in the B region therein, the nitrogen concentration is 5×10^{14} atoms/cm^3 and V/G (relative value) is 1.3 to 2.1;and, in the C region therein, the nitrogen concentration is 5×10^{15} atoms/cm^3 and V/G (relative value) is 1.3 to 2.1.

[0053]

As shown in the graphs, it has been found out that the precipitation valley region is the region in which voids having a size of 50 to 150 nm are present in the substrate within the range of the densities of 10^4 to $2\times10^5/cm^3$. Herein, the void size is represented by a diameter of a sphere having the same volume as the mean volume of the voids. Inside the precipitation valley region is the region in which the maximum value of the void size is 150 nm or more, or the density of the voids having a size of 50 to 150 nm exceeds $2\times10^5/cm^3$. Outside the precipitation valley region is the region in which the void size is equal to or less than 50 nm, or the void density is less than $10^4/cm^3$. In both the inside and outside the precipitation valley region, the oxygen precipitate density is larger than the precipitation valley region.

[0054]

The reason why the oxygen precipitate density of the

region in which the voids having a size of 50 to 150 nm are present in the density range of 10^4 to $2\times10^5/cm^3$ is smaller than the surrounding area is not known. The voids are formed when atomic vacancies aggregate in a temperature zone around 1100°C during crystal growth; however, the remaining atomic vacancies not aggregated as voids conceivably serve as nuclei of oxygen precipitates in a lower temperature zone (around 1000°C) during crystal growth. In the region in which the voids having the size of 50 to 150 nm are present in the range of the density of 10^4 to $2\times10^5/cm^3$ is expected in the state wherein the remaining vacancy concentration is the smallest according to other mechanisms.

[0055]

The reason that the precipitation valley region is changed in a substrate plane by increasing the crystal cooling rate of 1100 to 1000°C is conceivably that the radial distribution of the void density is changed by rapid cooling of 1100 to 1000°C.

[0056]

The crystal cooling rate in the temperature zone of 1100 to 1000°C upon crystal growth in the CZ method causes the shift of the precipitation valley region shown in Fig. 4 conceivably for the below reason.

[0057]

Supersaturated atomic vacancies introduced from a

solid-liquid interface upon crystal growth aggregate at around 1100°C, thereby forming voids. When the crystal cooling rate of 1100 to 1000°C is high, the time that the atomic vacancies aggregate is not sufficient, and the void size becomes small. As a result, the region in which the voids having a size of 50 to 150 nm are present in the range of the density of 10^4 to $2\times10^5/cm^3$ shown in the nitrogen concentration V/G map is shifted. In the NF region between the V region and OSF region shown in Fig. 3a, voids having a size of 50 nm or less are conceivably present.

[0058]

Specific examples of silicon single crystal manufacturing and annealed wafer manufacturing will next be described.

[0059]

As a silicon single crystal manufacturing method, the CZ method in which a crystal is pulled from a melt in a crucible while growing the crystal is widely performed. In such a silicon single crystal manufacturing method, in the first place, polycrystalline silicon is put in a crucible made of quartz as a raw material, and the raw material is melted by a heater (in-furnace structures such as the heater and a heat insulating material are collectively referred to as a hot zone) surrounding it. Then, a seed crystal is lowered from above the melt in the crucible and brought into contact with the melt surface. A

single crystal having a predetermined diameter is fabricated by upwardly pulling up the seed crystal while rotating the seed crystal and controlling the pulling speed V. As the crystal grows, the silicon melt decreases; and, in accordance with this, crystal growth environments such as heat conduction and flow in the silicon melt is varied. In order to stabilize crystal growth by maintaining these environments constant as much as possible, various arrangement has been made in actual crystal manufacturing steps. For example, generally, the crucible position is pulled up in accordance with the pulled crystal weight in order to keep the position of silicon melt surface constant with respect to the heater during crystal pulling. The variation in the heat transition conditions of the crystal side in the process in which the crystal is grown is extremely small compared with the melt side, is generally determined by the furnace structure and the hot zone structure in the furnace, and is slowly varied little in accordance with the crystal length.

[0060]

Generally, the temperature gradient G in the crystal growth interface is not uniform in a crystal plane. The crystal-side temperature gradient in the crystal growth interface is larger in the crystal outer peripheral portion than the crystal center portion. This is for the reason that the crystal side surface is more readily cooled by radiation cooling

from the crystal side surface. Therefore, even at a same pulling speed V, V/G becomes lower in the crystal outer peripheral portion, and the OSF region which causes epilayer defect generation is readily generated in the crystal outer peripheral portion. The crystal-side temperature gradient G in the crystal pulling direction in the crystal growth interface is strictly measured by repeating experiments in which, for example, crystal growth is actually carried out by inserting a thermo couple in a crystal.

[0061]

The V/G of the crystal growth interface and the crystal cooling rate at 1100 to 1000°C during crystal growth can be controlled by respectively changing G in the solid-liquid interface and G in the temperature zone of 1100 to 1000°C; however, in order to independently control them, the structure of the pulling furnace has to be changed.

[0062]

In order to reduce V/G, the pulling speed has to be reduced; however, as a result, the crystal cooling rate at 1100 to 1000°C during crystal growth is also reduced. Therefore, in order to reduce V/G of the crystal growth interface while increasing the crystal cooling rate at 1100 to 1000°C during crystal growth, special treatment such as increasing the cooling power of a heat shielding plate which is placed so as to surround the crystal is required.

[0063]

In order to manufacture a nitrogen-doped CZ-silicon single crystal, for example, there are a method in which a nitrogen gas is introduced during raw-material melting or a method in which a nitride is incorporated into a deposited silicon substrate by the CVD method or the like during raw material melting. The segregation coefficient k which is a rate of an impurity incorporated in a crystal after solidification with respect to the concentration in the melt is 7×10^{-4} in the case of nitrogen (W. Zulehner and D. Huber, Crystal Growth, Properties and Applications, p28, Springer-Verlag, New York, 1982).

[0064]

The nitrogen concentration introduced from the melt to the crystal can be expressed as the following expression by use of the solidification rate g = (weight of crystallized silicon)/(initial melt weight) of the crystal at that point.

(nitrogen concentration in crystal) =

$k \times$ (initial melt nitrogen concentration) $\times (1-g)^{k-1}$

This relation is generally maintained constant regardless of conditions such as the structure of the pulling furnace and the pulling speed; therefore, nitrogen concentration control in the crystal can be generally uniquely controlled by the nitrogen concentration of the initial melt.

[0065]

In the manufacturing of a silicon single crystal according to the CZ method, quartz is used as the crucible. The quartz crucible melts into the silicon melt little by little during crystal pulling; therefore, oxygen is present in the silicon melt. The oxygen melted from the quartz crucible moves due to flow and diffusion of the silicon melt, and the most part thereof evaporates from the melt surface in the form of an SiO gas. However, a part thereof is introduced into the crystal. The oxygen introduced at a high temperature is supersaturated in the process that the crystal is cooled, thereby causing aggregation and forming minute oxygen clusters during crystal cooling. These clusters serve as precipitation nuclei, are precipitated as SiOx in the process of device heat treatment after it is made into a silicon single crystal wafer, and become oxygen precipitates.

[0066]

Substrates for annealed wafers are generated from a resultant silicon single crystal ingot. Generally, the silicon single crystal is sliced by use of a wire saw or a inner blade slicer, and substrates are fabricated through steps of chamfering, etching, and mirror polishing. When an additional heat treatment step for oxygen precipitation acceleration or defect elimination is to be added, generally, a heat treatment process is carried out thereafter. However, in the case of the substrate described in the present invention to which nitrogen

is added, such step is not required, and it can be fabricated in the steps same as a general silicon substrate.

[0067]

The heat-treating furnace which carries out annealing may be a commercially available furnace, and no particular regulation is imposed thereon. However, it has to be arranged that an oxide film does not grow equal to or more than 2 nm during heat treatment. This is for the reason that, when the oxide film adheres on the surface, contraction/elimination of defects during annealing is inhibited. Specifically, an arrangement such as reducing the amount of impurities incorporated in an atmospheric gas during heat treatment as much as possible or reducing inclusion of air from the surrounding area as much as possible upon insertion of a wafer into a furnace is required. The used atmospheric gas is desirably a rare gas such as argon in which, for example, impurities are suppressed to 5ppma or less.

[0068]

Quartz or the like is used as the members which retain a wafer. These members are significantly deteriorated when the annealing temperature is increased too much. Therefore, they have to be frequently replaced, which is a factor of increased manufacturing cost. The annealing temperature is preferably 1250°C or less. When the annealing temperature is lowered too much, the contraction speed of defects become slow; therefore,

elimination takes time, and productivity is lowered. The annealing temperature is preferably 1150°C or more. When the annealing time is short, defects remain in the substrate surface since the defects are not sufficiently eliminated when the annealing time is short. When the annealing time is long, productivity is lowered since the time required for one annealing is lengthened. Therefore, the annealing time is desirably 10 minutes or more and two hours or less.

[0069]

The oxygen precipitation nuclei formed in a nitrogen-doped substrate which is used as a substrate are thermally stable by virtue of the effect of nitrogen and are not eliminated even during rapid temperature increase during the annealing step. An additional heat treatment step for oxygen precipitation acceleration or defect elimination is sometimes carried out during the annealing step. In that case, before the annealing step, heat treatment is carried out at a temperature lower than that of the annealing step. However, when such additional step is added in that manner, the time of the entire annealing step is lengthened; thus, productivity is lowered, and manufacturing cost is increased. In this regard, in the case of the nitrogen-doped substrate described in the present invention, such step is not required.

[EXAMPLE]

[0070]

Silicon single crystal manufacturing apparatuses used in this example are those used in general silicon single crystal manufacturing according to the CZ method. The apparatuses are a first pulling furnace in which a heat shielding plate is cooled in a particular method in order to increase the cooling speed of 1100 to 1000°C and a second furnace having a general cooling speed. When the present invention is to be carried out, no particular limitations are imposed on the pulling furnaces as long as the growth conditions of the present invention can be carried out.

[0071]

A silicon single crystal grown by utilizing the apparatuses has a conduction type: p-type (boron doped) and a crystal diameter: 8 inches (200 mm).

[0072]

Nitrogen doping was performed by putting substrates having nitride films in silicon melts.

[0073]

Relative V/G values are defined in the following manner. In a pulling furnace having the same structure as the furnace in which the nitrogen added crystal was pulled, crystals to which nitrogen and carbon were not added were pulled at various pulling speeds V, radial distribution of distribution pits was checked by the method described later, and the boundary position of the I region was obtained. For example, when the pulling

speed is low, the wafer edge side is in the I region, and dislocation pits are generated therein. In that case, the in-plane distribution of the dislocation pits was checked, and the position where the dislocation pit density is lower than $10/cm^2$ was set as the boundary of the I region. The V/G value at that position is set as (V/G)crit, and a relative V/G value of the nitrogen-added crystal pulled in the pulling furnace having the same structure is set as (V/G)/(V/G)crit. In other words, when the relative V/G value is 1, V/G is equal to (V/G)crit.

[0074]

Crystals to which nitrogen is not added are pulled from the first pulling furnace and the second pulling furnace. The relative V/G values are obtained, and a nitrogen concentration-V/G map is generated.

[0075]

As a cooling rate from 1100 to 1000°C during crystal growth, when the minimum value among crystal growth axial direction temperature gradients in the range of 1100 to 1000°C was G2 (°C/mm), V×G2 was calculated and it was employed as a representative value.

[0076]

Substrates (silicon wafers) were sliced from the same part in the single crystals, and the substrates after mirror processing were subjected to annealing, thereby producing

annealed wafers.

[0077]

The nitrogen concentrations were measured by using a secondary ion mass spectrometer (SIMS) after sampling samples from the annealed wafers and performing polishing of 20 μm in order to remove nitrogen out diffusion layers of the surfaces thereof.

[0078]

In the V region of the substrates, excessive atomic vacancies were introduced from liquid-solid interfaces during crystal growth, and, as a result, voids are generated. Therefore, the V region of the substrates can be specifically defined by the density of the voids.

[0079]

Regarding the voids in the substrates, void radial distribution of the substrates are measured by use of LSTD scanner (MO-6) produced by Mitsui Mining and Smelting Co., Ltd., which is a commercially available defect evaluation apparatus. This MO-6 emits a visible-light laser from the Brewster angle, and detects a scattered image of p-polarization as a defect image by a camera disposed in the vertical direction. Since the laser permeates merely up to 5 μm from the substrate surface, defects in the depth of 5 μm from the substrate surface can be measured. Upon measurement, the detection sensitivity was adjusted so that a void having a size of 50 nm or more when

converted into a sphere can be measured. The volume density of the voids was calculated from the area density of the measured voids and the measurement depth 5 μm. Then, the region where the volume density of the voids was equal to or more than $1\times10^5/cm^3$ was determined as the V region.

[0080]

Meanwhile, in the I region of the substrates, excessive interstitial atoms were introduced from the solid-liquid interface during crystal growth, and, as a result, they appear as dislocation pits. Therefore, the I region can be defined by the density of the dislocation pits.

[0081]

The dislocation pits were measured according to the below method. First, the substrate is etched by 5 μm by a Wright etch solution, and the number of rhombus-shaped or stream-line-shaped dislocation pits which were generated in the surface and had a size of 1 μm or more was counted through observation by an optical microscope. The measurement was carried out at a pitch of 10 mm in the radial direction of the substrate, and the dislocation pit area density was calculated from the visual field area. Then, the area where the dislocation pit density is $10/cm^2$ or more was determined as the I region.

[0082]

The OSF evaluation of the substrate was performed

according to the below method. First, the substrate was subjected to oxidation treatment in a vapor-containing oxygen atmosphere at 1100°C for an hour. Then, after an oxide film is removed by a hydrofluoric acid, it was etched by an amount corresponding to the thickness of 5 μm by the Wright etch solution, and elliptical, half-moon-like, or rod-like OSF pits formed on the surface were observed by an optical microscope. The number of the OSF pits was counted by scanning a visual field having a diameter of 2.5 mm in the substrate diameter direction by an optical microscope, and the OSF area density (pits/cm^2) was by dividing the number of the OSF pits by the observation area. The region where the OSF area density is equal to or more than 100/cm^2 was determined as the OSF region.

[0083]

The oxygen precipitation characteristics evaluation of the annealed wafer was carried out according to the below method. First, an annealed wafer was subjected to double heat treatment at 780°C for three hours and at 1000°C for sixteen hours. Then, the wafer was cleaved, and the internal oxygen precipitate densities were measured by BMD analyzer MO-4 produced by Mitsui Mining and Smelting Co., Ltd. The positions of the measurement points in the plane were located from the substrate center to 10 mm from the edge at a pitch of 10 mm. The minimum value of the obtained oxygen precipitate densities and the oxygen precipitate density radial distributionvariation represented

by the below expression were obtained.

[0084]

The oxygen precipitate density radial distribution variation = (oxygen precipitate density maximum value -oxygen precipitate density minimum value)/oxygen precipitate density maximum value

The evaluation results including comparative examples are shown in Table 1.

[0085]

[Table 1]

【Table 1】

Substrate Nitrogen Concentration (atoms/cm^3)	Pulling Furnace	Pulling Speed V (mm/min)	Range of Relative V/G Value		Cooling Rate of 1000 to 1100℃ (℃/min)	$(V/G)_1$	$(V/G)_2$	Precipitate Density Minimum Value (/cm^3)	Precipitate Density in/plane Variation	Remarks
5.0E+14	1	1.5	1.3	-2.1	8.0	0.70	2.64	1.0E+09	0.2	Example 1
2.0E+15	1	1.5	1.3	-2.1	8.0	0.24	11.82	4.0E+09	0.3	Example 2
4.0E+15	1	1.5	1.3	-2.1	8.0	0.06	87.36	9.0E+09	0.2	Example 3
1.0E+15	1	0.8	0.6	-1.0	4.0	0.49	4.35	2.0E+09	0.1	Example 4
3.0E+15	1	0.8	0.6	-1.0	4.0	0.12	32.14	4.0E+09	0.1	Example 5
5.0E+15	1	0.8	0.6	-1.0	4.0	0.03	237.46	9.0E+09	0.2	Example 6
1.0E+14	1	1.0	1.3	-1.5	5.0	0.93	1.77	5.0E+08	0.2	Example 7
2.0E+14	1	1.0	1.3	-1.5	5.0	0.87	1.95	6.0E+08	0.3	Example 8
5.0E+14	1	1.0	1.3	-1.5	5.0	0.70	2.64	1.0E+09	0.2	Example 9
1.0E+14	1	0.8	1.0	-1.2	4.0	0.93	1.77	5.0E+08	0.1	Example10
2.0E+14	1	0.8	1.0	-1.2	4.0	0.87	1.95	7.0E+08	0.2	Example11
5.0E+14	1	0.8	1.0	-1.2	4.0	0.70	2.64	1.0E+09	0.1	Example12
5.0E+13	1	0.8	1.3	-2.1	4.0	0.97	1.68	1.0E+08	0.9	Comp. Ex. 1
1.0E+14	1	0.8	0.6	-1.0	4.0	0.93	1.77	5.0E+08	0.6	Comp. Ex. 2
1.0E+14	1	1.5	1.3	-2.1	4.0	0.93	1.77	5.0E+08	0.7	Comp. Ex. 3
1.0E+15	2	1.2	1.3	-2.1	1.0	0.49	4.35	1.0E+09	0.8	Comp. Ex. 4

$(V/G)_1$: $\exp(-7.1\times10^{-16}\times$Nitrogen Concentration[atoms/cm^3]$)$

$(V/G)_2$: $1.6\times\exp(1.0\times10^{-15}\times$Nitrogen Concentration[atoms/cm^3]$)$

[0086]

Herein, $(V/G)_1$ and $(V/G)_2$ are the V/G lower limit value and the V/G upper limit value, respectively, which were obtained from the nitrogen concentrations of the pulled crystals by using respective expressions.

[0087]

The annealed wafers which satisfy the conditions that the substrate nitrogen concentration is equal to or more than 5×10^{14} atoms/cm^3 and equal to or less than 5×10^{15} atoms/cm^3 and the range of the relative V/G value is equal to or more than $\exp(-7.1 \times 10^{-16} \times$ nitrogen concentration (atoms/cm^3)) and equal to or less than $1.6 \exp(1.0 \times 10^{-15} \times$ nitrogen concentration (atoms/cm^3)), and using the substrates of which cooling rate of 1100 to 1000°C is equal to or more than 4°C/minute had the oxygen precipitate density minimum value of 5×10^8/cm^3 or more and the oxygen precipitate density radial distribution variation of 0.5 or less, and the oxygen precipitate radial distribution thereof was good. The substrate before carrying out annealing did not include the V region and the I region as defective regions, and the regions in which voids having a size of 50 to 150 nm were in the density range of 10^4 to 2×10^5/cm^3 were not present in the substrates.

[0088]

In the examples, the OSF was not present in the substrates (substrates of the annealed wafers of Examples 1 to 3) sliced

from the crystals pulled at the cooling rate of 1100 to 1000°C of 8°C/minute by use of the first pulling furnace when the nitrogen concentration is equal to or more than 5×10^{14} atoms/cm^3 and equal to or less than 4×10^{15} atoms/cm^3 and the relative V/G was equal to or more than 1.3 and equal to or less than 2.1 and the substrates (substrates of the annealed wafers of Examples 7 to 9) sliced from the crystals at the cooling rate of 1100 to 1000°C of 5°C/minute when the nitrogen concentration was equal to or more than 1×10^{14} atoms/cm^3 and equal to or less than 5×10^{14} atoms/cm^3 and the relative V/G was equal to or more than 1.3 and equal to or less than 1.5.

[0089]

The annealed wafer having the substrate nitrogen concentration of less than 1×10^{14} atoms/cm^3 had the oxygen precipitate density minimum value of less than 5×10^{8}/cm^3 and quality of oxygen precipitation was inferior to the Examples (Comparative Example 1).

[0090]

When the minimum value of the relative V/G was less than $\exp(-7.1 \times 10^{-16} \times$ nitrogen concentration (atoms/cm^3)), the I region was present in the substrate; therefore, the oxygen precipitate density radial distribution variation exceeds 0.5, and quality of oxygen precipitation was inferior to the Examples (Comparative Example 2).

[0091]

When the maximum value of the relative V/G exceeded 1.6 $\exp(1.0 \times 10^{-15} \times$ nitrogen concentration (atoms/cm^3)), the precipitation valley region was present in the substrate; therefore, the oxygen precipitate density radial distribution variation exceeded 0.5, and quality of oxygen precipitation was inferior to the Examples (Comparative Example 3).

[0092]

When the cooling rate of 1100 to 1000°C was less than 4°C/minute, the precipitation valley region was present in the substrate, the oxygen precipitate density radial distribution variation 0.5, and quality of oxygen precipitation was inferior to the Examples (Comparative Example 4).

[0093]

The embodiments and Examples of the present invention have been described hereinabove. However, the present invention is not limited to these Examples and embodiments, various modifications can be made by those skilled in the art, and such modified embodiments and Examples also includes the technical ideas of the present invention. Therefore, the technical range of the present invention is determined merely by the invention specifying notes according to claims which are reasonable for the above description.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[0094]

[FIG.1]

Figs. 1(a) and 1(b) are explanatory drawings for explaining the relation between defective regions and a nitrogen concentration in a silicon ingot which is pulled in accordance with the CZ method. Herein, Fig. 1(a) is a graph showing the relation between the defective regions which are present in a substrate before epitaxial deposition and nitrogen concentration, and Fig. 1(b) is a schematic drawing showing the defective regions and nitrogen concentration distribution in a silicon crystal ingot during pulling.

[FIG.2]

Fig. 2(a) is a graph showing the relation between the nitrogen concentration and V/G, and Fig. 2(b) is a chart showing oxygen precipitate radial distribution in substrate plane, whether the oxygen precipitate density is equal to or more than $5\times10^{8}/cm^{3}$ or not, and whether the oxygen precipitate density radial distribution variation is equal to or less than 0.5 or not.

[FIG.3]

Figs. 3(a) and 3(b) are explanatory drawings for explaining conditions for manufacturing annealed wafers in which oxygen precipitates are uniform. Fig. 3(a) is a graph showing the relation between the nitrogen concentration and V/G, and Fig. 3(b) is a chart showing oxygen precipitate distribution in the substrate plane, whether the oxygen precipitate density is $5\times10^{8}/cm^{3}$ or not, and whether the oxygen precipitate density

radial distribution is equal to or less than 0.5 or not.

[FIG.4]

Figs. 4(a) and 4(b) are graphs explaining radial distribution of voids and in-plane distribution of oxygen precipitates. Fig. 4(a) is a graph showing the relation between the nitrogen concentration and V/G, and Fig. 4(b) includes graphs showing results of densities of voids, which have a size of 50 to 150 nm in respective regions of A, B, and C, measured in the substrate radial direction.

[CLAIMS]

1. An annealed wafer having a surface defect-free layer and excellent gettering ability in the entire wafer surface, wherein

a minimum value of an oxygen precipitate density in the annealed wafer plane is $5\times10^{8}/cm^{3}$ or more, and an oxygen precipitate density radial distribution variation is 0.5 or less.

2. A method for manufacturing an annealed wafer, comprising annealing a silicon single crystal substrate which does not include a V region (region in which volume density of voids having a size of 50 nm or more is $1\times10^{5}/cm^{3}$ or more) and an I region (region in which density of dislocation pits having a size of 1 μm or more is $10/cm^{2}$ or more) as defective regions, and does not include a region in which the size of voids is 50 nm to 150 nm and the density of the voids is $10^{4}/cm^{3}$ or more and $10^{5}/cm^{3}$ or less.

3. The method for manufacturing an annealed wafer according to claim 2, wherein

a silicon single crystal is grown in the following range as crystal growth conditions at manufacturing a silicon single crystal by the Czochralski method:

a V/G upper limit value ($mm^{2}/°C$ min) is $1.6 \times \exp(1.0 \times 10^{-15}$

× nitrogen concentration (atoms/cm^3)) × (V/G)crit; and

a V/G lower limit value (mm^2/°C min) is exp(-7.1 × 10^{-16} × nitrogen concentration (atoms/cm^3)) × (V/G)crit

(wherein, V is a pulling speed (mm/min), G is a mean temperature gradient (°C/mm) in a crystal growth axial direction from a melting point to 1350°C, (V/G)crit is a lower limit value of V/G which does not include the I region as a defective region in the silicon single crystal to which nitrogen is not added, wherein the I region is a region to which excessive interstitial atoms are introduced from solid-liquid interface during crystal growth and a dislocation pit is generated);

a substrate is sliced from the nitrogen-added grown silicon single crystal in which the nitrogen concentration is 1×10^{14} atoms/cm^3 or more and 5×10^{15} atoms/cm^3 or less and serves as a substrate; and

the substrate is subjected to heat treatment at 1150°C or more and 1250°C or less for 10 minutes or more and two hours or less in a rare gas having an impurity of 5 ppm or less or in a non-oxidative atmosphere in which an oxide film thickness after the heat treatment is suppressed to 2 nm or less.

4. The method for manufacturing an annealed wafer according to claim 3, wherein

as the crystal growth conditions at manufacturing the silicon single crystal by the Czochralski method, a cooling rate

of 1100 to 1000°C is 4°C/minute or more.