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GALLIUM NITRIDE SINGLE CRYSTAL SUBSTRATE AND METHOD FOR PRODUCING THE SAME

Abstract

There is provided a gallium nitride single crystal substrate, which is a gallium nitride single crystal substrate having a diameter of 50 mm or more, with a low-index crystal plane closest to a main surface being (0001), and in which an average density of etch pits during etching applied to the main surface using an alkaline etching solution is less than 1×10.sup.6 cm.sup.−2; and in histograms of diameters of the etch pits in multiple different regions on the main surface, and among peaks appearing in the histograms, when a diameter of a first peak which is a smallest diameter is denoted as a, a diameter of a second peak which is a second smallest diameter is denoted as b, frequency of the first peak (the number of etch pits) is denoted as A, frequency of the second peak is denoted as B, the number of the etch pits constituting the first peak is denoted as α, and the number of the etch pits constituting the second peak is denoted as β, at least one of the following conditions (1), (2), and (3) is satisfied: (1) variation in a/b values in the multiple histograms is within ±5% of an average value. (2) variation in A/B values in the multiple histograms is within ±15% of an average value. (3) variation in α/β values in the multiple histograms is within ±30% of an average value.

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Background/Summary

TECHNICAL FIELD
[0001] The present invention relates to a gallium nitride single crystal substrate and a method for producing the same.
DESCRIPTION OF RELATED ART
[0002] For example, patent document 1 discloses a method for producing a gallium nitride single crystal substrate, the method including: preparing a base substrate composed of a single crystal of a group III nitride semiconductor, having a mirror-finished main surface, with a low index crystal plane being (0001) closest to the main surface; a first step of epitaxially growing a single crystal of a group III nitride semiconductor having a top surface in which (0001) is exposed directly on the main surface of the base substrate, and causing multiple recesses to generate on the top surface composed of an inclined interface other than (0001), gradually expanding the inclined interface upwardly toward the top of the main surface of the base substrate, causing (0001) to disappear from the top surface, and growing a first layer whose surface is composed only of the inclined interface; and a second step of epitaxially growing the single crystal of the group III nitride semiconductor on the first layer, causing the inclined interface to disappear, and growing a second layer having a mirror-finished surface, wherein in the first step, multiple recesses are formed on the top surface of the single crystal, and (0001) is caused to disappear, thereby forming multiple valleys and multiple peaks on the surface of the first layer.
[0003] Further for example, non-patent document 1 discloses a method for producing a gallium nitride single crystal substrate by a VAS (Void-Assisted Separation) method.
[0004] [Patent Document 1] JP 2020-33211 A.
[0005] [Non-patent Document 1] Jpn. J. Appl. Phys. Vol. 42 (2003) pp. L1-L3.
SUMMARY OF THE INVENTION
[0006] An object of the present invention is to suppress cracks that occur during growth or machining when producing a gallium nitride single crystal substrate with low dislocation density.
[0007] According to one aspect of the present disclosure, there is provided a gallium nitride single crystal substrate,
[0008] which is a gallium nitride single crystal substrate having a diameter of 50 mm or more, with a low-index crystal plane closest to a main surface being (0001), and
[0009] in which an average density of etch pits during etching applied to the main surface using an alkaline etching solution is less than 1×10.sup.6 cm.sup.−2; and
[0010] in histograms of diameters of the etch pits in multiple different regions on the main surface, and among peaks appearing in the histograms, when a diameter of a first peak which is a smallest diameter is denoted as a, a diameter of a second peak which is a second smallest diameter is denoted as b, frequency of the first peak (the number of etch pits) is denoted as A, frequency of the second peak is denoted as B, the number of the etch pits constituting the first peak is denoted as α, and the number of the etch pits constituting the second peak is denoted as β, at least one of the following conditions (1), (2), and (3) is satisfied: [0011] (1) variation in a/b values in the multiple

histograms is within ±5% of an average value; [0012] (2) variation in A/B values in the multiple histograms is within ±15% of an average value; [0013] (3) variation in α/β values in the multiple histograms is within ±30% of an average value.
[0014] According to another aspect of the present disclosure, there is provided a method for producing a gallium nitride single crystal substrate, the method including the steps of: [0015] (a) preparing a base substrate composed of a gallium nitride single crystal having (0001) that is a low-index crystal plane closest to a main surface, and having a uniform dislocation density distribution in a plane; [0016] (b) epitaxially growing the gallium nitride single crystal on the main surface of the base substrate; and [0017] (c) obtaining a gallium nitride single crystal substrate having a diameter of 50 mm, from the gallium nitride single crystal epitaxially grown in the step (b),
[0018] wherein in the step (b), the gallium nitride single crystal is epitaxially grown using only (0001) as a growth plane, without generating any inclined interface other than (0001) throughout an entire growth period; and
[0019] the gallium nitride single crystal substrate obtained in the step (c) is used as a new base substrate, and the steps (b) and (c) are repeated at least once or more.
[0020] According to the present disclosure, when producing a gallium nitride single crystal substrate with low dislocation density, cracks that occur during growth or machining can be suppressed.

Description

BRIEF DESCRIPTION OF THE DRAWINGS
[0021] FIG. **1** is a flowchart illustrating a method for producing a gallium nitride single crystal substrate according to one embodiment of the present invention.
[0022] FIG. **2**A is a schematic cross-sectional view illustrating a part of a method for producing a gallium nitride single crystal substrate according to one embodiment of the present invention.
[0023] FIG. **2**B is a schematic cross-sectional view illustrating a part of a method for producing a gallium nitride single crystal substrate according to one embodiment of the present invention.
[0024] FIG. **2**C is a schematic cross-sectional view illustrating a part of a method for producing a gallium nitride single crystal substrate according to one embodiment of the present invention.
[0025] FIG. **3** is an SEM image illustrating an example of etch pits formed on the main surface of the gallium nitride single crystal substrate according to one embodiment of the present invention.
[0026] FIG. **4** illustrates histograms of etch pit diameters for VAS substrate.
[0027] FIG. **5** illustrates histograms of etch pit diameters for the substrate of example 1.
[0028] FIG. **6** illustrates histograms of etch pit diameters for the substrate of comparative example 1.
DETAILED DESCRIPTION OF THE INVENTION
Findings Obtained by the Inventors
[0029] First, the findings obtained by the inventors will be described.
[0030] It is known that when the c-plane of a gallium nitride (GaN) single crystal substrate is etched with, for example, an alkaline etching solution, etch pits corresponding to dislocations are formed. Further, a method for identifying the type of dislocation (edge, mixture, screw) based on the size (diameter) of the etch pits is also known to those skilled in the art. However, this method is not necessarily universally applicable. The size of the etch pits formed by alkaline etching corresponds to the size of the strain of a crystal lattice around a dislocation core. This is because the size of an etch pit depends not only on the type of dislocation, but also on the impurities trapped in the dislocation, the precipitates on the dislocation, the distance between the dislocation and other nearby dislocations, and so on.
[0031] For the reason described above, although it is difficult to identify the type of dislocation

(edge, mixed, screw) based on the size of the etch pit, it can be said that dislocations that form large etch pits also have a large strain field around the dislocation core. Dislocations having a large strain field are likely to have a large Burgers vector, and such dislocations become hollow-core micropipe defects, and likely to become anomalous diffusion paths for impurities.

[0032] The size of the etch pit also depends greatly on etching conditions. Therefore, it is meaningless to discuss the absolute value of the size of the etch pit. However, among various types of the etch pits of different sizes detected by etching, the smallest etch pit is highly likely to correspond to an edge dislocation having a smallest strain field around the dislocation core. Therefore, the inventors have found a technique for determining the presence or absence of dislocation defects that adversely affect the properties of the device fabricated on a gallium nitride single crystal substrate, by examining a histogram of etch pit diameters and using the diameter of the smallest peak that appears in the histogram as a standard to examine the diameters and number of other etch pits. Then, when the diameter of a standard etch pit is taken as a, it was found that an etch pit having a diameter exceeding 4 a corresponds to a dislocation having accumulated the above-described large strain, and that such a dislocation is highly likely to have an adverse effect on the properties of the device.

[0033] Further, as described in patent document 1, when the dislocation density is reduced by forcibly changing the propagation direction of dislocations by means of a growth (hereinafter also referred to as 3D growth) with an inclined interface as a growth plane to annihilate dislocations, it was found that the type and density of the dislocations are likely to be varied in the plane, although the dislocation density of an entire substrate is reduced. When the type and density of the dislocations are varied in the plane, a large stress field is formed locally, making it easier for cracks to be introduced into the crystal.

[0034] The inventors have conducted extensive research into the relationship between the histogram of the diameters of etch pits formed by alkaline etching and the occurrence of cracks. As a result, when a histogram of diameters is created for each of multiple different regions in the plane, and the diameter of the first peak, which is the smallest diameter, is denoted as a, the diameter of the second peak, which is the second smallest diameter, is denoted as b, the frequency of the first peak (the number of etch pits) is denoted as A, the frequency of the second peak is denoted as B, the number of etch pits constituting the first peak is denoted as α, and the number of etch pits constituting the second peak is denoted as β, it has been found that when the variations in the a/b, A/B or α/β values in multiple histograms fall within a predetermined range, the occurrence of cracks can be dramatically reduced.

[0035] Further, the inventors have conducted extensive research into a method for producing a substrate having the above-described uniform in-plane histogram (in other words, a substrate having uniformly reduced dislocations in the plane). As a result, it is found that a substrate having the uniform in-plane histogram can be produced using a substrate with a uniform in-plane dislocation density distribution as a starting seed substrate by causing a growth (hereinafter, also referred to as 2D growth) of a gallium nitride single crystal, using only (0001) as a growth plane without generating any inclined interface other than (0001), and further by causing generational growth (details will be described later) without allowing a thick film to grow all at once, throughout an entire growth period.

One Embodiment of the Present Invention

[0036] Hereinafter, one embodiment of the present invention will be described with reference to the drawings.

[0037] Hereinafter, in a GaN crystal having a wurtzite structure, <0001> axis is referred to as “c-axis” and (0001) is referred to as “c-plane”. (0001) is sometimes referred to as “+c plane (gallium polar plane)” and (000-1) is sometimes referred to as “−c plane (nitrogen (N) polar plane).” Further, <1-100> axis is referred to as “m-axis” and {1-100} is referred to as “m-plane.” The m-axis may also be written as <10-10> axis. Further, <11-20> axis is referred to as “a-axis” and {11-

20} is referred to as "a-plane".

(1) Method for Producing a Gallium Nitride Single Crystal Substrate

[0038] The method for producing a gallium nitride single crystal substrate according to this embodiment will be described with reference to FIG. **1** and FIGS. **2**A to **2**C. FIG. **1** is a flowchart illustrating a method for producing a gallium nitride single crystal substrate according to this embodiment. FIGS. **2**A to **2**C are schematic cross-sectional views illustrating a part of the method for producing a gallium nitride single crystal substrate according to this embodiment.

[0039] As illustrated in FIG. **1**, the method for producing a gallium nitride single crystal substrate according to this embodiment includes, for example, a base substrate preparation step S**100**, a 2D growth step S**110**, and a slicing and machining step S**120**.

S**100**: Base Substrate Preparation Step

[0040] As illustrated in FIG. **2**A, in the base substrate preparation step S**100**, a base substrate **10** is prepared, which is composed of gallium nitride single crystal and in which a low-index crystal plane closest to a main surface **10***s* is (0001) (c-plane **10***c*) and the main surface **10***s* has a uniform in-plane dislocation density distribution. Specifically, it is preferable to prepare the base substrate **10** composed of gallium nitride single crystal by the VAS (Void-Assisted Separation) method described in non-patent document 1. A GaN substrate produced by the VAS method is characterized in the uniform in-plane dislocation density distribution, but c-plane warping occurs in the crystal such that the main surface **10***s* side is a concave surface. In order to fabricate a substrate having a uniform distribution of dislocation species, which is a feature of the gallium nitride single crystal substrate according to this embodiment, dislocations in the base substrate **10**, which serves as a starting substrate, must not have undergone a 3D growth process such as ELO (Epitaxial Lateral Overgrowth), and dislocations must not accumulate locally, i.e., dislocations must be uniformly distributed in the plane. The VAS method is a suitable means for obtaining such a substrate, but the substrate produced by the VAS method has a fair amount of c-plane warping, and the size of this warping is in a trade-off relationship with the in-plane uniformity of dislocation density. In this embodiment, emphasis is placed on the in-plane uniformity of dislocation density, and the c-plane warping in the base substrate **10** is tolerated by taking measures to alleviate the c-plane warping in the subsequent crystal growth step (for example, the generational growth described below).

[0041] The base substrate **10** may be a substrate doped with a dopant such as germanium (Ge), silicon (Si), or oxygen (O), or may be a so-called undoped substrate that is not intentionally doped with a dopant.

S**110**: 2D Growth Step

[0042] In the 2D growth step S**110**, on the main surface **10***s* of the base substrate **10** prepared in the base substrate preparation step S**100**, a single crystal of GaN is epitaxially grown with the c-plane **30***c* as a growth plane, as illustrated in FIG. **2**B. Specifically, for example, by supplying GaCl gas and NH.sub.3 gas to the heated base substrate **10** by the HVPE method, epitaxial growth is caused directly on the main surface **10***s* of the base substrate **10** to grow a growth layer **30**.

[0043] At this time, depending on the growth conditions, as described in patent document 1, an inclined interface other than the c-plane may be generated on the growth surface, resulting in 3D growth. In the epitaxial crystal growth, there are three types of crystal growth modes in the initial stage of the growth, and these modes are changed depending on the crystal growth conditions. Of the above three modes, the VW (Volmer-Weber) mode and the SK (Stranski-Krastanov) mode are growth modes that induce 3D growth. In contrast, in the 2D growth step S**110**, it is necessary to epitaxially grow the GaN single crystal (i.e., grow it in 2D) using only the c-plane as a growth plane throughout an entire growth period, without generating any inclined interfaces other than the c-plane. To achieve the 2D growth, the crystal growth conditions can be adjusted to produce an FM (Frank-van der Merwe) mode, which is different from the above growth mode.

[0044] In the 3D growth, the propagation direction of dislocations is forcibly bent and locally accumulated, and therefore multiple dislocations are combined with each other to efficiently reduce the dislocation density, and meanwhile dislocations with large Burgers vectors are likely to occur, resulting in dislocation species with various crystal strains being scattered in the substrate plane. In such a region, a large local stress field is formed, which may cause cracks to occur during crystal growth or cooling.

[0045] In the 2D growth, the propagation direction of dislocations is not forcibly bent, but in the process of growing the crystal thicker, there is a certain probability that propagating dislocations that are inclined in a direction of travel will meet and disappear, or they will form dislocation loops and stop propagating, thus gradually reducing the dislocation density.

[0046] Thus, although the 2D growth requires more time to reduce dislocations than the 3D growth, dislocations can be uniformly reduced in the plane because there is no change in the propagation direction of dislocations or no forced combining of dislocations. Another advantage is that dislocations with large Burgers vectors, which are the result of combining of a large number of dislocations, are less likely to occur.

[0047] In the 2D growth step S**110**, the growth layer **30** is grown under predetermined growth conditions so that the crystal growth proceeds in the FM mode. As a growth condition in this embodiment, for example, the growth temperature is preferably set to, for example, 980° C. or more and 1200° C. or less. Further, in the 2D growth step S**110**, the ratio of the supply rate of NH.sub.3 gas as a nitriding gas to the supply rate of GaCl gas as a group III source gas (hereinafter also referred to as the “V/III ratio”) is preferably set to, for example, 0.1 or more and 5 or less.

[0048] In the 2D growth step S**110**, a Si-doped GaN layer may be epitaxially grown as a growth layer **30** by supplying GaCl gas, NH.sub.3 gas, and dichlorosilane (SiH.sub.2Cl.sub.2) gas as an n-type dopant gas to the base substrate **10**, or a Ge-doped GaN layer may be epitaxially grown by supplying tetrachlorogermane (GeCl.sub.4) gas as an n-type dopant gas instead of the SiH.sub.2Cl.sub.2 gas. As the growth layer **30**, a GaN layer doped with iron (Fe), manganese (Mn), carbon (C), etc., may be epitaxially grown.

[0049] Other growth conditions in the 2D growth step S**110** are, for example, as follows.

[0050] Growth pressure: 90 to 105 kPa, preferably 90 to 95 kPa.

[0051] GaCl gas partial pressure: 1.5 to 15 kPa.

[0052] N.sub.2 gas flow rate/H.sub.2 gas flow rate: 0 to 1.

[0053] In the 2D growth step S**110**, it is preferable that the thickness of the growth layer **30** is set to, for example, 3 mm or more and 20 mm or less. If the thickness of the growth layer **30** is less than 3 mm, there is a possibility that the effect of reducing dislocations may not be sufficiently obtained. In addition, the c-plane warping that occurs in the base substrate **10** is inherited by the growth layer **30** grown thereon, and therefore due to the growth of the growth layer **30** to a certain thickness or more, stress is generated in the crystal to straighten the warping and flatten the c-plane, and the size of the c-plane warping becomes gradually small. If the thickness of the growth layer **30** is less than 3 mm, there is a possibility that a sufficient stress for straightening the c-plane warping cannot be obtained. Further, in the subsequent slicing and machining step S**120**, it is difficult to obtain a GaN single crystal substrate with a sufficient thickness. In contrast, by setting the thickness of the growth layer **30** to 3 mm or more, dislocations can be uniformly reduced in the plane, and the c-plane warping can be small. Further, in the subsequent slicing and machining step S**120**, a GaN single crystal substrate with a sufficient thickness can be obtained. On the other hand, if the thickness of the growth layer **30** exceeds 20 mm, the force attempting to straighten the c-plane warping may cause excessive strain to accumulate in the crystal, leading to the proliferation of dislocations in the crystal or the generation of microcracks. Further, if the internal residual stress in the GaN crystal becomes large, crystal fracture is more likely to occur in the slicing and machining step S**120**. In contrast, by setting the thickness of the growth layer **30** to 20 mm or less, the internal residual stress of the GaN crystal can be reduced, and cracks and fractures can be suppressed.

S**120**: Slicing and Machining Step

[0054] In the slicing and machining step S**120**, as illustrated in FIG. **2**C, for example, the growth layer **30** is sliced along a cutting plane approximately parallel to the main surface **30***s* (c-plane **30***c*) of the growth layer **30** using a wire saw, etc. Thereby, at least one gallium nitride single crystal substrate **50** (also referred to as a substrate **50**) having a diameter of 50 mm or more is obtained as an as-sliced substrate. At this time, it is preferable to slice the substrate **50** so that the thickness thereof is, for example, 300 μm or more and 500 μm or less.

[0055] As described above, due to the growth of the growth layer **30** to a certain thickness, stress is generated that attempts to straighten the c-plane warping during growth, and therefore the radius of curvature of the c-plane **50***c* of the substrate **50** cut out from the growth layer **30** becomes larger than the radius of curvature of the c-plane **10***c* of the base substrate **10**. Further, the growth layer **30** is separated from the base substrate **10** by the slicing and machining step S**120**, and the growth layer **30** is released from the constraints imposed on the growth layer **30** from the base substrate **10** due to the c-plane warping, and therefore the radius of curvature of the c-plane **50***c* of the cut-out substrate **50** becomes further larger than before the base substrate **10** was separated. Thereby, the internal residual stress in the cut substrate **50** is also reduced.

[0056] Specifically, the radius of curvature of the c-plane **50***c* of the substrate **50** is, for example, preferably 60 m or more, and more preferably 80 m or more. Thereby, the variation in the off-angle θ of the c-axis relative to the normal on the major surface **50** of the substrate **50** (the maximum and minimum difference in the off-angle θ in the plane of the substrate) can be smaller than the variation in the off-angle of the c-axis of the base substrate **10**.

[0057] Once the substrate **50** is obtained as an as-sliced substrate, both surfaces of the substrate **50** may be polished, for example, by a polishing device.

Generational Growth

[0058] In this embodiment, the substrate **50** obtained in the slicing and machining step S**120** is used as a new base substrate **10**, and the 2D growth step S**110** and the slicing and machining step S**120** are repeated at least once or more (preferably four times or more). This type of growth is referred to as a generational growth in this specification. By performing such a generational growth rather than a growth caused all at once, the c-plane warp is alleviated each time the substrate **50** is cut out. This method enables to overcome the drawbacks of the substrate, even when the substrate with uniform dislocation density distribution is adopted at the expense of c-plane warping. Further, by performing generational growth, the internal residual stress of the resulting GaN crystal can be further reduced. By reducing the internal residual stress, the propagation direction of dislocations is more easily maintained even in the new 2D growth step S**110** in which the substrate **50** is used as the base substrate **10**, thereby making it easier to uniformly reduce dislocations in the plane. Specifically, by repeating the generational growth and increasing the cumulative growth thickness of the growth layer **30** to 12 mm or more, the dislocation density can be reduced to 5×10.sup.5 cm.sup.−3 or less. There is no particular upper limit in the number of times that the generational growth is performed, but from the viewpoint of efficiently producing a large-diameter GaN single crystal substrate, it is preferable to perform the growth **10** times or less, for example.

[0059] Through the above steps, the substrate **50** according to this embodiment is produced.

Fabrication Step of a Semiconductor Stack and a Fabrication Step of a Semiconductor Device

[0060] After the substrate **50** is produced, for example, a semiconductor functional layer composed of a group III nitride semiconductor may be epitaxially grown on the substrate **50** to fabricate a semiconductor stack. After the semiconductor stack is fabricated, electrodes, etc., are formed on the semiconductor stack, and the semiconductor stack is diced to cut out chips of a predetermined size. In this way, a semiconductor device may be fabricated. Since the dislocations in the substrate **50** are uniformly reduced in the plane, the properties of the semiconductor device fabricated on the substrate **50** are uniform in the plane, thus improving reliability.

(2) Gallium Nitride Single Crystal Substrate (Free-Standing Nitride Semiconductor Substrate, Nitride Crystal Substrate)

[0061] Next, the gallium nitride single crystal substrate **50** according to this embodiment will be described.
[0062] In this embodiment, the substrate **50** obtained by the above-described producing method is a free-standing substrate composed of single crystal GaN.
[0063] The diameter of the substrate **50** is, for example, 50 mm or more, and the thickness of the substrate **50** is, for example, 300 μm or more and 1 mm or less.
[0064] The conductivity of the substrate **50** is not particularly limited, but when the substrate **50** is used for producing a semiconductor device as a vertical Schottky barrier diode (SBD), the substrate **50** is, for example, an n-type, and the n-type impurity in the substrate **50** is, for example, Si or Ge, and the n-type impurity concentration in the substrate **50** is, for example, 1.0×10.sup.18 cm.sup.−3 or more and 1.0×10.sup.20 cm.sup.−3 or less.
[0065] The substrate **50** has, for example, a main surface **50***s* which serves as an epitaxial growth plane. In this embodiment, the low-index crystal plane closest to the main surface **50***s* is, for example, a c-plane **50***c*.
[0066] The main surface **50***s* of the substrate **50** is, for example, mirror-finished, and the root-mean-square roughness RMS of the main surface **50***s* of the substrate **50** is, for example, less than 1 nm.
[0067] Further, in this embodiment, the impurity concentration in the substrate **50** obtained by the above-described producing method is lower than that in a substrate obtained by liquid phase growth such as the flux method or ammonothermal method.
[0068] Specifically, the hydrogen concentration in the substrate **50** is, for example, less than 1×10.sup.17 cm.sup.−3, and preferably 5×10.sup.16 cm.sup.−3 or less. Further, the oxygen concentration in the substrate **50** is, for example, 5×10.sup.16 cm.sup.−3 or less, and preferably 3×10.sup.16 cm.sup.−3 or less.
Curving of the C-Plane and Variation in the Off-Angle
[0069] In this embodiment, since the substrate **50** is produced by generational growth, the radius of curvature of the c-plane **50***c* of the substrate **50** is larger than, for example, the radius of curvature of the c-plane **10***c* of the base substrate **10** used in the method for producing the substrate **50** described above. Specifically, the radius of curvature of the c-plane **50***c* of the substrate **50** is, for example, preferably 60 m or more, and more preferably 80 m or more.
[0070] In this embodiment, the upper limit of the radius of curvature of the c-plane **50***c* of the substrate **50** is not particularly limited, and is preferably as large as possible. When the c-plane **50***c* of the substrate **50** is substantially flat, the radius of curvature of the c-plane **50***c* may be considered to be infinite.
[0071] Further, in this embodiment, the large radius of curvature of the c-plane **50***c* of the substrate **50** allows the variation in the off-angle θ of the c-axis relative to the normal on main surface **50***s* of the substrate **50** to be smaller than the variation in the off-angle of the c-axis of base substrate **10**.
[0072] Specifically, when an X-ray rocking curve measurement was performed for (0002) of the substrate **50** and the off-angle θ of the c-axis with respect to the normal on the main surface **50***s* was measured based on a diffraction peak angle of the (0002), the variation calculated from the maximum and minimum difference in the size of the off-angle θ within a diameter of 25 mm from the center of the main surface **50***s* is, for example, 0.024° or less, and preferably 0.018° or less.
[0073] In this embodiment, the lower limit of the variation in the off-angle θ of the c-axis of the substrate **50** is not particularly limited, and the smaller the better. When the c-plane **50***c* of the substrate **50** is substantially flat, the variation in the off-angle θ of the c-axis of the substrate **50** may be considered to be 0°.
[0074] Further, in this embodiment, since the curvature of the c-plane **50***c* is isotropically small with respect to the main surface **50***s* of the substrate **50**, the radius of curvature of the c-plane **50***c* has little directional dependency.
[0075] Specifically, the difference between the radius of curvature of the c-plane **50***c* in the

direction along the a-axis, as determined by the above-described measurement method, and the radius of curvature of the c-plane **50***c* in the direction along the m-axis, is, for example, 50% or less, and preferably 20% or less, of the larger of these radii of curvature.

Dislocation Density

[0076] In this embodiment, by the above-described producing method, the dislocation density on the surface of substrate **50** is lower than the dislocation density on the main surface **10***s* of base substrate **10**.

[0077] When the substrate **50** is produced using the base substrate **10** composed of high-purity GaN single crystal fabricated by the VAS method, the substrate **50** contains few non-radiative centers caused by foreign matters or point defects. Accordingly, when the main surface of the substrate **50** of the present application is observed using a multiphoton excitation microscope, etc., 95% or more (preferably 99% or more) of dark spots correspond to dislocations rather than non-radiative centers caused by foreign matters or point defects. The “multiphoton excitation microscope” is sometimes called a two-photon excitation microscope.

[0078] In this embodiment, by the above-described producing method, dislocations are uniformly reduced in the plane, and therefore regions with particularly high dislocation density due to dislocation concentration are not formed, and regions with low dislocation density are uniformly formed. Specifically, in this embodiment, when the main surface **50***s* of the substrate **50** is observed with a multiphoton excitation microscope in a field of view of 250 μm square and the dislocation density is calculated from a dark spot density, there is no region where the dislocation density exceeds 1×10.sup.6 cm.sup.−2, and the region where the dislocation density is less than 5×10.sup.5 cm.sup.−2 occupies 80% or more, preferably 90% or more, and more preferably 95% or more of the main surface **50***s*.

[0079] In other words, in this embodiment, the dislocation density averaged over an entire main surface **50***s* of the substrate **50** is, for example, less than 1×10.sup.6 cm.sup.−2, preferably less than 5.5×10.sup.5 cm.sup.−2, and more preferably 3×10.sup.5 cm.sup.−2 or less.

Etch Pit Histogram

[0080] When the main surface **50***s* of the substrate **50** is etched with an alkaline etching solution, etch pits as illustrated in FIG. **3** are formed. In this embodiment, the substrate **50** was immersed for 20 minutes in a molten liquid (temperature 470° C.) of a 1:1 mixture of potassium hydroxide (KOH) and sodium hydroxide (NaOH) to perform etching. Then, the main surface **50***s* of the substrate **50** after etching was observed using an SEM, and the diameter of each etch pit was calculated by image analysis. A histogram of etch pit diameters was created from the obtained data on the etch pit diameters. The etch pit diameter may be the maximum diameter of each etch pit region obtained by image analysis, or may be an equivalent circle diameter. In this embodiment, the diameter of the smallest peak (hereinafter also referred to as a first peak) among the peaks appearing in the histogram of etch pit diameters was standardized as a, and the horizontal axis was divided into classes in increments of 0.1 a. The vertical axis indicates the number (frequency) of the etch pits in a measurement area.

[0081] The average density (number per unit area) of the etch pits formed during etching applied to the main surface **50***s* of the substrate **50** of this embodiment under the above-described conditions, nearly matches the dislocation density determined by observation using the multiphoton excitation microscope. The size of the etch pits can be changed by adjusting etching conditions, but if they are present at too high a density, adjacent etch pits will overlap, making it difficult to measure the diameter of the etch pits, and therefore in order to perform a meaningful measurement, the average density of the etch pits is preferably less than 1×10.sup.6 cm.sup.−2, more preferably less than 5.5×10.sup.5 cm.sup.−2, and even more preferably 3×10.sup.5 cm.sup.−2 or less. The histograms of the average density of the etch pits and the diameters of the etch pits are preferably measured from a region having an area of 1 mm.sup.2 or more.

[0082] When the histogram of etch pit diameters is created for each of multiple different regions on the main surface **50***s* of the substrate **50**, and among the peaks appearing in the histogram, the diameter of the first peak, which is the smallest diameter, is denoted as a, the diameter of the second peak, which is the second smallest diameter, is denoted as b, the frequency of the first peak (the number of etch pits) is denoted as A, the frequency of the second peak is denoted as B, the number of etch pits constituting the first peak is denoted as α, and the number of etch pits constituting the second peak is denoted as β, the substrate **50** of this embodiment satisfies at least one of the following conditions (1), (2), and (3): [0083] (1) variation in a/b values in the multiple histograms is within ±5% of an average value. [0084] (2) variation in A/B values in the multiple histograms is within ±15% of an average value. [0085] (3) variation in α/β values in the multiple histograms is within ±30% of an average value.

[0086] The substrate **50** from which such a histogram is obtained has dislocations uniformly reduced in the plane, and is therefore unlikely to cause cracks to occur during crystal growth or machining. On the other hand, the substrate having variations exceeding the conditions (1), (2) and (3) has a large localized stress field, and is likely to cause cracks to occur during crystal growth or machining. In order to accurately determine the conditions (1), (2), and (3), it is preferable to create histograms of etch pit diameters in three or more (more preferably five or more) different regions on the main surface **50***s*.

[0087] The substrate **50** preferably satisfies two of the conditions (1), (2), and (3), and more preferably satisfies all of the conditions (1), (2), and (3). This allows the rate of crack occurrence to be more dramatically reduced during crystal growth or machining.

[0088] Further, the substrate **50** preferably satisfies at least one of the following conditions (4), (5) and (6), more preferably satisfies two of them, and particularly preferably satisfies all of them: [0089] (4) difference between maximum and minimum values of a/b in the multiple histograms is 0.1 or less. [0090] (5) difference between maximum and minimum values of A/B in the multiple histograms is 0.5 or less. [0091] (6) difference between maximum and minimum values of α/β in the multiple histograms is 0.8 or less.

[0092] Also, the substrate **50** preferably satisfies at least one of the following conditions (7), (8) and (9), more preferably satisfies two of them, and particularly preferably satisfies all of them: [0093] (7) standard deviation of a/b in the multiple histograms is 0.03 or less. [0094] (8) standard deviation of A/B in the multiple histograms is 0.20 or less. [0095] (9) standard deviation of β/α in the multiple histograms is 0.3 or less.

[0096] Also, the substrate **50** preferably satisfies at least one of the following conditions (10) and (11), and more preferably satisfies both of them: [0097] (10) A/α is 0.5 or more, and more preferably 0.7 or more in the multiple histograms. [0098] (11) B/β is 0.5 or more, and more preferably 0.7 or more in the multiple histograms.

[0099] Further, it is preferable that the number of the etch pits of the substrate **50** is 90% or more, and more preferably 95% or more in the multiple histograms.

[0100] In the substrate **50** of this embodiment, the total number of the etch pits having a diameter exceeding 4 a is preferably α/1000 or less. This can also be said to mean that there are substantially no etch pits having a diameter exceeding 4 a, but since large etch pits may be formed due to scratches or foreign matters on the substrate **50**, the total number of the etch pits is expressed as α/1000 or less. In the substrate **50** of this embodiment, dislocations are less likely to combine with each other due to the above-described producing method, and therefore it can be said that there are substantially no dislocation species or dislocation accumulation regions that would generate large local stress. Accordingly, the occurrence of cracks during crystal growth or machining can be suppressed.

[0101] In substrate **50** of this embodiment, the total number of the etch pits having a diameter of 2 a or more is preferably 1/10 or less, and more preferably 1/100 or less of the number of the etch pits constituting the first peak. The etch pits having a diameter of 2 a or more may correspond to dislocations that generate large local stress, and therefore by setting the total number of the etch

pits having a diameter of 2 a or more to 1/10 or less (more preferably 1/100 or less) of the number of the etch pits constituting the first peak, the occurrence of cracks can be suppressed.
[0102] In the substrate **50** of this embodiment, the number of the etch pits constituting the first peak is preferably 50% or more (more preferably 70% or more) of the total. In this embodiment, as described above, the dislocations are less likely to combine with each other, and therefore the proportion of dislocations with small strain fields is high, which suppresses the occurrence of cracks.
[0103] In the substrate **50** of this embodiment, when the frequency of the first peak is A, it is preferable that there are two peaks, the first peak and the second peak, that appear in the diameter histogram and have a frequency of A/10 or more. It can be said that the number of peaks appearing in the histogram of the etch pits corresponds to the number of component species of dislocation defects corresponding to the etch pits. Crystals in which many peaks are observed are not only characterized by simple edge or mixed dislocations, but also by a wide variety of impurities and point defects that are in combination with these dislocations. That is, they are crystals in which there is a high possibility that many impurity levels and defect levels are generated. It can be said that a large stress field occurs locally, and cracks are likely to occur during crystal growth or machining. In contrast, the crystal in which the histogram shows two peaks, the first peak and the second peak, with a frequency of A/10 or more, suggests that the only types of dislocations present in the crystal are simple edge dislocations and mixed dislocations. That is, it can be said that this is a substrate in which cracks are unlikely to occur during crystal growth or machining.
[0104] Further, the substrate **50** of this embodiment has a second peak in a diameter range of more than a and less than 2 a, and the number β of the etch pits constituting the second peak is preferably smaller than the number a of the etch pits constituting the first peak. The diameter of the etch pit constituting the second peak is in the range of more than a and less than 2 a. This means that it is highly likely that these etch pits correspond to a simple mixed dislocation. Also, the small number of etch pits constituting the second peak, in other words, the large number of etch pits constituting the first peak, means that the dislocations in the crystal are mainly composed of dislocations with little strain around the dislocation core. These features mean that the substrate **50** is a substrate in which cracks are unlikely to occur during crystal growth or machining.
Other Embodiments
[0105] The embodiment of the present invention has been specifically described above. However, the present invention is not limited to the above embodiment, and various modifications can be made without departing from the spirit and scope of the present invention.
[0106] The above embodiment mainly shows a case where the substrate **50** is an n-type. However, the substrate **50** may be a p-type or may have semi-insulating properties. For example, when the substrate **50** is used to produce a semiconductor device such as a high electron mobility transistor (HEMT), the substrate **50** preferably has semi-insulating properties.
[0107] The above embodiment shows a case where the growth layer **30** is sliced using a wire saw in the slicing and machining step S**120**, but for example, an outer circumferential blade slicer, an inner circumferential blade slicer, an electric discharge machine, etc., may also be used.
EXAMPLE
[0108] Next, examples of the present invention will be described. These examples are merely examples of the present invention, and the present invention is not limited to these examples.
(1) Fabrication of a Gallium Nitride Single Crystal Substrate
[0109] Gallium nitride single crystal substrates of example 1 and comparative example 1 were fabricated as follows.
[Fabrication Conditions for the Gallium Nitride Single Crystal Substrate in Example 1] (Base Substrate)
[0110] Material: GaN.
[0111] Fabrication method: VAS method.

[0112] Diameter: 2 inches.
[0113] Thickness: 400 μm.
[0114] Low-index crystal plane closest to the main surface: c-plane.
[0115] No pattern machining for the mask layer, etc., on the main surface.
[0116] Root mean square roughness RMS of the main surface: 2 nm.
[0117] Off-angle on the main surface: 0.4° in the m direction.
[0118] Radius of curvature of the main surface: 5 m.
[0119] Dislocation density of the main surface: 3×10^{6} cm^{-2} (growth layer).
[0120] Material: GaN.
[0121] Growth method: HVPE, 2D growth.
[0122] Growth temperature: 980° C. to 1,200° C.
[0123] V/III ratio: 0.1 to 5.
[0124] Thickness of the growth layer: 3 mm (slicing conditions).
[0125] Thickness of the gallium nitride single crystal substrate: 400 μm (generational growth).
[0126] Number of generational growths: 4 times.
[Fabrication Conditions for the Gallium Nitride Single Crystal Substrate in Comparative Example 1] (Base Substrate)
[0127] Same as example 1.
[0128] Material: GaN.
[0129] Growth method: HVPE, 3D growth.
[0130] First growth condition:
[0131] Growth temperature was 980° C. to 1,020° C., and V/III ratio was 2 to 20.
[0132] Thickness from the main surface of the base substrate to the surface of the first layer: 1 mm (second layer).
[0133] Material: GaN.
[0134] Growth method: HVPE, 2D growth.
[0135] Second growth condition:
[0136] Growth temperature was 1,050° C. to 1,080° C., and V/III ratio was 2 to 5.
[0137] Thickness from the main surface of the base substrate to the surface of the second layer: 2 mm (slicing condition).
[0138] Same as example 1.
(Generational Growth)
[0139] In comparative example 1, generational growth was not performed.
(2) Evaluation of the Etch Pit Histogram
[0140] The main surfaces of the base substrate (VAS substrate), the gallium nitride single crystal substrate of example 1, and the gallium nitride single crystal substrate of comparative example 1 were etched with an alkaline etching solution under the following conditions to form etch pits.
[0141] Etching solution: Alkaline melt consisting of 500 g KOH and 500 g NaOH.
[0142] Melting temperature: 470° C.
[0143] Immersion time: 20 minutes.
[0144] The main surface of the substrate formed with etch pits was observed using a SEM (SU5000, manufactured by Hitachi High-Technologies Corporation). A measurement field was 127 μm×95.3 μm (magnification 1000 times), and etch pits were measured by image analysis for an image (1143 μm×1048 μm) obtained by combining 9 horizontal×11 vertical (total of 99) SEM images. Specifically, using image processing software (Image J), the image was binarized, etch pit areas were filled in, and the larger one of the width and height of the etch pit area was calculated as the diameter of the etch pit. When the etch pit areas were filled in, areas showing small particles and linear pit areas caused by machining scratches, etc., were removed.
[0145] From the obtained data on the etch pit diameters, a histogram of etch pit diameters was created. In this example, among the peaks appearing in the histogram of etch pit diameters, the

diameter of the peak (first peak) appearing on the smallest diameter side was standardized as 1, and the horizontal axis was divided into classes in increments of 0.1. The histograms were created in five regions: the center of the substrate (0 mm, 0 mm), the right side of the substrate (20 mm, 0 mm), the left side of the substrate (−20 mm, 0 mm), the top side of the substrate (0 mm, 20 mm), and the bottom side of the substrate (0 mm, −20 mm), with the center of the substrate as an origin, the left and right direction in a plan view as x direction, and the top and bottom direction in a plan view as y direction.

[0146] FIG. **4** illustrates a histogram of the VAS substrate, FIG. **5** illustrates a histogram of example 1, and FIG. **6** illustrates a histogram of comparative example 1. In each histogram, the horizontal axis indicates the normalized etch pit diameter, and the vertical axis indicates the number (frequency) of etch pits in the measurement area. Further, table 1 shows an average density of etch pits, a/b value, A/B value, α/β value, etc., in each histogram for the VAS substrate, example 1, and comparative example 1.

TABLE-US-00001 TABLE 1 Variation from Variation from Variation from Substrate Properties Measurement position a/b average value A/B average value α/β average value VAS substrate Average density Center of substrate 0.71 −1.2% 1.49 −11.0% 1.83 0.5% of etch pits Right side of substrate 0.77 6.9% 1.71 2.1% 1.75 −4.0% 3.0 × 10.sup.5 cm.sup.−2 Left side of substrate 0.72 −0.1% 1.71 1.8% 1.83 0.5% Top side of substrate 0.68 −5.4% 1.56 −6.9% 1.65 −6.6% Bottom side of substrate 0.72 −0.1% 1.91 14.0% 1.99 9.6% Radius of curvature Average value 0.72 — 1.68 — 1.81 — 5 m Maximum value − 0.09 — 0.42 — 0.34 — minimum value Standard deviation 0.03 — 0.14 — 0.11 — Example 1 Average density Center of substrate 0.75 −1.0% 2.49 1.8% 3.30 −7.2% of etch pits Right side of substrate 0.75 −1.0% 2.48 1.4% 3.38 −2.8% 5.0 × 10.sup.5 cm.sup.−2 Left side of substrate 0.75 −1.0% 2.53 3.5% 3.38 −2.8% Top side of substrate 0.77 1.5% 2.41 −1.3% 3.62 7.0% Bottom side of substrate 0.77 1.5% 2.31 −5.4% 3.58 5.8% Radius of curvature Average value 0.76 — 2.45 — 3.45 — 60 m Maximum value − 0.02 — 0.22 — 0.32 — minimum value Standard deviation 0.01 — 0.08 — 0.13 — Comparative Average density Center of substrate 0.73 −8.4% 1.32 34.6% 1.57 7.0% example 1 of etch pits Right side of substrate 0.82 2.9% 1.17 19.5% 1.91 30.4% 5.0 × 10.sup.5 cm.sup.−2 Left side of substrate 0.85 5.7% 0.99 0.7% 1.02 −30.2% Top side of substrate 0.79 −1.8% 0.78 −22.3% 1.72 16.9% Bottom side of substrate 0.81 1.5% 0.66 −32.5% 1.11 −24.1% Radius of curvature Average value 0.80 — 0.98 — 1.47 — 40 m Maximum value − 0.11 — 0.68 — 0.89 — minimum value Standard deviation 0.04 — 0.25 — 0.34 —

[0147] As illustrated in FIG. **4** and Table 1, in the VAS substrate, a histogram shape was uniform in the plane, and the above conditions (2) and (3) were satisfied. That is, although the VAS substrate has a relatively large average density of etch pits (in other words, dislocation density), it can be said to be a base substrate having a uniform in-plane distribution of dislocation density.

[0148] Further, as illustrated in FIG. **5** and Table 1, in the substrate of example 1, the histogram shape was uniform in the plane, and all of the above conditions (1), (2), and (3) were satisfied. Further, the average density of etch pits was smaller than that of the VAS substrate. That is, the substrate of example 1 can be said to be a substrate in which dislocations are uniformly reduced in the plane. Further, the variation from the average value of a/b value, A/B value, and α/β value of the substrate of example 1 was smaller than that of the VAS substrate.

[0149] Further, as illustrated in FIG. **6** and table 1, in the substrate of comparative example 1, the histogram shape was varied in the plane, and the above conditions (1), (2), and (3) were not satisfied. That is, the substrate of comparative example 1 can be said to be a substrate in which the dislocation density was reduced, but the density and type of dislocations were varied in the plane.

[0150] Table 2 shows the occurrence rates of cracks (growth cracks) occurring during the preparation of the substrate and cracks (machining cracks) occurring during machining of the substrate, that is, the VAS substrate, the substrate of example 1, and the substrate of comparative example 1. As shown in table 2, it can be said that the occurrence rates of cracks can be reduced for a substrate having higher in-plane uniformity of the histogram.

TABLE-US-00002 TABLE 2

Substrate	Growth cracks	Machining cracks	Total
VAS substrate	5%	5%	10%
Example 1	1%	1%	2%
Comparative example 1	20%	30%	50%

(3) Evaluation of the Radius of Curvature of the C-Plane

[0151] The radius of curvature of the c-plane of the base substrate (VAS substrate), the substrate of example 1, and the substrate of comparative example 1 was measured. As a result, the VAS substrate was 5 m, the substrate of example 1 was 60 m, and the substrate of comparative example 1 was 40 m.

[0152] As described above, it was confirmed that by using the VAS substrate having a uniform in-plane dislocation density distribution as a base substrate and repeating 2D growth and generational growth, the substrate having uniformly reduced dislocations in the plane could be produced. Further, it was confirmed that the rate of crack occurrence could be reduced for the substrate having higher in-plane histogram uniformity. Further, it was confirmed that the substrate of example 1, which underwent repeated generational growth, had a larger radius of curvature of the c-plane than the VAS substrate, which was the starting seed substrate, and than the substrate of comparative example 1, which did not undergo generational growth.

Preferable Aspect of the Present Invention

[0153] Preferable aspects of the present invention will be described below.

(Supplementary Description 1)

[0154] A gallium nitride single crystal substrate,

[0155] which is a gallium nitride single crystal substrate having a diameter of 50 mm or more, with a low-index crystal plane closest to a main surface being (0001), and

[0156] in which an average density of etch pits during etching applied to the main surface using an alkaline etching solution is less than 1×10.sup.6 cm.sup.−2; and

[0157] in histograms of diameters of the etch pits in multiple different regions on the main surface, and among peaks appearing in the histograms, when a diameter of a first peak which is a smallest diameter is denoted as a, a diameter of a second peak which is a second smallest diameter is denoted as b, frequency of the first peak (the number of etch pits) is denoted as A, frequency of the second peak is denoted as B, the number of the etch pits constituting the first peak is denoted as α, and the number of the etch pits constituting the second peak is denoted as β, at least one of the following conditions (1), (2), and (3) is satisfied: [0158] (1) variation in a/b values in the multiple histograms is within ±5% of an average value. [0159] (2) variation in A/B values in the multiple histograms is within ±15% of an average value. [0160] (3) variation in α/β values in the multiple histograms is within ±30% of an average value.

(Supplementary Description 2)

[0161] The gallium nitride single crystal substrate according to supplementary description 1, which satisfies two of the conditions (1), (2), and (3).

(Supplementary Description 3)

[0162] The gallium nitride single crystal substrate according to supplementary description 1, which satisfies all of the conditions (1), (2), and (3).

(Supplementary Description 4)

[0163] The gallium nitride single crystal substrate according to supplementary description 1, which satisfies at least any one of the following conditions (4), (5), and (6): [0164] (4) difference between maximum and minimum values of a/b in the multiple histograms is 0.1 or less. [0165] (5) difference between maximum and minimum values of A/B in the multiple histograms is 0.5 or less. [0166] (6) difference between maximum and minimum values of α/β in the multiple histograms is 0.8 or less.

[0167] More preferably, two of the conditions (4), (5) and (6) are satisfied, and particularly preferably, all of the conditions (4), (5) and (6) are satisfied.

(Supplementary Description 5)

[0168] The gallium nitride single crystal substrate according to supplementary description 1, which satisfies at least any one of the following conditions (7), (8), and (9): [0169] (7) standard deviation of a/b in the multiple histograms is 0.03 or less. [0170] (8) standard deviation of A/B in the multiple histograms is 0.20 or less. [0171] (9) standard deviation of β/α in the multiple histograms is 0.3 or less.
[0172] More preferably, two of the conditions (7), (8), and (9) are satisfied, and particularly preferably, all of the conditions (7), (8), and (9) are satisfied.
(Supplementary Description 6)
[0173] The gallium nitride single crystal substrate according to supplementary description 1, which satisfies at least one of the following conditions (10) and (11):
[0174] (10) A/α is 0.5 or more, and more preferably 0.7 or more in the multiple histograms.
[0175] (11) B/β is 0.5 or more, and more preferably 0.7 or more in the multiple histograms.
[0176] More preferably, both of the conditions (10) and (11) are satisfied.
(Supplementary Description 7)
[0177] The gallium nitride single crystal substrate according to supplementary description 1, wherein in the multiple histograms, α+β represents 90% or more of a total number of etch pits.
(Supplementary Description 8)
[0178] The gallium nitride single crystal substrate according to supplementary description 1, wherein a total number of etch pits having a diameter exceeding 4 a is α/1000 or less in the histogram.
(Supplementary Description 9)
[0179] The gallium nitride single crystal substrate according to supplementary description 1, wherein a radius of curvature of (0001) is 60 nm or more.
(Supplementary Description 10)
[0180] The gallium nitride single crystal substrate according to any one of supplementary descriptions 1 to 9, wherein an average density of etch pits and the histogram are measured from a region having an area of 1 mm.sup.2 or more.
(Supplementary Description 11)
[0181] A method for producing a gallium nitride single crystal substrate, the method including the steps of: [0182] (a) preparing a base substrate composed of a gallium nitride single crystal having (0001) that is a low-index crystal plane closest to a main surface, and having a uniform dislocation density distribution in a plane; [0183] (b) epitaxially growing the gallium nitride single crystal on the main surface of the base substrate; and [0184] (c) obtaining a gallium nitride single crystal substrate having a diameter of 50 mm, from the gallium nitride single crystal epitaxially grown in the step (b),
[0185] wherein in the step (b), the gallium nitride single crystal is epitaxially grown using only (0001) as a growth plane, without generating any inclined interface other than (0001) throughout an entire growth period; and
[0186] the gallium nitride single crystal substrate obtained in the step (c) is used as a new base substrate, and the steps (b) and (c) are repeated at least once or more.
(Supplementary Description 12)
[0187] The method for producing a gallium nitride single crystal substrate according to supplementary description 11, wherein the base substrate prepared in the step (a) is a substrate fabricated by a VAS method.
(Supplementary Description 13)
[0188] The method for producing a gallium nitride single crystal substrate according to supplementary description 11, wherein in the step (b), the gallium nitride single crystal is grown to at least 3 mm or more.
(Supplementary Description 14)
[0189] The method for producing a gallium nitride single crystal substrate according to claim 11,

wherein each time the steps (b) and (c) are repeated, the dislocation density of the obtained gallium nitride single crystal substrate is reduced compared to that of the base substrate, and a radius of curvature of (0001) is larger than that of the base substrate.

Claims

1. A gallium nitride single crystal substrate, which is a gallium nitride single crystal substrate having a diameter of 50 mm or more, with a low-index crystal plane closest to a main surface being (0001), and in which an average density of etch pits during etching applied to the main surface using an alkaline etching solution is less than 1×10.sup.6 cm.sup.−2; and in histograms of diameters of the etch pits in multiple different regions on the main surface, and among peaks appearing in the histograms, when a diameter of a first peak which is a smallest diameter is denoted as a, a diameter of a second peak which is a second smallest diameter is denoted as b, frequency of the first peak is denoted as A, frequency of the second peak is denoted as B, the number of the etch pits constituting the first peak is denoted as α, and the number of the etch pits constituting the second peak is denoted as β, at least one of the following conditions (1), (2), and (3) is satisfied: (1) variation in a/b values in the multiple histograms is within ±5% of an average value. (2) variation in A/B values in the multiple histograms is within ±15% of an average value. (3) variation in α/β values in the multiple histograms is within ±30% of an average value.
2. The gallium nitride single crystal substrate according to claim 1, which satisfies two of the conditions (1), (2), and (3).
3. The gallium nitride single crystal substrate according to claim 1, which satisfies all of the conditions (1), (2), and (3).
4. The gallium nitride single crystal substrate according to claim 1, wherein in the histogram, a total number of etch pits having a diameter exceeding 4 a is α/1000 or less.
5. The gallium nitride single crystal substrate according to claim 1, wherein a radius of curvature of (0001) is 60 m or more.
6. The gallium nitride single crystal substrate according to claim 1, wherein an average density of etch pits and the histogram are measured from a region having an area of 1 mm.sup.2 or more.
7. A method for producing a gallium nitride single crystal substrate, the method comprising the steps of: (a) preparing a base substrate composed of a gallium nitride single crystal having (0001) that is a low-index crystal plane closest to a main surface, and having a uniform dislocation density distribution in a plane; (b) epitaxially growing the gallium nitride single crystal on the main surface of the base substrate; and (c) obtaining a gallium nitride single crystal substrate having a diameter of 50 mm, from the gallium nitride single crystal epitaxially grown in the step (b), wherein in the step (b), the gallium nitride single crystal is epitaxially grown using only (0001) as a growth plane, without generating any inclined interface other than (0001) throughout an entire growth period; and the gallium nitride single crystal substrate obtained in the step (c) is used as a new base substrate, and the steps (b) and (c) are repeated at least once or more.