

DESCRIPTION

Title of Invention

SLURRY AND POLISHING METHOD

Technical Field

5 [0001] The present invention relates to a slurry and a polishing method.

Background Art

[0002] In the manufacturing steps for semiconductor elements of recent years, the importance of processing technologies for density increase and micronization is increasing more and more. CMP (Chemical
10 mechanical polishing) technology, which is one of the processing technologies, has become an essential technology for the formation of a shallow trench isolation (hereinafter, referred to as "STI"), flattening of a pre-metal insulating material or an interlayer insulating material, formation of a plug or an embedded metal wiring, and the like in the
15 manufacturing steps for semiconductor elements.

[0003] Regarding polishing liquids that are most commonly used, for example, silica-based polishing liquids containing silica (silicon oxide) particles such as fumed silica and colloidal silica as abrasive grains are mentioned. Silica-based polishing liquids have a feature of high
20 flexibility of use, and by appropriately selecting the content of abrasive grains, pH, additives, and the like, polishing of a wide variety of materials can be achieved regardless of whether the material is an insulating material or an electroconductive material.

[0004] Meanwhile, as a polishing liquid mainly used for insulating
25 materials such as silicon oxide, a demand for a polishing liquid containing cerium compound particles as abrasive grains is also

increasing. For example, a cerium oxide-based polishing liquid containing cerium oxide particles as abrasive grains can polish silicon oxide at a high rate even when the abrasive grain content is lower than that in the silica-based polishing liquid (for example, see Patent Literatures 1 and 2 described below).

[0005] In recent years, in the manufacturing steps for semiconductor elements, it is required to achieve further micronization of wiring, and polishing scratches generated at the time of polishing are becoming problematic. That is, when polishing is performed using a conventional cerium oxide-based polishing liquid, even if minute polishing scratches are generated, there has been no problem as long as the sizes of the polishing scratches are smaller than conventional wiring widths; however, in a case where it is directed to achieve further micronization of the wiring, even minute polishing scratches become problematic.

[0006] With regard to this problem, an investigation has been conducted on polishing liquids that use particles of cerium hydroxide (for example, see Patent Literatures 3 to 5 described below). Furthermore, methods for producing particles of cerium hydroxide have also been investigated (for example, see Patent Literatures 6 and 7 described below).

Citation List

Patent Literature

[0007] Patent Literature 1: Japanese Unexamined Patent Publication No. H10-106994

Patent Literature 2: Japanese Unexamined Patent Publication

No. H08-022970

Patent Literature 3: International Publication WO 2002/067309

Patent Literature 4: International Publication WO 2012/070541

Patent Literature 5: International Publication WO 2012/070542

5 Patent Literature 6: Japanese Unexamined Patent Publication
No. 2006-249129

Patent Literature 7: International Publication WO 2012/070544

Summary of Invention

Technical Problem

10 [0008] Incidentally, in recent years, 3D-NAND devices in which the
cell portions of a device are laminated in the longitudinal direction have
come to the fore. In the present technology, the level differences of the
insulating materials during cell formation are several times higher
compared to the conventional planar types. According to this, in order
15 to maintain the throughput of the device production, it is necessary to
rapidly resolve the high level differences as described above in a CMP
step or the like, and it is necessary to improve the polishing rate for an
insulating material.

[0009] The present invention is directed to solve the problems
20 described above, and an object of the present invention is to provide a
slurry capable of improving the polishing rate for an insulating material,
and a polishing method using the slurry.

Solution to Problem

[0010] A slurry of an aspect of the present invention is a slurry
25 containing abrasive grains and a liquid medium, in which the abrasive
grains include first particles and second particles in contact with the first

particles, a particle size of the second particles is smaller than a particle size of the first particles, the first particles contain cerium oxide, the second particles contain a cerium compound, and in a case where a content of the abrasive grains is 0.1% by mass, a BET specific surface area of a solid phase obtained when the slurry is subjected to centrifugal separation for 60 minutes at a centrifugal acceleration of 1.1×10^4 G is 40 m²/g or more.

[0011] According to such a slurry, it is possible to improve the polishing rate for an insulating material, and therefore, an insulating material can be polished at a high polishing rate.

[0012] A polishing method of another aspect of the present invention includes a step of polishing a surface to be polished by using the above-described slurry. According to such a polishing method, the above-described effects similar to those obtainable with the above-described slurry can be obtained by using the above-described slurry.

Advantageous Effects of Invention

[0013] According to the present invention, it is possible to provide a slurry capable of improving the polishing rate for an insulating material (for example, silicon oxide). According to the present invention, a polishing method using the above-described slurry can be provided.

[0014] According to the present invention, it is possible to provide use of a slurry in polishing of a surface to be polished containing silicon oxide. According to the present invention, it is possible to provide use of a slurry in a flattening step of a base substrate surface that is the manufacturing technology of semiconductor elements. According to

the present invention, it is possible to provide use of a slurry for a flattening step of an STI insulating material, a pre-metal insulating material, or an interlayer insulating material.

Description of Embodiments

5 [0015] Hereinafter, embodiments of the present invention will be described in detail. However, the present invention is not limited to the following embodiments.

[0016] <Definition>

10 In the present specification, a numerical range that has been indicated by use of "to" indicates the range that includes the numerical values which are described before and after "to", as the minimum value and the maximum value, respectively. In the numerical ranges that are described stepwise in the present specification, the upper limit value or the lower limit value of the numerical range of a certain stage can be

15 arbitrarily combined with the upper limit value or the lower limit value of the numerical range of another stage. In the numerical ranges that are described in the present specification, the upper limit value or the lower limit value of the numerical value range may be replaced with the value shown in the examples. "A or B" may include either one of A

20 and B, and may also include both of A and B. Materials listed as examples in the present specification can be used singly or in combinations of two or more, unless otherwise specifically indicated. In the present specification, when a plurality of substances corresponding to each component exist in the composition, the content

25 of each component in the composition means the total amount of the plurality of substances that exist in the composition, unless otherwise

specified. The term "step" includes not only an independent step but also a step by which an intended action of the step is achieved, though the step cannot be clearly distinguished from other steps.

[0017] As described later, a slurry of the present embodiment contains abrasive grains. The abrasive grains are also referred to as "abrasive particles"; however, in the present specification, the term "abrasive grains" is used. Abrasive grains are generally solid particles, and it is considered that at the time of polishing, an object to be removed is removed by the mechanical action (physical action) of the abrasive grains and the chemical action of the abrasive grains (mainly the surface of the abrasive grains); however, it is not limited to this. The polishing rate in the case of using the slurry of the present embodiment can be compared, for example, on the basis of a polishing rate obtained when the content of the abrasive grains (the total amount of particles) is adjusted to 0.1% by mass on the basis of the total mass of the slurry.

[0018] <Slurry>

The slurry of the present embodiment contains abrasive grains and a liquid medium as essential components. The slurry of the present embodiment can be used as, for example, a polishing liquid (CMP polishing liquid). In the present specification, the term "polishing liquid" (abrasive) is defined as a composition to be brought into contact with a surface to be polished, at the time of polishing. The term "polishing liquid" itself does not at all limit the components that are contained in the polishing liquid.

[0019] The abrasive grains include composite particles including first particles and second particles in contact with the first particles. The

particle size of the second particles is smaller than the particle size of the first particles. The first particles contain cerium oxide and the second particles contain a cerium compound. In a case where a content of the abrasive grains is 0.1% by mass, a BET specific surface area of a solid phase obtained when the slurry of the present embodiment is subjected to centrifugal separation for 60 minutes at a centrifugal acceleration of 1.1×10^4 G is 40 m²/g or more.

[0020] The polishing rate for an insulating material (for example, silicon oxide) can be improved by using the slurry of the present embodiment. According to such a slurry, even in a case where the content of the abrasive grains is small, a high polishing rate for an insulating material can be obtained. The reasons why the polishing rate for an insulating material is improved in this way are, for example, the reasons to be as follows. However, the reasons are not limited to the reasons to be as follows.

[0021] That is, polishing of an insulating material proceeds by the mechanical action and the chemical action between surfaces of the abrasive grains contributing to polishing and the surface of the insulating material.

The first particles containing cerium oxide and having a larger particle size than that of the second particles have strong mechanical action (mechanical property) with respect to an insulating material as compared to the second particles. On the other hand, the second particles containing a cerium compound and having a smaller particle size than that of the first particles have small mechanical action with respect to an insulating material as compared to the first particles, but

have strong chemical action (chemical property) with respect to an insulating material since the specific surface area (surface area per unit mass) in the whole particle is large. Therefore, a synergetic effect of improving the polishing rate is easily obtained by using the first particles having strong mechanical action and the second particles having strong chemical action.

Further, in the present embodiment, the BET specific surface area of the solid phase obtained by centrifugal separation is $40 \text{ m}^2/\text{g}$ or more. In this case, since the abrasive grains recovered as solid phases have a high specific surface area so that the aforementioned interaction between the abrasive grains and an insulating material is strong, the polishing rate is easily improved.

As described above, by using the slurry of the present embodiment, it is speculated that the polishing rate for an insulating material can be improved.

[0022] As the BET specific surface area of the solid phase, the BET specific surface area after drying the solid phase obtained by centrifugal separation of the slurry can be used. The BET specific surface area of the solid phase is preferably $41 \text{ m}^2/\text{g}$ or more from the viewpoint of easily improving the polishing rate for an insulating material. The BET specific surface area of the solid phase is preferably $70 \text{ m}^2/\text{g}$ or less, more preferably $60 \text{ m}^2/\text{g}$ or less, further preferably $50 \text{ m}^2/\text{g}$ or less, particularly preferably $45 \text{ m}^2/\text{g}$ or less, extremely preferably $43 \text{ m}^2/\text{g}$ or less, and highly preferably $42 \text{ m}^2/\text{g}$ or less, from the viewpoint of easily improving the polishing rate for an insulating material. From the above-described viewpoints, the BET specific surface area of the solid

phase is more preferably 40 to 70 m²/g.

[0023] The BET specific surface area of the solid phase can be measured utilizing a gas adsorption method, for example, by using a specific surface area/fine pore size analysis device (trade name: QUADRASORB evo) manufactured by Quantachrome Instruments under the following conditions. As the BET specific surface area of the solid phase, an average value of two measurements can be used.

Pretreatment: Vacuum deaeration (100°C, 2 hours)

Measurement method: Constant volume method

Adsorption gas: Nitrogen gas

Measurement temperature: 77.35 K (-195.8°C)

Measurement cell size: 1.5 cm³

Measurement item: A value of P/P₀ was changed in a range of 0 to 0.3 to measure several points

Analysis item: Specific surface area by BET multipoint method

Number of times of measurement: Changing a sample and performing measurement twice

[0024] A solid phase for measuring the BET specific surface area can be recovered from the slurry, for example, by centrifugal separation and vacuum drying under the following conditions.

[Centrifugal separation conditions]

Apparatus: Centrifugal separator (trade name: himac CR7) manufactured by Hitachi Koki Co., Ltd.

Separation condition: 60 minutes at centrifugal acceleration of 1.1×10⁴ G

[Vacuum drying conditions]

Apparatus: Vacuum dryer (trade name: Standard Type ADP200)
manufactured by Yamato Scientific Co., Ltd.

Drying condition: 24 hours at room temperature (25°C)

[0025] (Abrasive grains)

5 The abrasive grains of the slurry of the present embodiment
include composite particles including first particles and second particles
in contact with the first particles. The particle size of the second
particles is smaller than the particle size of the first particles. The
magnitude relationship in particle size between the first particles and the
10 second particles can be determined from SEM images of the composite
particles, or the like.

[0026] The particle size of the first particles is preferably in the
following range. The lower limit of the particle size of the first
particles is preferably 15 nm or more, more preferably 25 nm or more,
15 further preferably 35 nm or more, particularly preferably 40 nm or
more, extremely preferably 50 nm or more, highly preferably 80 nm or
more, and even more preferably 100 nm or more, from the viewpoint
that the polishing rate for an insulating material is further improved.
The upper limit of the particle size of the first particles is preferably
20 1000 nm or less, more preferably 800 nm or less, further preferably 600
nm or less, particularly preferably 400 nm or less, extremely preferably
300 nm or less, highly preferably 200 nm or less, and even more
preferably 150 nm or less, from the viewpoint of improving the
dispersibility of the abrasive grains and the viewpoint of easily
25 suppressing scratches at a polished surface. From the above-described
viewpoints, the particle size of the first particles is more preferably 15 to

1000 nm. The average particle size (average secondary particle size) of the first particles may be in the above ranges.

[0027] The particle size of the second particles is preferably in the following range. The lower limit of the particle size of the second particles is preferably 1 nm or more, more preferably 2 nm or more, and further preferably 3 nm or more, from the viewpoint that the polishing rate for an insulating material is further improved. The upper limit of the particle size of the second particles is preferably 50 nm or less, more preferably 30 nm or less, further preferably 25 nm or less, particularly preferably 20 nm or less, extremely preferably 15 nm or less, and highly preferably 10 nm or less, from the viewpoint of improving the dispersibility of the abrasive grains and the viewpoint of easily suppressing scratches at a polished surface. From the above-described viewpoints, the particle size of the second particles is more preferably 1 to 50 nm. The average particle size (average secondary particle size) of the second particles may be in the above ranges.

[0028] The average particle size (average secondary particle size) of the abrasive grains (the entire abrasive grains including composite particles) in the slurry is preferably in the following range. The lower limit of the average particle size of the abrasive grains is preferably 16 nm or more, more preferably 20 nm or more, further preferably 30 nm or more, particularly preferably 40 nm or more, extremely preferably 50 nm or more, highly preferably 100 nm or more, even more preferably 120 nm or more, and further preferably 140 nm or more, from the viewpoint that the polishing rate for an insulating material is further improved. The upper limit of the average particle size of the abrasive

grains is preferably 1050 nm or less, more preferably 1000 nm or less, further preferably 800 nm or less, particularly preferably 600 nm or less, extremely preferably 500 nm or less, highly preferably 400 nm or less, even more preferably 300 nm or less, further preferably 200 nm or less, particularly preferably 160 nm or less, and extremely preferably 155 nm or less, from the viewpoint of improving the dispersibility of the abrasive grains and the viewpoint of easily suppressing scratches at a polished surface. From the above-described viewpoints, the average particle size of the abrasive grains is more preferably 16 to 1050 nm.

[0029] The average particle size can be measured, for example, using a light diffraction scattering type particle size distribution meter (for example, trade name: N5 manufactured by Beckman Coulter, Inc. or trade name: MICROTRAC MT3300EXII manufactured by MicrotracBEL Corp.).

[0030] The first particles contain cerium oxide (for example, ceria) and the second particles contain a cerium compound. Examples of the cerium compound of the second particles include cerium hydroxide and cerium oxide. As the cerium compound of the second particles, a compound different from cerium oxide can be used. The cerium compound preferably contains cerium hydroxide. The abrasive grains containing cerium hydroxide have higher reactivity (chemical action) with an insulating material (for example, silicon oxide) by the action of the hydroxyl group than particles composed of silica, cerium oxide, or the like, and an insulating material can be polished at a higher polishing rate. The cerium hydroxide is, for example, a compound containing tetravalent cerium (Ce^{4+}) and at least one hydroxide ion (OH^-). The

cerium hydroxide may contain an anion (for example, nitrate ion NO_3^- and sulfate ion SO_4^{2-}) other than a hydroxide ion. For example, the cerium hydroxide may also contain an anion (for example, nitrate ion NO_3^- and sulfate ion SO_4^{2-}) bonded to tetravalent cerium.

5 [0031] The cerium hydroxide can be prepared by reacting a cerium salt with an alkali source (base). The cerium hydroxide is preferably prepared by mixing a cerium salt with an alkali liquid (for example, alkali aqueous solution). Thereby, it is possible to obtain particles having an extremely fine particle size, and easily obtain an excellent
10 effect of reducing polishing scratches. Such a technique is disclosed in, for example, Patent Literatures 6 and 7. The cerium hydroxide can be obtained by mixing a cerium salt solution (for example, a cerium salt aqueous solution) with alkali liquid. Examples of the cerium salt include $\text{Ce}(\text{NO}_3)_4$, $\text{Ce}(\text{SO}_4)_2$, $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$, and $\text{Ce}(\text{NH}_4)_4(\text{SO}_4)_4$.

15 [0032] It is considered that particles including $\text{Ce}(\text{OH})_a\text{X}_b$ (in the formula, $a + b \times c = 4$) composed of tetravalent cerium (Ce^{4+}), one to three hydroxide ions (OH^-), and one to three anions (X^c) are generated (incidentally, such particles are also "cerium hydroxide") depending on production conditions of cerium hydroxide and the like. It is
20 considered that, in $\text{Ce}(\text{OH})_a\text{X}_b$, an electron-withdrawing anion (X^c) acts to enhance reactivity of the hydroxide ion and the polishing rate is improved with the increase in abundance of $\text{Ce}(\text{OH})_a\text{X}_b$. Examples of the anions (X^c) include NO_3^- and SO_4^{2-} . It is considered that the particles containing cerium hydroxide can contain not only $\text{Ce}(\text{OH})_a\text{X}_b$
25 but also $\text{Ce}(\text{OH})_4$, CeO_2 , or the like.

[0033] The containing of $\text{Ce}(\text{OH})_a\text{X}_b$ in the particles containing cerium

hydroxide can be confirmed by a method for detecting a peak corresponding to the anions (X^-) with FT-IR ATR method (Fourier transform Infra Red Spectrometer Attenuated Total Reflection method) after washing the particles with pure water well. The existence of the anions (X^-) can also be confirmed by XPS method (X-ray Photoelectron Spectroscopy).

[0034] The composite particles including the first particles and the second particles can be obtained by bringing the first particles and the second particles into contact with each other using a homogenizer, a nanomizer, a ball mill, a bead mill, a sonicator, or the like; by bringing the first particles and the second particles each having opposing charges to each other into contact with each other; by bringing the first particles and the second particles into contact with each other in a state of a small content of the particles; or the like.

[0035] The lower limit of the content of cerium oxide in the first particles is preferably 50% by mass or more, more preferably 70% by mass or more, further preferably 90% by mass or more, and particularly preferably 95% by mass or more, on the basis of the entire first particles (the entire first particles contained in the slurry; the same applies hereinafter), from the viewpoint that the polishing rate for an insulating material is further improved. The first particles may be an embodiment substantially composed of cerium oxide (an embodiment in which substantially 100% by mass of the first particles are cerium oxide).

[0036] The lower limit of the content of the cerium compound in the second particles is preferably 50% by mass or more, more preferably

70% by mass or more, further preferably 90% by mass or more, and particularly preferably 95% by mass or more, on the basis of the entire second particles (the entire second particles contained in the slurry; the same applies hereinafter), from the viewpoint that the polishing rate for an insulating material is further improved. The second particles may be an embodiment substantially composed of a cerium compound (an embodiment in which substantially 100% by mass of the second particles are a cerium compound).

[0037] The content of the second particles can be estimated on the basis of a value of absorbance of equation below which is obtained by a spectrophotometer when light having a specific wavelength is transmitted through the slurry. That is, in a case where particles absorb light having a specific wavelength, the light transmittance of a region containing these particles is decreased. The light transmittance is decreased not only by absorption of the particles but also by scattering, but in the second particles, the influence of scattering is small. Therefore, in the present embodiment, the content of the second particles can be estimated on the basis of a value of absorbance calculated by equation below.

$$\text{Absorbance} = -\text{LOG}_{10}(\text{Light transmittance [\%]}/100)$$

[0038] The lower limit of the content of the first particles in the abrasive grains is preferably 50% by mass or more, more preferably more than 50% by mass, further preferably 60% by mass or more, particularly preferably 70% by mass or more, extremely preferably 75% by mass or more, and highly preferably 80% by mass or more, on the basis of the entire abrasive grains (the entire abrasive grains contained

in the slurry; the same applies hereinafter), from the viewpoint that the polishing rate for an insulating material is further improved. The upper limit of the content of the first particles in the abrasive grains is preferably 95% by mass or less, more preferably 93% by mass or less, further preferably 90% by mass or less, particularly preferably 88% by mass or less, extremely preferably 86% by mass or less, highly preferably 85% by mass or less, and even more preferably 82% by mass or less, on the basis of the entire abrasive grains, from the viewpoint that the polishing rate for an insulating material is further improved. From the above-described viewpoints, the content of the first particles in the abrasive grains is more preferably 50 to 95% by mass on the basis of the entire abrasive grains.

[0039] The lower limit of the content of the second particles in the abrasive grains is preferably 5% by mass or more, more preferably 7% by mass or more, further preferably 10% by mass or more, particularly preferably 12% by mass or more, extremely preferably 14% by mass or more, highly preferably 15% by mass or more, and even more preferably 18% by mass or more, on the basis of the entire abrasive grains (the entire abrasive grains contained in the slurry), from the viewpoint that the polishing rate for an insulating material is further improved. The upper limit of the content of the second particles in the abrasive grains is preferably 50% by mass or less, more preferably less than 50% by mass, further preferably 40% by mass or less, particularly preferably 30% by mass or less, extremely preferably 25% by mass or less, and highly preferably 20% by mass or less, on the basis of the entire abrasive grains, from the viewpoint that the polishing rate for an

insulating material is further improved. From the above-described viewpoints, the content of the second particles in the abrasive grains is more preferably 5 to 50% by mass on the basis of the entire abrasive grains.

5 [0040] The lower limit of the content of cerium oxide in the abrasive grains is preferably 50% by mass or more, more preferably more than 50% by mass, further preferably 60% by mass or more, particularly preferably 70% by mass or more, extremely preferably 75% by mass or more, and highly preferably 80% by mass or more, on the basis of the
10 entire abrasive grains (the entire abrasive grains contained in the slurry), from the viewpoint that the polishing rate for an insulating material is further improved. The upper limit of the content of cerium oxide in the abrasive grains is preferably 95% by mass or less, more preferably 93% by mass or less, further preferably 90% by mass or less,
15 particularly preferably 88% by mass or less, extremely preferably 86% by mass or less, highly preferably 85% by mass or less, and even more preferably 82% by mass or less, on the basis of the entire abrasive grains, from the viewpoint that the polishing rate for an insulating material is further improved. From the above-described viewpoints,
20 the content of cerium oxide in the abrasive grains is more preferably 50 to 95% by mass on the basis of the entire abrasive grains.

[0041] The lower limit of the content of cerium hydroxide in the abrasive grains is preferably 5% by mass or more, more preferably 7% by mass or more, further preferably 10% by mass or more, particularly
25 preferably 12% by mass or more, extremely preferably 14% by mass or more, highly preferably 15% by mass or more, and even more

preferably 18% by mass or more, on the basis of the entire abrasive grains (the entire abrasive grains contained in the slurry), from the viewpoint that the polishing rate for an insulating material is further improved. The upper limit of the content of cerium hydroxide in the abrasive grains is preferably 50% by mass or less, more preferably less than 50% by mass, further preferably 40% by mass or less, particularly preferably 30% by mass or less, extremely preferably 25% by mass or less, and highly preferably 20% by mass or less, on the basis of the entire abrasive grains, from the viewpoint that the polishing rate for an insulating material is further improved. From the above-described viewpoints, the content of cerium hydroxide in the abrasive grains is more preferably 5 to 50% by mass on the basis of the entire abrasive grains.

[0042] The lower limit of the content of the first particles is preferably 50% by mass or more, more preferably more than 50% by mass, further preferably 60% by mass or more, particularly preferably 70% by mass or more, extremely preferably 75% by mass or more, and highly preferably 80% by mass or more, on the basis of the total amount of the first particles and the second particles, from the viewpoint that the polishing rate for an insulating material is further improved. The upper limit of the content of the first particles is preferably 95% by mass or less, more preferably 93% by mass or less, further preferably 90% by mass or less, particularly preferably 88% by mass or less, extremely preferably 86% by mass or less, highly preferably 85% by mass or less, and even more preferably 82% by mass or less, on the basis of the total amount of the first particles and the second particles,

from the viewpoint that the polishing rate for an insulating material is further improved. From the above-described viewpoints, the content of the first particles is more preferably 50 to 95% by mass on the basis of the total amount of the first particles and the second particles.

5 [0043] The lower limit of the content of the second particles is preferably 5% by mass or more, more preferably 7% by mass or more, further preferably 10% by mass or more, particularly preferably 12% by mass or more, extremely preferably 14% by mass or more, highly preferably 15% by mass or more, and even more preferably 18% by
10 mass or more, on the basis of the total amount of the first particles and the second particles, from the viewpoint that the polishing rate for an insulating material is further improved. The upper limit of the content of the second particles is preferably 50% by mass or less, more preferably less than 50% by mass, further preferably 40% by mass or
15 less, particularly preferably 30% by mass or less, extremely preferably 25% by mass or less, and highly preferably 20% by mass or less, on the basis of the total amount of the first particles and the second particles, from the viewpoint that the polishing rate for an insulating material is further improved. From the above-described viewpoints, the content
20 of the second particles is more preferably 5 to 50% by mass on the basis of the total amount of the first particles and the second particles.

[0044] The lower limit of the content of the first particles in the slurry is preferably 0.005% by mass or more, more preferably 0.008% by mass or more, further preferably 0.01% by mass or more, particularly
25 preferably 0.05% by mass or more, extremely preferably 0.07% by mass or more, and highly preferably 0.08% by mass or more, on the basis of

the total mass of the slurry, from the viewpoint that the polishing rate for an insulating material is further improved. The upper limit of the content of the first particles in the slurry is preferably 5% by mass or less, more preferably 3% by mass or less, further preferably 1% by mass or less, particularly preferably 0.5% by mass or less, extremely preferably 0.3% by mass or less, highly preferably 0.2% by mass or less, and even more preferably 0.1% by mass or less, on the basis of the total mass of the slurry, from the viewpoint that the polishing rate for an insulating material is further improved and the viewpoint of enhancing the storage stability of the slurry. From the above-described viewpoints, the content of the first particles in the slurry is more preferably 0.005 to 5% by mass on the basis of the total mass of the slurry.

[0045] The lower limit of the content of the second particles in the slurry is preferably 0.005% by mass or more, more preferably 0.008% by mass or more, further preferably 0.01% by mass or more, particularly preferably 0.012% by mass or more, extremely preferably 0.015% by mass or more, highly preferably 0.018% by mass or more, and even more preferably 0.02% by mass or more, on the basis of the total mass of the slurry, from the viewpoint of further enhancing a chemical interaction between the abrasive grains and a surface to be polished so that the polishing rate for an insulating material is further improved. The upper limit of the content of the second particles in the slurry is preferably 5% by mass or less, more preferably 3% by mass or less, further preferably 1% by mass or less, particularly preferably 0.5% by mass or less, extremely preferably 0.1% by mass or less, highly

preferably 0.05% by mass or less, even more preferably 0.04% by mass or less, further preferably 0.035% by mass or less, and further preferably 0.03% by mass or less, on the basis of the total mass of the slurry, from the viewpoints of easily avoiding the aggregation of the abrasive grains, and easily obtaining a more favorable chemical interaction between the abrasive grains and a surface to be polished to easily utilize the properties of the abrasive grains effectively. From the above-described viewpoints, the content of the second particles in the slurry is more preferably 0.005 to 5% by mass on the basis of the total mass of the slurry.

[0046] The lower limit of the content of cerium oxide in the slurry is preferably 0.005% by mass or more, more preferably 0.008% by mass or more, further preferably 0.01% by mass or more, particularly preferably 0.05% by mass or more, extremely preferably 0.07% by mass or more, and highly preferably 0.08% by mass or more, on the basis of the total mass of the slurry, from the viewpoint that the polishing rate for an insulating material is further improved. The upper limit of the content of cerium oxide in the slurry is preferably 5% by mass or less, more preferably 3% by mass or less, further preferably 1% by mass or less, particularly preferably 0.5% by mass or less, extremely preferably 0.3% by mass or less, highly preferably 0.2% by mass or less, and even more preferably 0.1% by mass or less, on the basis of the total mass of the slurry, from the viewpoint that the polishing rate for an insulating material is further improved and the viewpoint of enhancing the storage stability of the slurry. From the above-described viewpoints, the content of cerium oxide in the slurry is more preferably 0.005 to 5% by

mass on the basis of the total mass of the slurry.

[0047] The lower limit of the content of cerium hydroxide in the slurry is preferably 0.005% by mass or more, more preferably 0.008% by mass or more, further preferably 0.01% by mass or more, particularly preferably 0.012% by mass or more, extremely preferably 0.015% by mass or more, highly preferably 0.018% by mass or more, and even more preferably 0.02% by mass or more, on the basis of the total mass of the slurry, from the viewpoint of further enhancing a chemical interaction between the abrasive grains and a surface to be polished so that the polishing rate for an insulating material is further improved. The upper limit of the content of cerium hydroxide in the slurry is preferably 5% by mass or less, more preferably 3% by mass or less, further preferably 1% by mass or less, particularly preferably 0.5% by mass or less, extremely preferably 0.1% by mass or less, highly preferably 0.05% by mass or less, even more preferably 0.04% by mass or less, further preferably 0.035% by mass or less, and further preferably 0.03% by mass or less, on the basis of the total mass of the slurry, from the viewpoints of easily avoiding the aggregation of the abrasive grains, and easily obtaining a more favorable chemical interaction between the abrasive grains and a surface to be polished to easily utilize the properties of the abrasive grains effectively. From the above-described viewpoints, the content of cerium hydroxide in the slurry is more preferably 0.005 to 5% by mass on the basis of the total mass of the slurry.

[0048] The lower limit of the content of the abrasive grains in the slurry is preferably 0.01% by mass or more, more preferably 0.05% by mass

or more, further preferably 0.08% by mass or more, and particularly preferably 0.1% by mass or more, on the basis of the total mass of the slurry, from the viewpoint that the polishing rate for an insulating material is further improved. The upper limit of the content of the abrasive grains in the slurry is preferably 10% by mass or less, more preferably 5% by mass or less, further preferably 1% by mass or less, particularly preferably 0.5% by mass or less, extremely preferably 0.1% by mass or less, highly preferably 0.2% by mass or less, even more preferably 0.15% by mass or less, further preferably 0.135% by mass or less, particularly preferably 0.13% by mass or less, and extremely preferably 0.12% by mass or less, on the basis of the total mass of the slurry, from the viewpoint of enhancing the storage stability of the slurry. From the above-described viewpoints, the content of the abrasive grains in the slurry is more preferably 0.01 to 10% by mass on the basis of the total mass of the slurry.

[0049] The first particles can have a negative zeta potential. The second particles can have a positive zeta potential. The zeta potential represents the surface potential of a particle. The zeta potential can be measured, for example, using a dynamic light scattering type zeta potential measuring apparatus (for example, trade name: DelsaNano C manufactured by Beckman Coulter, Inc.). The zeta potential of the particles can be adjusted using an additive. For example, by bringing monocarboxylic acid (for example, acetic acid) into contact with particles containing cerium oxide, particles having a positive zeta potential can be obtained. Furthermore, by bringing ammonium dihydrogen phosphate, a material having carboxyl group (for example,

polyacrylic acid) or the like into contact with particles containing cerium oxide, particles having a negative zeta potential can be obtained.

[0050] The slurry of the present embodiment may contain particles other than the composite particles including the first particles and the second particles. Examples of such other particles include the first particles not in contact with the second particles; the second particles not in contact with the first particles; and third particles composed of silica, alumina, zirconia, yttria, or the like (particles not including the first particles and the second particles).

[0051] (Liquid medium)

The liquid medium is not particularly limited; however, water such as deionized water or ultrapure water is preferred. The content of the liquid medium may be the balance of the slurry remaining after excluding the contents of other constituent components, and the content is not particularly limited.

[0052] (Optional components)

The slurry of the present embodiment may further contain optional additives for the purpose of adjusting the polishing characteristics, and the like. Examples of the optional additives include a material having a carboxyl group (excluding a compound corresponding to a polyoxyalkylene compound or a water-soluble polymer), a polyoxyalkylene compound, a water-soluble polymer, an oxidizing agent (for example, hydrogen peroxide), and a dispersant (for example, a phosphoric acid-based inorganic salt). The respective additives can be used singly or in combination of two or more kinds thereof.

[0053] Optional additives (a water-soluble polymer or the like) have an effect by which the dispersion stability of the abrasive grains in the slurry can be enhanced, and an insulating material (for example, silicon oxide) can be polished at a higher rate. Furthermore, since an insulating material (for example, silicon oxide) can be polished at a high rate, the level difference elimination property is improved, and high flattening properties can also be obtained. This is considered to be because the polishing rate for convex portions is improved to a large extent compared to concave portions.

[0054] Examples of the material having a carboxyl group include monocarboxylic acids such as acetic acid, propionic acid, butyric acid, and valeric acid; hydroxy acids such as lactic acid, malic acid, and citric acid; dicarboxylic acids such as malonic acid, succinic acid, fumaric acid, and maleic acid; polycarboxylic acids such as polyacrylic acid and polymaleic acid; and amino acids such as arginine, histidine, and lysine.

[0055] Examples of the polyoxyalkylene compound include a polyalkylene glycol and a polyoxyalkylene derivative.

[0056] Examples of the polyalkylene glycol include polyethylene glycol, polypropylene glycol, and polybutylene glycol. The polyalkylene glycol is preferably at least one selected from the group consisting of polyethylene glycol and polypropylene glycol, and is more preferably polyethylene glycol.

[0057] A polyoxyalkylene derivative is, for example, a compound obtained by introducing a functional group or a substituent to a polyalkylene glycol, or a compound obtained by adding a polyalkylene oxide to an organic compound. Examples of the functional group or a

substituent include an alkyl ether group, an alkyl phenyl ether group, a phenyl ether group, a styrenated phenyl ether group, a glyceryl ether group, an alkylamine group, a fatty acid ester group, and a glycol ester group. Examples of the polyoxyalkylene derivative include a polyoxyethylene alkyl ether, polyoxyethylene bisphenol ether (for example, manufactured by NIPPON NYUKAZAI CO., LTD., BA GLYCOL series), polyoxyethylene styrenated phenyl ether (for example, manufactured by Kao Corporation, EMULGEN series), a polyoxyethylene alkyl phenyl ether (for example, manufactured by DKS Co. Ltd., NOIGEN EA series), a polyoxyalkylene polyglyceryl ether (for example, manufactured by Sakamoto Yakuhin Kogyo Co., Ltd., SC-E series and SC-P series), a polyoxyethylene sorbitan fatty acid ester (for example, manufactured by DKS Co. Ltd., SORGEN TW series), a polyoxyethylene fatty acid ester (for example, manufactured by Kao Corporation, EMANON series), a polyoxyethylene alkylamine (for example, manufactured by DKS Co. Ltd., AMIRADIN D), and other compounds having a polyalkylene oxide added thereto (for example, manufactured by Nissin Chemical Co., Ltd., SURFINOL 465, and manufactured by NIPPON NYUKAZAI CO., LTD., TMP series).

[0058] A water-soluble polymer has an effect of adjusting the polishing characteristics such as the dispersion stability of the abrasive grains, flattening properties, in-plane uniformity, polishing selectivity for silicon oxide with respect to silicon nitride (polishing rate for silicon oxide/polishing rate for silicon nitride), and polishing selectivity for silicon oxide with respect to polysilicon (polishing rate for silicon oxide/polishing rate for polysilicon). Here, the "water-soluble

polymer" is defined as a polymer which is dissolved in 100 g of water in an amount of 0.1 g or more. A polymer that corresponds to the polyoxyalkylene compound is not to be included in the "water-soluble polymer".

5 [0059] The water-soluble polymer is not particularly limited, and examples include acrylic polymers such as polyacrylamide and polydimethylacrylamide; polysaccharides such as carboxymethyl cellulose, agar, curdlan, dextrin, cyclodextrin, and pullulan; vinyl-based polymers such as polyvinyl alcohol, polyvinylpyrrolidone, and
10 polyacrolein; glycerin-based polymers such as polyglycerin and a polyglycerin derivative; and polyethylene glycol.

[0060] In the case of using a water-soluble polymer, the lower limit of the content of the water-soluble polymer is preferably 0.001% by mass or more, more preferably 0.01% by mass or more, further preferably
15 0.1% by mass or more, particularly preferably 0.3% by mass or more, and extremely preferably 0.5% by mass or more, on the basis of the total mass of the slurry, from the viewpoint that an effect of adding a water-soluble polymer is obtained while sedimentation of the abrasive grains is suppressed. The upper limit of the content of the
20 water-soluble polymer is preferably 10% by mass or less, more preferably 8% by mass or less, further preferably 6% by mass or less, particularly preferably 5% by mass or less, extremely preferably 3% by mass or less, and highly preferably 1% by mass or less, on the basis of the total mass of the slurry, from the viewpoint that an effect of adding a
25 water-soluble polymer is obtained while sedimentation of the abrasive grains is suppressed.

[0061] (Characteristics of slurry)

In a case where the content of the abrasive grains is 0.1% by mass, the absorbance for light having a wavelength of 380 nm in the liquid phase (supernatant solution) obtained when the slurry of the present embodiment is subjected to centrifugal separation for 5 minutes at a centrifugal acceleration of 5.8×10^4 G preferably exceeds 0. Thereby, the polishing rate for an insulating material can be further improved. The reasons why the polishing rate for an insulating material is improved in this way are, for example, the reasons to be as follows. However, the reasons are not limited to the reasons to be as follows.

[0062] In the aforementioned centrifugal separation, the composite particles are easy to be selectively removed, a liquid phase containing, as solid contents, particles that are free (hereinafter, referred to as "free particles"; for example, second particles not in contact with the first particles) can be obtained, and in a case where the absorbance exceeds 0, the abrasive grains contain free particles in addition to the composite particles in the slurry. Since the free particles have a smaller particle size than that of the composite particles, the free particles have a high diffusion rate in the slurry and are preferentially adsorbed to a surface of an insulating material to coat the surface. In this case, as well as acting directly on the insulating material, the composite particles can act on the free particles adsorbed to the insulating material to act indirectly on the insulating material (for example, the mechanical action can be transferred to the insulating material through the free particles adsorbed to the insulating material). Thereby, the polishing rate for an insulating

material is improved.

[0063] In a case where the content of the abrasive grains is 0.1% by mass, the absorbance for light having a wavelength of 380 nm in the liquid phase obtained when the slurry of the present embodiment is subjected to centrifugal separation for 5 minutes at a centrifugal acceleration of 5.8×10^4 G is preferably in the following range. The absorbance is more preferably 0.001 or higher, further preferably 0.002 or higher, particularly preferably 0.003 or higher, extremely preferably 0.005 or higher, highly preferably 0.01 or higher, even more preferably 0.03 or higher, further preferably 0.05 or higher, particularly preferably 0.08 or higher, extremely preferably 0.09 or higher, highly preferably 0.1 or higher, and even more preferably 0.15 or higher, from the viewpoint that the polishing rate for an insulating material is further improved. In a case where the content of free particles in the slurry is large, it is speculated that the amount of adsorption of free particles with respect to the insulating material is increased, and thus the polishing rate for an insulating material is further improved. The absorbance is preferably 0.5 or less, more preferably 0.4 or less, further preferably 0.3 or less, particularly preferably 0.25 or less, and extremely preferably 0.2 or less, from the viewpoint that the polishing rate for an insulating material is further improved. From the above-described viewpoints, the absorbance is more preferably more than 0 and 0.5 or less. The above-described absorbance can be adjusted by adjusting the content of free particles in the abrasive grains. For example, the above-described absorbance can be decreased by increasing the surface area of the first particles with which the second particles are in contact, adjusting a state

to an insufficient dispersion state when the first particles and the second particles are brought into contact with each other (by decreasing a dispersion time, decreasing the number of rotations in stirring of a liquid containing the first particles and the second particles, weakening electrostatic repulsion generated between particles, or the like), and the like.

[0064] The light transmittance for light having a wavelength of 500 nm in a liquid phase obtained when the slurry of the present embodiment (for example, the slurry having a content of the abrasive grains of 0.1% by mass) is subjected to centrifugal separation for 5 minutes at a centrifugal acceleration of 5.8×10^4 G is preferably 50%/cm or more, more preferably 60%/cm or more, further preferably 70%/cm or more, particularly preferably 80%/cm or more, extremely preferably 90%/cm or more, and highly preferably 92%/cm or more, from the viewpoint that the polishing rate for an insulating material is further improved. The upper limit of the light transmittance is 100%/cm.

[0065] The lower limit of the pH of the slurry of the present embodiment is preferably 2.0 or more, more preferably 2.5 or more, further preferably 2.8 or more, particularly preferably 3.0 or more, extremely preferably 3.2 or more, highly preferably 3.5 or more, even more preferably 4.0 or more, further preferably 4.2 or more, and particularly preferably 4.3 or more, from the viewpoint that the polishing rate for an insulating material is further improved. The upper limit of the pH is preferably 7.0 or less, more preferably 6.5 or less, further preferably 6.0 or less, particularly preferably 5.0 or less, extremely preferably 4.8 or less, highly preferably 4.7 or less, even

more preferably 4.6 or less, further preferably 4.5 or less, and particularly preferably 4.4 or less, from the viewpoint that the storage stability of the slurry is further improved. From the above-described viewpoints, the pH is more preferably 2.0 to 7.0. The pH of the slurry is defined as the pH at a liquid temperature of 25°C.

[0066] The pH of the slurry can be adjusted by means of an acid component such as an inorganic acid or an organic acid; an alkali component such as ammonia, sodium hydroxide, tetramethylammonium hydroxide (TMAH), imidazole, or an alkanolamine; or the like. A buffering agent may be added in order to stabilize the pH. A buffering agent may be added as a buffer solution (a liquid containing a buffering agent). Examples of such a buffer solution include an acetate buffer solution and a phthalate buffer solution.

[0067] The pH of the slurry of the present embodiment can be measured by a pH meter (for example, Model No. PHL-40 manufactured by DKK-TOA CORPORATION). Specifically, for example, a pH meter is subjected to two-point calibration using a phthalate pH buffer solution (pH: 4.01) and a neutral phosphate pH buffer solution (pH: 6.86) as standard buffer solutions, subsequently the electrode of the pH meter is introduced into the slurry, and the value after being stabilized after a lapse of two minutes or longer is measured. The liquid temperatures of the standard buffer solutions and the slurry are all set to 25°C.

[0068] In a case where the slurry of the present embodiment is used as a CMP polishing liquid, the constituent components of the polishing liquid may be stored as a one-pack polishing liquid, or may be stored as

a multi-pack (for example, two-pack) polishing liquid set in which the constituent components of the polishing liquid are divided into a slurry and an additive liquid such that a slurry (first liquid) containing abrasive grains and a liquid medium, and an additive liquid (second liquid) containing additives and a liquid medium are mixed to form the polishing liquid. The additive liquid may contain, for example, an oxidizing agent. The constituent components of the polishing liquid may be stored as a polishing liquid set divided into three or more liquids.

[0069] In the polishing liquid set, the slurry and the additive liquid are mixed immediately before polishing or during polishing to prepare the polishing liquid. Furthermore, a one-pack polishing liquid may be stored as a stock solution for a polishing liquid with a reduced liquid medium content and used by dilution with a liquid medium at the time of polishing. A multi-pack polishing liquid set may be stored as a stock solution for a slurry and a stock solution for an additive liquid with reduced liquid medium contents, and used by dilution with a liquid medium at the time of polishing.

[0070] <Polishing method>

The polishing method of the present embodiment (such as a polishing method of a base substrate) includes a polishing step of polishing a surface to be polished (such as a surface to be polished of a base substrate) by using the slurry. The slurry in the polishing step may be a polishing liquid obtained by mixing the slurry and the additive liquid of the above-described polishing liquid set.

[0071] In the polishing step, for example, in a state where a material to

be polished of the base substrate that has the material to be polished is pressed against a polishing pad (polishing cloth) of a polishing platen, the slurry is supplied between the material to be polished and the polishing pad, and the base substrate and the polishing platen are moved relative to each other to polish the surface to be polished of the material to be polished. In the polishing step, for example, at least a part of a material to be polished is removed by polishing.

[0072] As the base substrate that is to be polished, a substrate to be polished or the like is exemplified. As the substrate to be polished, for example, a base substrate in which a material to be polished is formed on a substrate for semiconductor element production (for example, a semiconductor substrate in which an STI pattern, a gate pattern, a wiring pattern, or the like is formed) is exemplified. Examples of the material to be polished include an insulating material such as silicon oxide. The material to be polished may be a single material or a plurality of materials. In a case where a plurality of materials are exposed on a surface to be polished, they can be considered as a material to be polished. The material to be polished may be in the form of a film (film to be polished) or may be an insulating film such as a silicon oxide film.

[0073] By polishing a material to be polished (for example, an insulating material such as silicon oxide) formed on such a substrate with the slurry and removing an excess part, it is possible to eliminate irregularities on the surface of a material to be polished and to produce a smooth surface over the entire surface of the polished material.

[0074] In the polishing method of the present embodiment, as a

polishing apparatus, it is possible to use a common polishing apparatus which has a holder capable of holding a base substrate having a surface to be polished and a polishing platen to which a polishing pad can be pasted. A motor or the like in which the number of rotations can be changed is attached to each of the holder and the polishing platen. As the polishing apparatus, for example, polishing apparatus: F-REX300 manufactured by EBARA CORPORATION, or polishing apparatus: MIRRA manufactured by Applied Materials, Inc. can be used.

[0075] As the polishing pad, common unwoven cloth, a foamed body, an unfoamed body, and the like can be used. As the material for the polishing pad, it is possible to use a resin such as polyurethane, an acrylic resin, polyester, an acrylic-ester copolymer, polytetrafluoroethylene, polypropylene, polyethylene, poly-4-methylpentene, cellulose, cellulose ester, polyamide (for example, Nylon (trade name) and aramid), polyimide, polyimidamide, a polysiloxane copolymer, an oxirane compound, a phenolic resin, polystyrene, polycarbonate, or an epoxy resin. Particularly, from the viewpoint of obtaining further excellent polishing rate and flattening properties, the material for the polishing pad is preferably at least one selected from the group consisting of a foamed polyurethane and a non-foamed polyurethane. It is preferable that the polishing pad is subjected to groove processing, by which the slurry accumulates thereon.

[0076] Polishing conditions are not limited, but the upper limit of the rotation speed of a polishing platen is preferably 200 min^{-1} ($\text{min}^{-1} = \text{rpm}$) or less such that the base substrate is not let out, and the upper

limit of the polishing pressure to be applied to the base substrate (processing load) is preferably 100 kPa or less from the viewpoint of easily suppressing the generation of polishing scratches. The slurry is preferably continuously supplied to the polishing pad with a pump or the like during polishing. There are no limitations on the supply amount for this, however, it is preferable that the surface of the polishing pad is always covered with the slurry.

[0077] The slurry and the polishing method of the present embodiment are preferably used for polishing a surface to be polished containing silicon oxide. The slurry and the polishing method of the present embodiment can be suitably used in formation of an STI and polishing of an interlayer insulating material at a high rate. The lower limit of the polishing rate for an insulating material (for example, silicon oxide) is preferably 360 nm/min or more, more preferably 400 nm/min or more, further preferably 450 nm/min or more, and particularly preferably 500 nm/min or more.

[0078] The present embodiment can also be used in polishing of a pre-metal insulating material. Examples of the pre-metal insulating material include silicon oxide, phosphorus-silicate glass, boron-phosphorus-silicate glass, silicon oxyfluoride, and fluorinated amorphous carbon.

[0079] The present embodiment can also be applied to materials other than the insulating material such as silicon oxide. Examples of such a material include high permittivity materials such as Hf-based, Ti-based, and Ta-based oxides; semiconductor materials such as silicon, amorphous silicon, SiC, SiGe, Ge, GaN, GaP, GaAs, and organic

semiconductors; phase-change materials such as GeSbTe; inorganic electroconductive materials such as ITO; and polymer resin materials such as polyimide-based, polybenzoxazole-based, acrylic, epoxy-based, and phenol-based materials.

5 [0080] The present embodiment can be applied not only to film-like objects to be polished, but also to various types of substrates made of glass, silicon, SiC, SiGe, Ge, GaN, GaP, GaAs, sapphire, plastics, or the like.

10 [0081] The present embodiment can be used not only for the production of semiconductor elements, but also for the production of image display devices such as TFT or organic EL; optical components such as a photomask, a lens, a prism, an optical fiber, or a single crystal scintillator; optical elements such as an optical switching element or an optical waveguide; light-emitting elements such as a solid laser or a
15 blue laser LED; and magnetic storage devices such as a magnetic disc or a magnetic head.

[0082] According to the present embodiment, it is possible to provide a method for producing abrasive grains, the method including a step of bringing first particles containing cerium oxide into contact with second
20 particles containing a cerium compound. According to the present embodiment, it is possible to provide a method for producing a slurry, the method including a step of obtaining abrasive grains by the method for producing abrasive grains.

Examples

25 [0083] Hereinafter, the present invention will be specifically described based on Examples; however, the present invention is not limited to the

following Examples.

[0084] <Preparation of cerium oxide slurry>

Particles containing cerium oxide (first particles; hereinafter, referred to as "cerium oxide particles") and trade name: ammonium dihydrogen phosphate manufactured by Wako Pure Chemical Industries, Ltd. (molecular weight: 97.99) were mixed to prepare a cerium oxide slurry (pH: 7) containing 5.0% by mass (solid content amount) of the cerium oxide particles. The mixing amount of the ammonium dihydrogen phosphate was adjusted to 1% by mass on the basis of the total amount of the cerium oxide particles.

[0085] An adequate amount of the cerium oxide slurry was introduced into trade name: MICROTRAC MT3300EXII manufactured by MicrotracBEL Corp., and the average particle size of the cerium oxide particles was measured. The displayed average particle size value was obtained as the average particle size (average secondary particle size). The average particle size of the cerium oxide particles in the cerium oxide slurry was 145 nm.

[0086] An adequate amount of the cerium oxide slurry was introduced into trade name: DelsaNano C manufactured by Beckman Coulter, Inc. and measurement was performed twice at 25°C. The average value of the displayed zeta potentials was obtained as the zeta potential. The zeta potential of the cerium oxide particles in the cerium oxide slurry was -55 mV.

[0087] <Preparation of cerium hydroxide slurry>

(Synthesis of cerium hydroxide)

480 g of an aqueous 50% by mass $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ solution

(trade name: CAN50 liquid manufactured by Nihon Kagaku Sangyo Co., Ltd.) was mixed with 7450 g of pure water to obtain a solution. Next, while this solution was stirred, 750 g of an aqueous solution of imidazole (10% by mass aqueous solution, 1.47 mol/L) was added dropwise thereto at a mixing rate of 5 mL/min, and thereby a precipitate containing cerium hydroxide was obtained. The cerium hydroxide was synthesized at a temperature of 20°C and a stirring speed of 500 min⁻¹. The stirring was performed using a 3-blade pitch paddle with a total blade section length of 5 cm.

[0088] The obtained precipitate (precipitate containing cerium hydroxide) was subjected to centrifugal separation (4000 min⁻¹, for 5 minutes), and then subjected to solid-liquid separation with removal of a liquid phase by decantation. 10 g of the particles obtained by solid-liquid separation were mixed with 990 g of water, and then the particles were dispersed in water using an ultrasonic cleaner, thereby preparing a cerium hydroxide slurry (content of particles: 1.0% by mass) containing particles that contained cerium hydroxide (second particles; hereinafter, referred to as "cerium hydroxide particles").

[0089] (Measurement of average particle size)

When the average particle size (average secondary particle size) of the cerium hydroxide particles in the cerium hydroxide slurry was measured using trade name: N5 manufactured by Beckman Coulter, Inc., a value of 10 nm was obtained. The measuring method was as follows. First, about 1 mL of a measuring sample (cerium hydroxide slurry, aqueous dispersion liquid) containing 1.0% by mass of cerium hydroxide particles was introduced into a 1-cm square cell, and then the

cell was placed in the N5. Measurement was performed at 25°C with the refractive index set to 1.333 and the viscosity set to 0.887 mPa·s as the measuring sample information of N5 software, and the value displayed as Unimodal Size Mean was read off.

5 [0090] (Measurement of zeta potential)

An adequate amount of the cerium hydroxide slurry was introduced into trade name: DelsaNano C manufactured by Beckman Coulter, Inc. and measurement was performed twice at 25°C. The average value of the displayed zeta potentials was obtained as the zeta potential. The zeta potential of the cerium hydroxide particles in the cerium hydroxide slurry was +50 mV.

[0091] (Structural analysis of cerium hydroxide particles)

An adequate amount of the cerium hydroxide slurry was taken and vacuum-dried to isolate the cerium hydroxide particles, and then, sufficiently washed with pure water to obtain a sample. When the obtained sample was measured by FT-IR ATR method, a peak based on nitrate ion (NO_3^-) was observed in addition to a peak based on hydroxide ion (OH^-). Furthermore, when the same sample was measured by XPS (N-XPS) for nitrogen, a peak based on nitrate ion was observed while no peak based on NH_4^+ was observed. These results confirmed that the cerium hydroxide particles at least partially contained particles having nitrate ion bonded to a cerium element. Furthermore, since particles having hydroxide ion bonded to a cerium element were at least partially contained in the cerium hydroxide particles, it was confirmed that the cerium hydroxide particles contained cerium hydroxide. These results confirmed that the cerium hydroxide

contained a hydroxide ion bonded to a cerium element.

[0092] <Preparation of slurry>

(Example 1)

While stirring at a rotation speed of 300 rpm using a stirring
5 blade of two blades, 30 g of the cerium hydroxide slurry and 1930 g of
ion-exchange water were mixed to obtain a mixed liquid.
Subsequently, after mixing 40 g of the cerium oxide slurry in the mixed
liquid while stirring the mixed liquid, stirring was performed while
being irradiated with ultrasonic waves using an ultrasonic cleaner
10 (device name: US-105) manufactured by SND Co., Ltd. Thereby, a
test slurry containing composite particles including cerium oxide
particles and cerium hydroxide particles that were in contact with the
cerium oxide particles (content of cerium oxide particles: 0.1% by mass,
content of cerium hydroxide particles: 0.015% by mass, pH: 3.9,
15 average particle size of the abrasive grains: 155 nm) was prepared.

[0093] (Example 2)

While stirring at a rotation speed of 300 rpm using a stirring
blade of two blades, 35 g of the cerium hydroxide slurry and 1925 g of
ion-exchange water were mixed to obtain a mixed liquid.
20 Subsequently, after mixing 40 g of the cerium oxide slurry in the mixed
liquid while stirring the mixed liquid, stirring was performed while
being irradiated with ultrasonic waves using an ultrasonic cleaner
(device name: US-105) manufactured by SND Co., Ltd. Thereby, a
test slurry containing composite particles including cerium oxide
25 particles and cerium hydroxide particles that were in contact with the
cerium oxide particles (content of cerium oxide particles: 0.1% by mass,

content of cerium hydroxide particles: 0.0175% by mass, pH: 4.0, average particle size of the abrasive grains: 155 nm) was prepared.

[0094] (Example 3)

While stirring at a rotation speed of 300 rpm using a stirring
5 blade of two blades, 40 g of the cerium hydroxide slurry and 1920 g of
ion-exchange water were mixed to obtain a mixed liquid.
Subsequently, after mixing 40 g of the cerium oxide slurry in the mixed
liquid while stirring the mixed liquid, stirring was performed while
being irradiated with ultrasonic waves using an ultrasonic cleaner
10 (device name: US-105) manufactured by SND Co., Ltd. Thereby, a
test slurry containing composite particles including cerium oxide
particles and cerium hydroxide particles that were in contact with the
cerium oxide particles (content of cerium oxide particles: 0.1% by mass,
content of cerium hydroxide particles: 0.02% by mass, pH: 4.1, average
15 particle size of the abrasive grains: 155 nm) was prepared.

[0095] (Example 4)

While stirring at a rotation speed of 300 rpm using a stirring
blade of two blades, 50 g of the cerium hydroxide slurry and 1910 g of
ion-exchange water were mixed to obtain a mixed liquid.
20 Subsequently, after mixing 40 g of the cerium oxide slurry in the mixed
liquid while stirring the mixed liquid, stirring was performed while
being irradiated with ultrasonic waves using an ultrasonic cleaner
(device name: US-105) manufactured by SND Co., Ltd. Thereby, a
test slurry containing composite particles including cerium oxide
25 particles and cerium hydroxide particles that were in contact with the
cerium oxide particles (content of cerium oxide particles: 0.1% by mass,

content of cerium hydroxide particles: 0.025% by mass, pH: 4.3, average particle size of the abrasive grains: 155 nm) was prepared.

[0096] (Example 5)

While stirring at a rotation speed of 300 rpm using a stirring
5 blade of two blades, 70 g of the cerium hydroxide slurry and 1890 g of ion-exchange water were mixed to obtain a mixed liquid. Subsequently, after mixing 40 g of the cerium oxide slurry in the mixed liquid while stirring the mixed liquid, stirring was performed while being irradiated with ultrasonic waves using an ultrasonic cleaner
10 (device name: US-105) manufactured by SND Co., Ltd. Thereby, a test slurry containing composite particles including cerium oxide particles and cerium hydroxide particles that were in contact with the cerium oxide particles (content of cerium oxide particles: 0.1% by mass, content of cerium hydroxide particles: 0.035% by mass, pH: 4.5,
15 average particle size of the abrasive grains: 155 nm) was prepared.

[0097] (Example 6)

20 g of the cerium hydroxide slurry, 60 g of ion-exchange water, and 20 g of the cerium oxide slurry were sequentially added to a 1-mm-diameter cylindrical container containing zirconia beads to obtain
20 a mixed liquid. Subsequently, the mixed liquid was placed on a mixer rotor manufactured by AS ONE CORPORATION (device name: MR-5) and stirred at 100 rpm. Thereafter, 900 g of ion-exchange water was added and then stirred. Thereby, a test slurry containing composite particles including cerium oxide particles and cerium hydroxide
25 particles that were in contact with the cerium oxide particles (content of cerium oxide particles: 0.1% by mass, content of cerium hydroxide

particles: 0.02% by mass, pH: 4.1, average particle size of the abrasive grains: 155 nm) was prepared.

[0098] (Example 7)

25 g of the cerium hydroxide slurry, 55 g of ion-exchange water,
5 and 20 g of the cerium oxide slurry were sequentially added to a 1-mm-diameter cylindrical container containing zirconia beads to obtain a mixed liquid. Subsequently, the mixed liquid was placed on a mix rotor manufactured by AS ONE CORPORATION (device name: MR-5) and stirred at 100 rpm. Thereafter, 900 g of ion-exchange water was
10 added and then stirred. Thereby, a test slurry containing composite particles including cerium oxide particles and cerium hydroxide particles that were in contact with the cerium oxide particles (content of cerium oxide particles: 0.1% by mass, content of cerium hydroxide particles: 0.025% by mass, pH: 4.3, average particle size of the abrasive
15 grains: 155 nm) was prepared.

[0099] (Example 8)

30 g of the cerium hydroxide slurry, 50 g of ion-exchange water, and 20 g of the cerium oxide slurry were sequentially added to a 1-mm-diameter cylindrical container containing zirconia beads to obtain
20 a mixed liquid. Subsequently, the mixed liquid was placed on a mix rotor manufactured by AS ONE CORPORATION (device name: MR-5) and stirred at 100 rpm. Thereafter, 900 g of ion-exchange water was added and then stirred. Thereby, a test slurry containing composite particles including cerium oxide particles and cerium hydroxide
25 particles that were in contact with the cerium oxide particles (content of cerium oxide particles: 0.1% by mass, content of cerium hydroxide

particles: 0.035% by mass, pH: 4.4, average particle size of the abrasive grains: 155 nm) was prepared.

[0100] (Comparative Example 1)

While stirring at a rotation speed of 300 rpm using a stirring blade of two blades, 20 g of the cerium hydroxide slurry and 1940 g of ion-exchange water were mixed to obtain a mixed liquid. Subsequently, after mixing 40 g of the cerium oxide slurry in the mixed liquid while stirring the mixed liquid, stirring was performed while being irradiated with ultrasonic waves using an ultrasonic cleaner (device name: US-105) manufactured by SND Co., Ltd. Thereby, a test slurry containing composite particles including cerium oxide particles and cerium hydroxide particles that were in contact with the cerium oxide particles (content of cerium oxide particles: 0.1% by mass, content of cerium hydroxide particles: 0.01% by mass, pH: 4.1, average particle size of the abrasive grains: 220 nm) was prepared.

[0101] (Comparative Example 2)

After mixing 40 g of the cerium oxide slurry and 1960 g of ion-exchange water while stirring the mixed liquid at a rotation speed of 300 rpm using a stirring blade of two blades, stirring was performed while being irradiated with ultrasonic waves using an ultrasonic cleaner (device name: US-105) manufactured by SND Co., Ltd. Thereby, a test slurry containing cerium oxide particles (content of cerium oxide particles: 0.1% by mass, pH: 7.0, average particle size of the abrasive grains: 145 nm) was prepared.

[0102] (Comparative Example 3)

After mixing 200 g of the cerium hydroxide slurry and 1800 g of

ion-exchange water while stirring the mixed liquid at a rotation speed of 300 rpm using a stirring blade of two blades, stirring was performed while being irradiated with ultrasonic waves using an ultrasonic cleaner (device name: US-105) manufactured by SND Co., Ltd. Thereby, a test slurry containing cerium hydroxide particles (content of cerium hydroxide particles: 0.1% by mass, pH: 4.0, average particle size of the abrasive grains: 10 nm) was prepared.

[0103] <Measurement of pH of test slurry>

The aforementioned pH of each test slurry was measured using Model No. PHL-40 manufactured by DKK-TOA CORPORATION.

[0104] <Measurement of average particle size of abrasive grains>

Each test slurry mentioned above was introduced in an adequate amount into trade name: MICROTRAC MT3300EXII manufactured by MicrotracBEL Corp., measurement was then performed, and thereby the aforementioned average particle size of the abrasive grains was obtained. The displayed average particle size value was obtained as the average particle size (average secondary particle size) of the abrasive grains.

[0105] <Measurement of absorbance and light transmittance of supernatant solution>

The content of the abrasive grains (the total amount of particles) in the test slurry was adjusted to 0.1% by mass (diluted with ion-exchange water) to prepare a test liquid. 7.5 g of the test liquid was introduced in a centrifugal separator (trade name: Optima MAX-TL) manufactured by Beckman Coulter, Inc. and treated at a centrifugal acceleration of 5.8×10^4 G (58148 G) and at a setting

temperature of 25°C for 5 minutes to obtain a supernatant solution.

[0106] About 4 mL of the supernatant solution was introduced into a 1-cm square cell made of quartz, and then, the cell was placed in a spectrophotometer (device name: U3310) manufactured by Hitachi, Ltd.

5 Measurement of the absorbance was performed in a wavelength range of 200 to 600 nm, and a value of the absorbance in a wavelength of 380 nm was read from a chart thus obtained. The measurement results are shown in Table 1. Further, as for Examples 1 to 8, a value of the light transmittance in a wavelength of 500 nm was read from the chart thus
10 obtained, and as a result, the value was 92%/cm or more.

[0107] <BET specific surface area measurement>

The content of the abrasive grains (the total amount of particles) in the test slurry was adjusted to 0.1% by mass (diluted with ion-exchange water) to prepare a test liquid. Each test liquid was
15 subjected to centrifugal separation under the following conditions to obtain precipitate, and then the precipitate was vacuum-dried under the following conditions to recover a solid phase for measuring a BET specific surface area.

[Centrifugal separation conditions]

20 Apparatus: Centrifugal separator (trade name: himac CR7) manufactured by Hitachi Koki Co., Ltd.

Separation condition: 60 minutes at centrifugal acceleration of 1.1×10^4 G

[Vacuum drying conditions]

25 Apparatus: Vacuum dryer (trade name: Standard Type ADP200) manufactured by Yamato Scientific Co., Ltd.

Drying condition: 24 hours at room temperature

[0108] The BET specific surface area of the solid phase was measured by using a specific surface area/fine pore size analysis device (trade name: QUADRASORB evo) manufactured by Quantachrome Instruments under the following conditions. An average value of two measurements was obtained as the BET specific surface area of the solid phase. The measurement results are shown in Table 1.

Pretreatment: Vacuum deaeration (100°C, 2 hours)

Measurement method: Constant volume method

Adsorption gas: Nitrogen gas

Measurement temperature: 77.35 K (-195.8°C)

Measurement cell size: 1.5 cm³

Measurement item: Several points at the adsorption side in P/P_0 = 0 to 0.3

Analysis item: Specific surface area by BET multipoint method

Number of times of measurement: Changing a sample and performing measurement twice

[0109] <CMP evaluation>

The content of the abrasive grains (the total amount of particles) in the test slurry was adjusted to 0.1% by mass (diluted with ion-exchange water) to prepare a CMP polishing liquid. The substrate to be polished was polished by using this CMP polishing liquid under the polishing conditions below. Values of the pH in the CMP polishing liquid and the average particle size of the abrasive grains were the same as the values in the test slurry mentioned above.

[CMP polishing conditions]

Polishing apparatus: MIRRA (manufactured by Applied Materials, Inc.)

Flow rate of CMP polishing liquid: 200 mL/min

5 Substrate to be polished: As a blanket wafer having no pattern formed thereon, a substrate to be polished having a silicon oxide film (TEOS film) having a thickness of 2 μm , which had been formed by a plasma CVD method, on a silicon substrate was used.

Polishing pad: Foamed polyurethane resin having closed pores (manufactured by Dow Chemical Japan Ltd., Product No.: IC1010)

10 Polishing pressure: 13 kPa (2.0 psi)

Rotation numbers of substrate to be polished and polishing platen: Substrate to be polished/polishing platen = 93/87 rpm

Polishing time: 1 minute (60 seconds)

15 Washing of wafer: After a CMP treatment, washing was performed with water while applying an ultrasonic wave, and then drying was performed with a spin dryer.

[0110] The polishing rate for a silicon oxide film (SiO_2RR) that had been polished and washed under the above-described conditions was obtained by the formula below. The results are shown in Table 1.

20 The film thickness difference of the silicon oxide film before and after polishing was obtained using a light interference type film thickness measuring apparatus (trade name: F80 manufactured by Filmetrics Japan, Inc.).

25 Polishing rate (RR) = (Film thickness difference [nm] of silicon oxide film before and after polishing)/(Polishing time: 1 [min])

[0111] [Table 1]

	Example								Comparative Example		
	1	2	3	4	5	6	7	8	1	2	3
BET specific surface area [m ² /g]	43	42	40	41	40	40	41	42	39	19	199
Absorbance at 380 nm of supernatant solution	0.068	0.083	0.093	0.164	0.239	0.108	0.183	0.205	0.002	0	0.99
Polishing rate for silicon oxide [nm/min]	401	450	456	548	530	460	532	527	355	245	28

CLAIMS

1. A slurry comprising abrasive grains and a liquid medium,
wherein

the abrasive grains include first particles and second particles in
5 contact with the first particles,

a particle size of the second particles is smaller than a particle
size of the first particles,

the first particles contain cerium oxide,

the second particles contain a cerium compound, and

10 in a case where a content of the abrasive grains is 0.1% by mass,
a BET specific surface area of a solid phase obtained when the slurry is
subjected to centrifugal separation for 60 minutes at a centrifugal
acceleration of 1.1×10^4 G is $40 \text{ m}^2/\text{g}$ or more.

2. The slurry according to claim 1, wherein, in a case where a
15 content of the abrasive grains is 0.1% by mass, an absorbance for light
having a wavelength of 380 nm in a liquid phase obtained when the
slurry is subjected to centrifugal separation for 5 minutes at a centrifugal
acceleration of 5.8×10^4 G exceeds 0.

3. The slurry according to claim 1 or 2, wherein the cerium
20 compound contains cerium hydroxide.

4. The slurry according to any one of claims 1 to 3, wherein a
content of the abrasive grains is 0.01 to 10% by mass.

5. The slurry according to any one of claims 1 to 4, wherein the
slurry is used for polishing a surface to be polished containing silicon
25 oxide.

6. A polishing method comprising a step of polishing a surface to

be polished by using the slurry according to any one of claims 1 to 5.