DESCRIPTION

POLISHING SOLUTION COMPOSITION FOR SILICON OXIDE FILM POLISHING

Technical Field

[0001] The present invention relates to a silicon oxide film polishing composition, a method for manufacturing a semiconductor substrate using the same, a method for polishing a semiconductor substrate using the same, and the use of the silicon oxide film polishing composition for polishing a silicon oxide film on a polysilicon film.

Background Art

[0002] Recently, in the production methods of semiconductor substrates, a shallow trench isolation process (hereinafter, referred to as an STI process) is adopted to electrically separate semiconductor elements such as DRAM and a flash memory element. Such an STI process includes: forming a trench in a substrate to be polished that includes a silicon substrate and a polishing stop layer, by etching or photolithography; filling the trench with an insulating material such as silicon oxide; and removing a step height created by an excessive insulating material by polishing (planarization stage).

[0003] Various methods such as a reflow method, a spin-on-glass (SOG) method, and an etch-back method have been adopted for the planarization stage. However, since these methods did not give satisfactory results that meet a trend toward higher integration and higher performance of semiconductor elements, recently a chemical mechanical polishing method (hereinafter, referred to as a CMP method) is most widely adopted for the planarization stage.

[0004] The CMP method includes: supplying a slurry composition that contains polishing particles and various chemical components between a polishing pad of a polishing device and a substrate to be polished; and bringing the substrate and the polishing pad into contact with each other and moving them relatively, thereby mechanically polishing the substrate with the polishing particles and chemically polishing the substrate by the action of the chemical components (see, e.g., Patent Documents 1 and 3).

[0005] In the CMP method, a trench filled with an insulating material (e.g., silicon oxide) is formed by selectively removing the insulating material arranged on the upper side of a silicon substrate. In such a planarization stage, by stopping polishing when the upper surface of a polishing stop film is exposed, a step height between an active region and a non-active region due to excessive polishing can be minimized, whereby the performance of elements and the reliability of process can be maintained.

[0006] As the polishing stop film, conventionally a silicon nitride film has been used, and recently a polysilicon thin film is examined to simplify the production steps of semiconductor devices. Accordingly, "high polishing selectivity" is required that enables high-rate polishing of a silicon oxide film while minimizing the polishing of the polysilicon film (see Patent Document 2).

Prior Art Documents

Patent Documents

[0007] Patent Document 1: JP 2009–212378 A

Patent Document 2: JP 2013–507786 A

Patent Document 3: JP 2009–518852 A

Disclosure of Invention

Problem to be Solved by the Invention

[0008] Conventional polishing compositions that contain ceria particles do not make a sufficient difference in the polishing rate between the silicon oxide film and the polysilicon film, that is, their polishing selectivity is not sufficiently high, and they leave many polishing flaws on the polysilicon thin film.

[0009] Therefore, the present invention provides a silicon oxide film polishing composition exhibiting high polishing selectivity that enables high-rate polishing of a silicon oxide film while minimizing polishing of a polysilicon film (polishing stop film), and reducing polishing flaws, methods for manufacturing and polishing a semiconductor substrate using the same, and the use of the silicon oxide film polishing composition for polishing a silicon oxide film on a polysilicon film.

Means for Solving Problem

[0010] The silicon oxide film polishing composition of the present invention is a silicon oxide film polishing composition for polishing a silicon oxide film on a polysilicon film, including components A–C below:

component A: a water-soluble polymer containing a polyethylene glycol chain;

component B: ceria-coated silica particles in which surfaces of silica particles are at least partially coated with granular ceria; and

component C: an aqueous medium.

[0011] A method for manufacturing a semiconductor substrate of the present invention includes polishing a silicon oxide film on a polysilicon film of a substrate to be polished using a polishing composition until the silicon oxide film is removed, the substrate to be polished including the silicon oxide film and the polysilicon film arranged under and in contact with the silicon oxide film,

wherein the silicon oxide film polishing composition of the present invention is used as the polishing composition.

[0012] A method for polishing a semiconductor substrate of the present invention includes polishing a silicon oxide film on a polysilicon film of a substrate to be polished using a polishing composition until the silicon oxide film is removed, the substrate to be polished including the silicon oxide film and the polysilicon film arranged under and in contact with the silicon oxide film,

wherein the silicon oxide film polishing composition of the present invention is used as the polishing composition.

[0013] An exemplary use of the silicon oxide film polishing composition of the present invention is a use thereof for polishing a silicon oxide film on a polysilicon film.

[0014] An another exemplary use of the silicon oxide film polishing composition of the present invention is a use thereof for polishing, in a step of manufacturing a semiconductor substrate, a silicon oxide film on a polysilicon film of a substrate to be polished until the silicon oxide film is removed, the substrate to be polished including the silicon oxide film and the polysilicon film arranged under and in contact with the silicon oxide film.

Effects of the Invention

[0015] According to the present invention, it is possible to provide a silicon oxide film

polishing composition that exhibits high polishing selectivity that ensures an adequate polishing rate for a silicon oxide film for high productivity while minimizing polishing of a polysilicon film, and that reduces polishing flaws on the surface of the polysilicon film, methods for manufacturing and polishing a semiconductor substrate using the silicon oxide film polishing composition, and the use of the silicon oxide film polishing composition for polishing a silicon oxide film on a polysilicon film.

Description of the Invention

[0016] The present invention is based on the finding that a polishing composition including ceria-coated silica particles in which surfaces of silica particles are at least partially coated with granular ceria (hereinafter, also referred to as "ceria-coated silica particles" simply) as polishing particles and a water-soluble polymer containing a polyethylene glycol (PEG) chain as a polishing aid can exhibit high polishing selectivity that enables high-rate polishing of a silicon oxide film while minimizing polishing of a polysilicon film (polishing stop film), and reduce polishing flaws on the surface of the polysilicon film.

[0017] The precise mechanism for producing such effects of the present invention is uncertain, but the following are presumed. Under near-neutral conditions, the surface of the silicon oxide film is negatively charged and hydrophilic, whereas the surface of the polysilicon film is negatively charged and strongly hydrophobic. Since the water-soluble polymer included in the silicon oxide film polishing composition of the present invention (hereinafter, also referred to as "polishing composition" simply) contains a PEG chain that strongly interacts with a hydrophobic substance, it easily adsorbs to the polysilicon film due to the hydrophobic interaction yet hardly adsorbs to the negatively charged hydrophilic polishing particles or surface of the silicon oxide film due to the charge repulsion. Therefore, when the polysilicon film is exposed with the progress of polishing of the silicon oxide film, the polishing aid adsorbs to the polysilicon film selectively by the hydrophobic interaction. The polishing aid adsorbed to the polysilicon film forms a thick coat (adsorbed layer) on the polysilicon film, and the presence of this coat effectively reduces the polishing of the polysilicon film.

[0018] Ceria particles produced by a pulverization method, which are now widely

used as polishing particles, have many edges, whereas the ceria-coated silica particles included in the polishing composition of the present invention have a configuration in which the surfaces of silica particles are at least partially coated with granular ceria. With this configuration, the polishing composition of the present invention can reduce polishing flaws on the surface of the polysilicon film, as compared with the conventional polishing compositions that contain ceria particles produced by a pulverization method as polishing particles. Further, polishing particles in a spherical shape generally cannot produce high polishing rate because of their low frictional resistance to a surface to be polished, whereas the ceria-coated silica particles included in the polishing composition of the present invention have minute irregularities on their surfaces by coating silica particles with minute granular ceria. Therefore, for example, even if the shape of the silica particles is substantially spherical, this special particle configuration allows the polishing particles to have a higher frictional force to a surface to be polished than substantially spherical silica particles without such coating, thereby producing a high polishing rate.

[0019] The polishing composition of the present invention that includes the water-soluble polymer (component A) and the ceria-coated silica particles (component B) in combination can exhibit high polishing selectivity that enables high-rate polishing of a silicon oxide film while minimizing polishing of a polysilicon film, and reduce polishing flaws on the exposed polysilicon film. With this high polishing selectivity and the effect of reducing polishing flaws, the present invention can provide a highly smooth surface of a substrate to be polished including a silicon oxide film and a polysilicon film. Note that these are only assumptions, and the present disclosure is not limited to these mechanisms.

[0020] In one aspect, the present invention relates to a silicon oxide film polishing composition used at the time of polishing a silicon oxide film performed in a step of forming a shallow trench isolation structure in the production process of a semiconductor substrate, the composition including: a water-soluble polymer containing a PEG chain (component A); ceria-coated silica particles (component B); and an aqueous medium (component C). By using the polishing composition of the present invention, in the polishing of a silicon oxide film performed in a step of forming a shallow trench isolation structure, the adequate polishing rate for a silicon

oxide film for high productivity can be ensured while reducing excessive polishing of a polysilicon film, thereby achieving excellent polishing selectivity. Moreover, polishing flaws can be reduced.

[0021] In this specification, when the "polishing selectivity" is high, the ratio of the polishing rate for the silicon oxide film to the polishing rate for the polysilicon film (the polishing rate for the silicon oxide film / the polishing rate for the polysilicon film) becomes large.

[0022] [Component A: water-soluble polymer]

The polishing composition of the present invention includes a water-soluble polymer (component A) containing a PEG chain represented by $-(CH_2CH_2O)_n-$ (where n represents an average number of added moles of an ethylene oxide group (EO), and an integer), from the viewpoint of improving the polishing selectivity and reducing the polishing flaws. The water-soluble polymer containing a PEG chain is at least one selected from polyethylene glycol, a homopolymer having a PEG chain in the structure, and a copolymer having a PEG chain in the structure. The water-soluble polymer may be either a polymer containing a PEG chain in the main chain or a polymer containing a PEG chain in the side chain, preferably a water-soluble polymer containing a PEG chain in the side chain from the viewpoint of improving the polishing selectivity. The water-soluble polymer may be either in a non-neutralized state or in a state neutralized with alkali. The alkali to be used for neutralization is preferably potassium hydroxide, sodium hydroxide, or ammonia. Here, "water-soluble" indicates having a solubility of 2 g/100 ml or higher with respect to water (20°C).

[0023] The weight average molecular weight of the PEG chain contained in the component A is preferably 200 or more, more preferably 300 or more, further preferably 400 or more, still further preferably 600 or more, still further preferably 1000 or more, still further preferably 2000 or more, still further preferably 3000 or more, and still further preferably 4000 or more from the viewpoint of improving the polishing selectivity and reducing the polishing flaws, and preferably 200000 or less, more preferably 180000 or less, further preferably 150000 or less, still further preferably 130000 or less, still further preferably 90000 or less, still further preferably 25000 or less, still further preferably 18000 or less, still further preferably 10000 or

less, and still further preferably 6500 or less from the viewpoint of ensuring an adequate polishing rate for a silicon oxide film for high productivity. The average number of added moles in the PEG chain is preferably 5 or more, more preferably 9 or more, further preferably 13 or more, still further preferably 20 or more, still further preferably 45 or more, still further preferably 65 or more, and still further preferably 90 or more from the viewpoint of improving the polishing selectivity and reducing the polishing flaws, and preferably 250 or less, more preferably 200 or less, and further preferably 150 or less from the viewpoint of ensuring an adequate polishing rate for a silicon oxide film for high productivity.

[0024] When the water-soluble polymer (component A) included in the polishing composition of the present invention is the polymer containing a PEG chain in the main chain for example, the weight average molecular weight of the PEG chain is preferably 200 or more, more preferably 300 or more, further preferably 600 or more, still further preferably 1000 or more, still further preferably 2000 or more, still further preferably 3000 or more, and still further preferably 4000 or more from the viewpoint of reducing polishing of a polysilicon film, and preferably 200000 or less, more preferably 180000 or less, further preferably 150000 or less, still further preferably 130000 or less, still further preferably 90000 or less, still further preferably 25000 or less, still further preferably 18000 or less, still further preferably 10000 or less, and still further preferably 6500 or less from the viewpoint of ensuring an adequate polishing rate for a silicon oxide film for high productivity. The average number of added moles in the PEG chain of the polymer containing a PEG chain in the main chain is preferably 5 or more, more preferably 13 or more, further preferably 20 or more, still further preferably 45 or more, still further preferably 65 or more, and still further preferably 90 or more from the viewpoint of improving the polishing selectivity and reducing the polishing flaws, and preferably 250 or less, more preferably 200 or less, and further preferably 150 or less from the viewpoint of ensuring an adequate polishing rate for a silicon oxide film for high productivity.

[0025] When the water-soluble polymer (component A) included in the polishing composition of the present invention is the polymer containing a PEG chain in the side chain for example, the weight average molecular weight of the PEG chain is preferably 200 or more, more preferably 400 or more, further preferably 1000 or more,

and still further preferably 4000 or more from the viewpoint of reducing polishing of a polysilicon film, and preferably 10000 or less, more preferably 6500 or less, and further preferably 5500 or less from the viewpoint of ensuring an adequate polishing rate for a silicon oxide film for high productivity. The average number of added moles in the PEG chain of the polymer containing a PEG chain in the side chain is preferably 4 or more, more preferably 9 or more, further preferably 20 or more, still further preferably 45 or more, still further preferably 65 or more, and still further preferably 90 or more from the viewpoint of improving the polishing selectivity and reducing the polishing flaws, and preferably 250 or less, more preferably 200 or less, and further preferably 150 or less from the viewpoint of ensuring an adequate polishing rate for a silicon oxide film for high productivity.

[0026] The weight average molecular weight (Mw) of the PEG chain in the water-soluble polymer (component A) was measured using gel permeation chromatography (GPC) described in the examples below.

[0027] The water-soluble polymer (component A) included in the polishing composition of the present invention is preferably at least one selected from the group consisting of polyethylene glycol, a homopolymer of monomethoxypolyethyleneglycol mono(meth)acrylate, a copolymer of (meth)acrylic acid and monomethoxypolyethyleneglycol mono(meth)acrylate, a copolymer of (meth)acrylate and monomethoxypolyethyleneglycol mono(meth)acrylate, a copolymer of alkyl (meth)acrylate and (meth)acrylic acid and monomethoxypolyethyleneglycol mono(meth)acrylate, a copolymer of polyvinyl alcohol and polyethylene glycol, alkali metal salts of these, and ammonium salts of these, from the viewpoint of improving the polishing selectivity and reducing the polishing flaws. Preferable examples of the (meth)acrylate include: alkyl (meth)acrylate (the carbon number of the alkyl group is preferably 1 to 18, more preferably 8 to 16); (meth)acrylate having a hydroxyl group such as 2-hydroxyethyl (meth)acrylate and hydroxypropyl (meth)acrylate, 2-methoxyethyl (meth)acrylate, and 2-ethoxyethyl (meth)acrylate; and (meth)acrylate having a phosphate group such as phosphoric mono-(2-hydroxyethyl) methacrylate and phosphoric mono-(2-hydroxyethyl) alkyl methacrylate (the carbon number of the alkyl group is preferably 1 to 18, more preferably 1 to 16), from the viewpoint of improving the polishing selectivity and reducing the polishing flaws.

[0028] Among these, the water-soluble polymer (component A) included in the polishing composition of the present invention preferably contains an anionic group, from the viewpoint of improving the polishing selectivity and reducing the polishing flaws. When the water-soluble polymer (component A) contains an anionic group, it is possible to reduce the adsorption of the water-soluble polymer (component A) to the silicon oxide film and the adsorption of the ceria-coated silica particles to the component A that has adsorbed on the polysilicon film, by the charge repulsion. Thus, the polishing selectivity is improved and the polishing flaws are reduced. The component A is more preferably a water-soluble polymer containing an anionic group and containing a PEG chain in the side chain from the same viewpoint. The anionic group is preferably at least one selected from a carboxylic acid group, a sulfate group, and a phosphate group, more preferably at least one selected from a carboxylic acid group and a phosphate group, and further preferably a carboxylic acid group, from the viewpoint of the acid dissociation constant (pKa).

[0029] The water-soluble polymer (component A) containing an anionic group is preferably at least one selected from the group consisting of a copolymer of (meth)acrylic acid and monomethoxypolyethyleneglycol mono(meth)acrylate, a copolymer of (meth)acrylate having an anionic group and monomethoxypolyethyleneglycol mono(meth)acrylate, a copolymer of alkyl (meth)acrylate and (meth)acrylic acid and monomethoxypolyethyleneglycol mono(meth)acrylate, alkali metal salts of these, and ammonium salts of these, from the viewpoint of improving the polishing selectivity and reducing the polishing flaws, more preferably at least one selected from the group consisting of a copolymer of (meth)acrylic acid and monomethoxypolyethyleneglycol mono(meth)acrylate, a copolymer of (meth)acrylate having a carboxylic acid group and monomethoxypolyethyleneglycol mono(meth)acrylate, a copolymer of (meth)acrylate having a phosphate group and monomethoxypolyethyleneglycol mono(meth)acrylate, alkali metal salts of these, and ammonium salts of these, and further preferably at least one selected from the group consisting of a copolymer of methacrylic acid and monomethoxypolyethyleneglycol monomethacrylate, an alkali metal salt thereof, and an ammonium salt thereof.

[0030] The weight average molecular weight of the component A is preferably 200 or

more, more preferably 300 or more, further preferably 600 or more, still further preferably 1000 or more, still further preferably 2000 or more, still further preferably 3000 or more, and still further preferably 4000 or more from the viewpoint of improving the polishing selectivity and reducing the polishing flaws, and preferably 300000 or less, more preferably 270000 or less, further preferably 150000 or less, still further preferably 130000 or less, still further preferably 90000 or less, still further preferably 25000 or less, still further preferably 18000 or less, still further preferably 10000 or less, and still further preferably 6500 or less from the viewpoint of ensuring an adequate polishing rate for a silicon oxide film for high productivity.

[0031] When the water-soluble polymer (component A) included in the polishing composition of the present invention is the polymer containing a PEG chain in the main chain, the weight average molecular weight (Mw) is preferably 200 or more, more preferably 300 or more, further preferably 600 or more, still further preferably 1000 or more, still further preferably 2000 or more, still further preferably 3000 or more, and still further preferably 4000 or more from the viewpoint of improving the polishing selectivity and reducing the polishing flaws, and preferably 200000 or less, more preferably 180000 or less, further preferably 150000 or less, still further preferably 130000 or less, still further preferably 90000 or less, still further preferably 25000 or less, still further preferably 18000 or less, still further preferably 10000 or less, and still further preferably 6500 or less from the viewpoint of reducing the polishing flaws and ensuring an adequate polishing rate for a silicon oxide film for high productivity. When the water-soluble polymer (component A) is the polymer containing a PEG chain in the side chain, the weight average molecular weight (Mw) is preferably 10000 or more, more preferably 12000 or more, further preferably 15000 or more, still further preferably 16000 or more, and still further preferably 45000 or more from the viewpoint of the polishing selectivity, and preferably 300000 or less, more preferably 290000 or less, further preferably 280000 or less, and still further preferably 270000 or less from the viewpoint of reducing the polishing flaws and ensuring an adequate polishing rate for a silicon oxide film for high productivity, and further preferably 90000 or less, and still further preferably 70000 or less from the viewpoint of further improving the polishing selectivity and ease of blending.

[0032] The weight average molecular weight (Mw) of the water-soluble polymer was

measured using gel permeation chromatography (GPC) described in the examples below.

[0033] When the water-soluble polymer (component A) included in the polishing composition of the present invention is a copolymer of at least one monomer A selected from (meth)acrylic acid and (meth)acrylate and at least one monomer B selected from polyethylene glycol and polyethylene glycol esters, the molar ratio of the constitutional units derived from the monomer A to the constitutional units derived from the monomer B (the constitutional units derived from the monomer A / the constitutional units derived from the monomer B) included in the copolymer is preferably (5/95) or more, more preferably (25/75) or more, further preferably (40/60) or more, still further (55/45) or more, and preferably (99/1) or less, more preferably (95/5) or less, further preferably (90/10) or less, and still further preferably (85/15) or less.

[0034] When the total mass of the water-soluble polymer (component A), the ceria-coated silica particles (component B), and the aqueous medium (component C) is 100 mass%, the content of the water-soluble polymer (component A) in the polishing composition of the present invention is preferably 0.05 mass% or more, more preferably 0.1 mass% or more, further preferably 0.2 mass% or more, still further preferably 0.25 mass% or more, and preferably 5 mass% or less, more preferably 2.5 mass% or less, further preferably 1.0 mass% or less, and still further preferably 0.75 mass% or less, from the viewpoint of improving the polishing selectivity and reducing the polishing flaws.

[0035] [Component B: ceria-coated silica particles]

The polishing particles included in the polishing composition of the present invention include ceria-coated silica particles (component B) in which surfaces of silica particles are at least partially coated with granular ceria, from the viewpoint of ensuring an adequate polishing rate for a silicon oxide film for high productivity and reducing the polishing flaws.

[0036] The average secondary particle diameter of the ceria-coated silica particles measured by dynamic light scattering (DLS) is preferably 100 nm or more, more preferably 150 nm or more, and preferably 300 nm or less, more preferably 250 nm or less. The ceria-coated silica particles having a large average secondary particle diameter enhance the polishing rate for a silicon oxide film, whereas those having a

small average secondary particle diameter reduce polishing flaws. The average secondary particle diameter of the ceria-coated silica particles can be measured by the method described in the examples below. The average secondary particle diameter of the ceria-coated silica particles measured by the dynamic light scattering is also referred to as an average particle diameter thereof measured by the dynamic light scattering, that is, the concept of this term is broad, including primary particles or secondary particles of silica particles to which a plurality of primary particles or secondary particles of granular ceria adhere (are bonded).

[0037] Regarding the polishing particles included in the polishing composition of the present invention, ceria for coating the silica particles has crystallinity and a granular shape, preferably a substantially spherical shape from the viewpoint of improving the polishing rate for a silicon oxide film and reducing the polishing flaws. The average primary particle diameter of the granular ceria measured by the transmission electron microscope observation is preferably 5 nm or more, more preferably 7.5 nm or more, further preferably 10 nm or more, and preferably 40 nm or less, more preferably 30 nm or less, and further preferably 25 nm or less, from the viewpoint of the polishing rate. The granular ceria for coating the silica particles having an average primary particle diameter of preferably 5 nm or more facilitates the synthesis of the granular ceria. The granular ceria having an average primary particle diameter of preferably 40 nm or less can coat silica particles uniformly, thereby reducing the occurrence of the polishing flaws effectively. The average primary particle diameter of the granular ceria can be measured by the method described in the examples below.

[0038] The ζ potential (zeta potential) of the ceria-coated silica particles at pH 6 is preferably less than 0 mV, more preferably −25 mV or less, further preferably −40 mV or less from the viewpoint of dispersibility of the ceria-coated silica particles, and preferably −60 mV or more from the viewpoint of easy production of the polishing composition. The ζ potential can be measured by the method described in the examples below. The ζ potential at pH 4 is preferably less than 0 mV, more preferably −20 mV or less, further preferably −28 mV or less from the viewpoint of dispersibility of the ceria-coated silica particles, and preferably −60 mV or more from the viewpoint of easy production of the polishing composition. The preferable range of the ζ potential at pH 8 is the same as that at pH 6.

[0039] It is preferred that the silica particles coated with granular ceria are colloidal silica, and have a substantially spherical shape from the viewpoint of improving the polishing rate for a silicon oxide film and reducing the polishing flaws. The average primary particle diameter of the silica particles used for preparation of the ceria-coated silica particles, measured by the transmission electron microscope observation, is preferably 15 nm or more, more preferably 20 nm or more, further preferably 40 nm or more, and preferably 300 nm or less, more preferably 200 nm or less, and further preferably 150 nm or less from the viewpoint of the polishing rate. The silica particles having an average primary particle diameter of preferably 15 nm or more can enhance the polishing rate for a silicon oxide film effectively. The silica particles having an average primary particle diameter of preferably 300 nm or less can reduce the occurrence of the polishing flaws effectively. The average primary particle diameter of the silica particles can be measured by the method described in the examples below.

[0040] When the amount of the ceria for coating the silica particles with respect to the amount of the silica used in the production process of the ceria-coated silica particles is expressed by a mass ratio (silica/ceria), the ratio is preferably 0.5 or more, more preferably 0.67 or more, further preferably 0.8 or more, and preferably 4.0 or less, more preferably 3.0 or less, and further preferably 2.5 or less. When the coating amount of the ceria is large, it is possible to increase the polishing rate for a silicon oxide film. When the coating amount of the ceria is small, it is possible to reduce the generation of ceria aggregates resulting from ceria particles that have failed to coat silica particles and hence are in a free state, thereby reducing the occurrence of the polishing flaws. Incidentally, although the coating amount of the ceria varies depending on the particle diameter of the granular ceria, favorable polish properties can be obtained if approximately the above-described mass ratio is used for coating. Moreover, "the amount of the ceria for coating the silica particles" indicates the mass of the ceria that is converted from the used amount of a ceria supply source.

[0041] The ceria-coated silica particles can be produced, e.g., by depositing ceria on silica particles. Any conventionally known method that can produce cerium hydroxide or cerium oxide on silica particles may be used. For example, the method may be a method of depositing ceria on silica particles by dropping an aqueous

solution of cerium nitrate to a dispersion of silica particles, a method using thermal hydrolysis of cerium ammonium nitrate, a method using alkoxide, etc. In the case of producing cerium hydroxide on silica particles, the cerium hydroxide may be converted into cerium oxide by a hydrothermal treatment or baking. The ceria-coated silica particles produced by these methods may be loosened before use to separate the particles sticking together by baking.

[0042] When the total mass of the water-soluble polymer (component A), the ceria-coated silica particles (component B), and the aqueous medium (component C) is 100 mass%, the content of the ceria-coated silica particles (component B) in the polishing composition of the present invention is preferably 0.1 mass% or more, more preferably 0.2 mass% or more, further preferably 0.25 mass% or more, and still further preferably 0.5 mass% or more from the viewpoint of improving the polishing selectivity and ensuring an adequate polishing rate for a silicon oxide film for high productivity, and preferably 5.0 mass% or less, more preferably 2.5 mass% or less, further preferably 2.0 mass% or less, and still further preferably 1.5 mass% or less from the same viewpoint.

[0043] The mass ratio of the water-soluble polymer (component A) to the ceria-coated silica particles (component B) (the mass of the water-soluble polymer / the mass of the ceria-coated silica particles) in the polishing composition of the present invention is preferably 0.02 or more, more preferably 0.1 or more, further preferably 0.2 or more from the viewpoint of improving the polishing selectivity and reducing the polishing flaws, and preferably 25 or less, more preferably 10 or less, and further preferably 1 or less from the viewpoint of ensuring an adequate polishing rate for a silicon oxide film for high productivity.

[0044] [Aqueous medium: component C]

The polishing composition of the present invention includes an aqueous medium. Examples of the aqueous medium include water, and a mixture of water and a solvent soluble in water. Examples of the solvent soluble in water include lower alcohols such as methanol, ethanol, and isopropanol, and ethanol is preferred from the viewpoint of safety in the polishing step. More preferably, the aqueous medium is composed of water such as ion-exchanged water, distilled water, or ultrapure water, from the viewpoint of improving the quality of a semiconductor

substrate.

[0045] When the total mass of the water-soluble polymer (component A), the ceria-coated silica particles (component B), and the aqueous medium (component C) is 100 mass%, the content of the aqueous medium (component C) in the polishing composition of the present invention may be a remainder obtained by subtracting the copolymer (component A) and the ceria-coated silica particles (component B) from the total mass.

[0046] [Other components]

The polishing composition of the present invention may further include a pH adjuster, a polishing aid other than the component A, inorganic particles other than the component B (polishing particles), etc., as long as the effects of the present invention are not impaired. The content of the optional components is preferably 0.001 mass% or more, more preferably 0.0025 mass% or more, and further preferably 0.01 mass% or more from the viewpoint of ensuring the polishing rate for a silicon oxide film, and preferably 1 mass% or less, more preferably 0.5 mass% or less, and further preferably 0.1 mass% or less from the viewpoint of improving the polishing selectivity. It is preferred that the polishing composition of the present invention does not contain any fluorine compound from the viewpoint of improving the wettability of a surface of a substrate after polishing.

[0047] The pH of the polishing composition of the present invention can be adjusted as needed, as long as the effects of the present invention are not impaired. A pH adjuster to lower the pH is not particularly limited, so long as it is an acidic compound. Examples of the acidic compound include: inorganic acids such as hydrochloric acid, nitric acid, and sulfuric acid; and organic acids such as acetic acid, oxalic acid, citric acid, and malic acid. Among these, hydrochloric acid, nitric acid, and acetic acid are preferred, and hydrochloric acid and acetic acid are more preferred from the viewpoint of versatility.

[0048] A pH adjuster to increase the pH of the polishing composition is not particularly limited, so long as it is an alkaline compound. Examples of the alkaline compound include: inorganic alkaline compounds such as ammonia and potassium hydroxide; and organic alkaline compounds such as alkylamine and alkanolamine. Among these, ammonia and alkylamine are preferred, and ammonia is more

preferred from the viewpoint of improving the quality of a semiconductor substrate.

[0049] The polishing aid other than the component A is preferably an anionic compound or a non-ionic compound, more preferably an anionic surfactant or a non-ionic surfactant from the viewpoint of enhancing the dispersibility of the ceria-coated silica particles. Examples of the anionic surfactant include anionic polymers such as polyacrylic acid, alkyl ether acetate, alkyl ether phosphate, and alkyl ether sulfate. Examples of the non-ionic surfactant include non-ionic polymers such as polyacrylamide, and polyoxyalkylene alkyl ether.

[0050] The inorganic particles other than the component B are preferably silica particles or ceria particles, more preferably silica particles. The amount of the inorganic particles other than the component B with respect to 100 parts by mass of the component B in the polishing composition of the present invention is preferably 10 parts by mass or less, more preferably 1 part by mass or less, and further preferably 0 part by mass, from the viewpoint of the polishing rate and the polishing selectivity.

[0051] [Polishing composition]

The polishing composition of the present invention includes: a water-soluble polymer containing a PEG chain (component A); ceria-coated silica particles (component B); and an aqueous medium (component C). The polishing composition of the present invention can be produced, e.g., by a method including mixing of the water-soluble polymer (component A) and the aqueous medium (component C) and an aqueous dispersion of the ceria-coated silica particles (component B). It is preferred that the polishing composition is obtained by preparing an aqueous solution of the polishing aid in which a water-soluble polymer containing a PEG chain (polishing aid) is dissolved in an aqueous medium and preparing a dispersion of the ceria-coated silica particles in which the ceria-coated silica particles are dispersed in an aqueous medium, and then adding (dropping) the dispersion of the ceria-coated silica particles and as needed other components such as the pH adjuster to the aqueous solution of the polishing aid while stirring the aqueous solution of the polishing aid.

[0052] The ceria-coated silica particles can be dispersed in the aqueous medium, e.g., using an agitator such as a homomixer, a homogenizer, an ultrasonic disperser, a wet ball mill, or a bead mill. If coarse particles resulting from the aggregation or the like of the ceria-coated silica particles are present in the aqueous medium, it is preferred

that the coarse particles should be removed by centrifugation, filtration with a filter, etc. The ceria-coated silica particles are dispersed in the aqueous medium preferably in the presence of the water-soluble polymer containing a PEG chain.

[0053] The pH of the polishing composition of the present invention at 25°C is preferably 3 or more, more preferably 4 or more, further preferably 5 or more, and still further preferably 5.5 or more from the viewpoint of protecting a polishing device, improving the polishing rate for a silicon oxide film, improving the polishing selectivity, and improving the dispersibility of the ceria-coated silica particles,
and preferably 9 or less, more preferably 8.5 or less, further preferably 7.5 or less, and still further preferably 6.5 or less from the viewpoint of the easy control of the polishing conditions, improving the polishing selectivity, reducing polishing of a polysilicon film, and improving the dispersibility of the ceria-coated silica particles. The details of the measurement conditions of the pH are as described in the examples below.

[0054] The polishing composition in embodiments of this application is not limited to a single-liquid type that is put on the market with all the components being mixed beforehand, and can be a two-liquid type including separate components that are to be mixed at the time of use. In the two-liquid type polishing composition, the aqueous medium is divided into a first aqueous medium and a second aqueous medium, and the polishing composition may be composed of a dispersion of the ceria-coated silica particles and an aqueous solution of the polishing aid. The dispersion of the ceria-coated silica particles is obtained by dispersing ceria-coated silica particles and part of a water-soluble polymer containing a PEG chain in the first aqueous medium. The aqueous solution of the polishing aid is obtained by dissolving the remaining water-soluble polymer containing a PEG chain in the second aqueous medium.

[0055] The dispersion of the ceria-coated silica particles and the aqueous solution of the polishing aid may be mixed before being supplied to the surface of an object to be polished, or they may be separately supplied to the surface of a substrate to be polished and mixed thereon.

[0056] The content of each component described above is the amount when the polishing composition is being used in the polishing step. However, the polishing composition of this embodiment may be stored and supplied in a concentrated state as

long as the stability is not impaired. This is preferred because the production and transportation costs can be reduced. The concentrated liquid may be appropriately diluted with the above aqueous medium as needed for use in the polishing step. The dilution ratio is preferably 5 to 100 times.

[0057] [Production method and polishing method of semiconductor substrate]

The polishing composition of the present invention can be used suitably in the polishing performed in a formation step of an element isolation structure of a semiconductor substrate. A specific example of the production method of the semiconductor substrate of the present invention is as follows. First, a silicon substrate is exposed to oxygen inside an oxidation furnace to grow a silicon dioxide layer on its surface, and then a polysilicon film (polishing stop film) is formed on the silicon dioxide layer, e.g., by a CVD (chemical vapor deposition) method. Next, a trench is formed using a photolithography technique on a substrate that includes a silicon substrate and a polishing stop film arranged on one principal surface of the silicon substrate, e.g., a substrate in which a polysilicon film is formed on a silicon dioxide layer of a silicon substrate. Next, a silicon oxide (SiO_2) film for covering the trench is formed, e.g., by a CVD method using a silane gas and an oxygen gas to obtain a substrate to be polished with the polysilicon film being covered with the silicon oxide film. By forming the silicon oxide film, the trench is filled with silicon oxide of the silicon oxide film, and the surface of the polishing stop film that is opposite to the surface facing the silicon substrate side is covered with the silicon oxide film.

[0058] The surface of the silicon oxide film thus formed that is opposite to the surface facing the silicon substrate side has a step height formed correspondingly to the convexo-concave pattern of the lower layer. Next, the silicon oxide film is polished according to the CMP method at least until the surface of the polishing stop film (polysilicon film) that is opposite to the surface facing the silicon substrate side is exposed, more preferably until the surface of the silicon oxide film is flush with the surface of the polishing stop film. The polishing composition of the present invention is used in the polishing step according to the CMP method. In the polishing according to the CMP method, uneven portions on the surface of a substrate to be polished are planarized by supplying the polishing composition to a contact portion of a surface of the substrate to be polished and a polishing pad in a state where they are

in contact with each other, and moving them relatively. In the production method of the semiconductor substrate and the polishing method of the semiconductor substrate of the present invention, another insulating film may be formed between the silicon dioxide layer of the silicon substrate and the polishing stop film (polysilicon film).

[0059] The number of revolutions of the polishing pad is preferably 30 to 200 r/min, more preferably 45 to 150 r/min, and further preferably 60 to 100 r/min, regardless of whether the polishing composition is a single-liquid type or two-liquid type. The number of revolutions of the substrate to be polished is preferably 130 to 200 r/min, more preferably 45 to 150 r/min, and further preferably 60 to 100 r/min.

[0060] The polishing load of a polishing device equipped with a polishing pad is preferably 500 g weight/cm^2 or less, more preferably 400 g weight/cm^2 or less, and further preferably 350 g weight/cm^2 or less, regardless of whether the polishing composition is a single-liquid type or two-liquid type, from the viewpoint of preventing an adverse effect on planarization and the occurrence of flaws due to an excessive load. Meanwhile, the polishing load is preferably 20 g weight/cm^2 or more, more preferably 50 g weight/cm^2 or more, and further preferably 100g weight/cm^2 or more, from the viewpoint of shortening the polishing time.

[0061] The supply rate of the polishing composition is preferably 500 mL/min or less, more preferably 400 mL/min or less, and further preferably 300 mL/min or less from the viewpoint of the efficiency of polishing. Meanwhile, the supply rate of the polishing composition is preferably 10 mL/min or more, and more preferably 30 mL/min or more from the viewpoint of improving the polishing rate for a silicon oxide film.

[0062] In the production method of the semiconductor substrate and the polishing method of the substrate to be polished of the present disclosure, the ratio of the polishing rate for the silicon oxide film to the polishing rate for the polysilicon film (the polishing rate for the silicon oxide film / the polishing rate for the polysilicon film) is preferably as large as possible. Specifically, the ratio is preferably 50 or more, more preferably 52 or more, further preferably 54 or more, and still further preferably 55 or more.

[0063] The present disclosure relates to one or more following embodiments.

[0064] <1> A silicon oxide film polishing composition for polishing a silicon oxide film

on a polysilicon film, including components A–C below:

component A: a water-soluble polymer containing a polyethylene glycol (PEG) chain;

component B: ceria-coated silica particles in which surfaces of silica particles are at least partially coated with granular ceria; and

component C: an aqueous medium.

<2> The silicon oxide film polishing composition according to <1>, wherein the weight average molecular weight of the polyethylene glycol chain contained in the component A is preferably 200 or more, more preferably 300 or more, further preferably 400 or more, still further preferably 600 or more, still further preferably 1000 or more, still further preferably 2000 or more, still further preferably 3000 or more, and still further preferably 4000 or more, and preferably 200000 or less, more preferably 180000 or less, further preferably 150000 or less, still further preferably 130000 or less, still further preferably 90000 or less, still further preferably 25000 or less, still further preferably 18000 or less, still further preferably 10000 or less, and still further preferably 6500 or less.

<3> The silicon oxide film polishing composition according to <2>, wherein the average number of added moles of an ethylene oxide group in the PEG chain is preferably 5 or more, more preferably 9 or more, further preferably 13 or more, still further preferably 20 or more, still further preferably 45 or more, still further preferably 65 or more, and still further preferably 90 or more, and preferably 250 or less, more preferably 200 or less, and further preferably 150 or less.

<4> The silicon oxide film polishing composition according to <1>, wherein when the water-soluble polymer is a polymer containing a PEG chain in the main chain, the weight average molecular weight of the PEG chain is preferably 200 or more, more preferably 300 or more, further preferably 600 or more, still further preferably 1000 or more, still further preferably 2000 or more, still further preferably 3000 or more, and still further preferably 4000 or more, and preferably 200000 or less, more preferably 180000 or less, further preferably 150000 or less, still further preferably 130000 or less, still further preferably 90000 or less, still further preferably 25000 or less, still further preferably 18000 or less, still further preferably 10000 or less, and still further preferably 6500 or less.

<5> The silicon oxide film polishing composition according to <4>, wherein the average number of added moles of an ethylene oxide group in the PEG chain is preferably 5 or more, more preferably 13 or more, further preferably 20 or more, still further preferably 45 or more, still further preferably 65 or more, and still further preferably 90 or more, and preferably 250 or less, more preferably 200 or less, and further preferably 150 or less.

<6> The silicon oxide film polishing composition according to <1>, wherein when the water-soluble polymer is a polymer containing a PEG chain in the side chain, the weight average molecular weight of the PEG chain is preferably 200 or more, more preferably 400 or more, further preferably 1000 or more, and still further preferably 4000 or more, and preferably 10000 or less, more preferably 6500 or less, and further preferably 5500 or less.

<7> The silicon oxide film polishing composition according to <6>, wherein the average number of added moles of an ethylene oxide group in the PEG chain is preferably 4 or more, more preferably 9 or more, further preferably 20 or more, still further preferably 45 or more, still further preferably 65 or more, and still further preferably 90 or more, and preferably 250 or less, more preferably 200 or less, and further preferably 150 or less.

<8> The silicon oxide film polishing composition according to any one of <1>–<7>, wherein the water-soluble polymer preferably contains an anionic group, more preferably contains at least one anionic group selected from a carboxylic acid group, a sulfate group, and a phosphate group, further preferably contains at least one anionic group selected from a carboxylic acid group and a phosphate group, and still further preferably contains a carboxylic acid group.

<9> The silicon oxide film polishing composition according to any one of <1>–<8>, wherein the component A is preferably at least one water-soluble polymer selected from the group consisting of polyethylene glycol, a homopolymer of monomethoxypolyethyleneglycol mono(meth)acrylate, a copolymer of (meth)acrylic acid and monomethoxypolyethyleneglycol mono(meth)acrylate, a copolymer of (meth)acrylate and monomethoxypolyethyleneglycol mono(meth)acrylate, a copolymer of alkyl (meth)acrylate and (meth)acrylic acid and monomethoxypolyethyleneglycol mono(meth)acrylate, a copolymer of polyvinyl alcohol

and polyethylene glycol, alkali metal salts of these, and ammonium salts of these, more preferably at least one water-soluble polymer selected from the group consisting of polyethylene glycol, a homopolymer of monomethoxypolyethyleneglycol mono(meth)acrylate, a copolymer of (meth)acrylate and monomethoxypolyethyleneglycol mono(meth)acrylate, a copolymer of alkyl (meth)acrylate and (meth)acrylic acid and monomethoxypolyethyleneglycol mono(meth)acrylate, alkali metal salts of these, and ammonium salts of these, further preferably at least one water-soluble polymer selected from the group consisting of a copolymer of (meth)acrylic acid and monomethoxypolyethyleneglycol mono(meth)acrylate, a copolymer of (meth)acrylate having an anionic group and monomethoxypolyethyleneglycol mono(meth)acrylate, a copolymer of alkyl (meth)acrylate and (meth)acrylic acid and monomethoxypolyethyleneglycol mono(meth)acrylate, alkali metal salts of these, and ammonium salts of these, still further preferably at least one water-soluble polymer selected from the group consisting of a copolymer of (meth)acrylic acid and monomethoxypolyethyleneglycol mono(meth)acrylate, a copolymer of (meth)acrylate having a carboxylic acid group and monomethoxypolyethyleneglycol mono(meth)acrylate, a copolymer of (meth)acrylate having a phosphate group and monomethoxypolyethyleneglycol mono(meth)acrylate, alkali metal salts of these, and ammonium salts of these, and still further preferably at least one water-soluble polymer selected from the group consisting of a copolymer of methacrylic acid and monomethoxypolyethyleneglycol monomethacrylate, an alkali metal salt thereof, and an ammonium salt thereof.

<10> The silicon oxide film polishing composition according to <9>, wherein the (meth)acrylate is preferably at least one selected from: alkyl (meth)acrylate (the carbon number of the alkyl group is preferably 1 to 18, more preferably 8 to 16); (meth)acrylate having a hydroxyl group such as 2-hydroxyethyl (meth)acrylate and hydroxypropyl (meth)acrylate, 2-methoxyethyl (meth)acrylate, and 2-ethoxyethyl (meth)acrylate; and (meth)acrylate having a phosphate group such as phosphoric mono-(2-hydroxyethyl) methacrylate and phosphoric mono-(2-hydroxyethyl) alkyl methacrylate (the carbon number of the alkyl group is preferably 1 to 18, more preferably 1 to 16).

<11> The silicon oxide film polishing composition according to any one of

<1>—<10>,wherein when the water-soluble polymer (component A) is a copolymer of at least one monomer A selected from (meth)acrylic acid and (meth)acrylate and at least one monomer B selected from polyethylene glycol and polyethylene glycol esters, the molar ratio of the constitutional units derived from the monomer A to the constitutional units derived from the monomer B (the constitutional units derived from the monomer A / the constitutional units derived from the monomer B) contained in one molecule of the copolymer is preferably (5/95) or more, more preferably (25/75) or more, further preferably (40/60) or more, still further (55/45) or more, and preferably (99/1) or less, more preferably (95/5) or less, further preferably (90/10) or less, and still further preferably (85/15) or less.

<12> The silicon oxide film polishing composition according to any one of <1>—<11>, wherein the weight average molecular weight (Mw) of the water-soluble polymer (component A) is preferably 200 or more, more preferably 300 or more, further preferably 600 or more, still further preferably 1000 or more, still further preferably 2000 or more, still further preferably 3000 or more, and still further preferably 4000 or more, and preferably 300000 or less, more preferably 270000 or less, further preferably 150000 or less, still further preferably 130000 or less, still further preferably 90000 or less, still further preferably 25000 or less, still further preferably 18000 or less, still further preferably 10000 or less, and still further preferably 6500 or less.

<13> The silicon oxide film polishing composition according to any one of <1>—<11>, wherein

when the water-soluble polymer (component A) is the polymer containing a PEG chain in the main chain, the weight average molecular weight (Mw) is preferably 200 or more, more preferably 300 or more, further preferably 600 or more, still further preferably 1000 or more, still further preferably 2000 or more, still further preferably 3000 or more, and still further preferably 4000 or more, and preferably 200000 or less, more preferably 180000 or less, further preferably 150000 or less, still further preferably 130000 or less, still further preferably 90000 or less, still further preferably 25000 or less, still further preferably 18000 or less, still further preferably 10000 or less, and still further preferably 6500 or less, and

when the water-soluble polymer (component A) is the polymer containing a

PEG chain in the side chain, the weight average molecular weight (Mw) is preferably 10000 or more, more preferably 12000 or more, further preferably 15000 or more, still further preferably 16000 or more, and still further preferably 45000 or more, and preferably 300000 or less, more preferably 290000 or less, further preferably 280000 or less, and still further preferably 270000 or less, and further preferably 90000 or less, and still further preferably 70000 or less.

<14> The silicon oxide film polishing composition according to any one of <1>–<13>, wherein when the total mass of the water-soluble polymer (component A), the ceria-coated silica particles (component B), and the aqueous medium (component C) is 100 mass%, the content of the water-soluble polymer (component A) is preferably 0.05 mass% or more, more preferably 0.1 mass% or more, further preferably 0.2 mass% or more, still further preferably 0.25 mass% or more, and preferably 5 mass% or less, more preferably 2.5 mass% or less, further preferably 1.0 mass% or less, and still further preferably 0.75 mass% or less.

<15> The silicon oxide film polishing composition according to any one of <1>–<14>, wherein the component B represents ceria-coated silica particles in which silica particles that have an average primary particle diameter measured by transmission electron microscope observation of preferably 15 nm or more and 300 nm or less are coated with granular ceria that has an average primary particle diameter measured by the transmission electron microscope observation of preferably 5 nm or more and 40 nm or less, and

a mass ratio of silica to ceria (silica/ceria) is preferably 0.5 or more and 4.0 or less.

<16> The silicon oxide film polishing composition according to <15>, wherein the average primary particle diameter of the granular ceria is more preferably 7.5 nm or more, further preferably 10 nm or more, and more preferably 30 nm or less, and further preferably 25 nm or less.

<17> The silicon oxide film polishing composition according to <15> or <16>, wherein the average primary particle diameter of the silica particles is more preferably 20 nm or more, further preferably 40 nm or more, and more preferably 200 nm or less, and further preferably 150 nm or less.

<18> The silicon oxide film polishing composition according to any one of

<15>—<17>, wherein the mass ratio (silica/ceria) is more preferably 0.67 or more, further preferably 0.8 or more, and more preferably 3.0 or less, and further preferably 2.5 or less.

<19> The silicon oxide film polishing composition according to any one of <1>—<18>, wherein the average secondary particle diameter of the ceria-coated silica particles measured by dynamic light scattering is preferably 100 nm or more, more preferably 150 nm or more, and preferably 300 nm or less, more preferably 250 nm or less.

<20> The silicon oxide film polishing composition according to any one of <1>—<19>, wherein the ζ potential of the ceria-coated silica particles at pH 6 is preferably less than 0 mV, more preferably −25 mV or less, further preferably −40 mV or less, and preferably −60 mV or more.

<21> The silicon oxide film polishing composition according to any one of <1>—<20>, wherein the ζ potential of the ceria-coated silica particles at pH 4 is preferably less than 0 mV, more preferably −20 mV or less, further preferably −28 mV or less, and preferably −60 mV or more.

<22> The silicon oxide film polishing composition according to any one of <1>—<21>, wherein the ζ potential of the ceria-coated silica particles at pH 8 is preferably less than 0 mV, more preferably −25 mV or less, further preferably −40 mV or less, and preferably −60 mV or more.

<23> The silicon oxide film polishing composition according to any one of <1>—<22>, wherein when the total mass of the water-soluble polymer (component A), the ceria-coated silica particles (component B), and the aqueous medium (component C) is 100 mass%, the content of the ceria-coated silica particles (component B) is preferably 0.1 mass% or more, more preferably 0.2 mass% or more, further preferably 0.25 mass% or more, and still further preferably 0.5 mass% or more, and preferably 5.0 mass% or less, more preferably 2.5 mass% or less, further preferably 2.0 mass% or less, and still further preferably 1.5 mass% or less.

<24> The silicon oxide film polishing composition according to any one of <1>—<23>, wherein the mass ratio of the water-soluble polymer (component A) to the ceria-coated silica particles (component B) (the mass of the water-soluble polymer / the mass of the ceria-coated silica particles) is preferably 0.02 or more, more preferably 0.1

or more, further preferably 0.2 or more, and preferably 25 or less, more preferably 10 or less, and further preferably 1 or less.

<25> The silicon oxide film polishing composition according to any one of <1>—<24>, wherein the pH of the silicon oxide film polishing composition at 25°C is preferably 3 or more, more preferably 4 or more, further preferably 5 or more, and still further preferably 5.5 or more, and preferably 9 or less, more preferably 8.5 or less, further preferably 7.5 or less, and still further preferably 6.5 or less.

<26> The silicon oxide film polishing composition according to any one of <1>—<25>, wherein the ratio of the polishing rate for the silicon oxide film to the polishing rate for the polysilicon film (the polishing rate for the silicon oxide film / the polishing rate for the polysilicon film) is preferably 50 or more, more preferably 52 or more, further preferably 54 or more, and still further preferably 55 or more.

<27> The silicon oxide film polishing composition according to any one of <1>—<26>,

wherein the silicon oxide film polishing composition is a two-liquid type including separate components that are to be mixed at the time of use,

the aqueous medium (component C) is divided into a first aqueous medium and a second aqueous medium, and the silicon oxide film polishing composition is composed of a dispersion of the ceria-coated silica particles and an aqueous solution of a polishing aid, the dispersion of the ceria-coated silica particles being obtained by dispersing the ceria-coated silica particles and part of a water-soluble polymer containing a PEG chain in the first aqueous medium, and the aqueous solution of the polishing aid being obtained by dissolving the remaining water-soluble polymer containing a PEG chain in the second aqueous medium.

<28> A method for manufacturing a semiconductor substrate, including polishing a silicon oxide film on a polysilicon film of a substrate to be polished using a polishing composition until the silicon oxide film is removed, the substrate to be polished including the silicon oxide film and the polysilicon film arranged under and in contact with the silicon oxide film,

wherein the silicon oxide film polishing composition according to any one of <1> to <27> is used as the polishing composition.

<29> A method for polishing a semiconductor substrate, including polishing a

silicon oxide film on a polysilicon film of a substrate to be polished using a polishing composition until the silicon oxide film is removed, the substrate to be polished including the silicon oxide film and the polysilicon film arranged under and in contact with the silicon oxide film,

wherein the silicon oxide film polishing composition according to any one of <1> to <27> is used as the polishing composition.

<30> A use of the silicon oxide film polishing composition according to any one of <1> to <27> for polishing a silicon oxide film on a polysilicon film.

<31> A use of the silicon oxide film polishing composition according to any one of <1> to <27> for polishing, in a step of manufacturing a semiconductor substrate, a silicon oxide film on a polysilicon film of a substrate to be polished until the silicon oxide film is removed, the substrate to be polished including the silicon oxide film and the polysilicon film arranged under and in contact with the silicon oxide film.

Examples

[0065] 1. Preparation of polishing composition

[Preparation Example 1 of polishing composition]

Polyethylene glycol (water-soluble polymer (component A)) and ion-exchanged water were mixed uniformly to obtain an aqueous solution of the polishing aid. While stirring the aqueous solution of the polishing aid, a dispersion of the ceria-coated silica particles (dispersion medium: ion-exchanged water) and a 1N hydrochloric acid aqueous solution (pH adjuster) were added thereto, and ion-exchanged water was further added to adjust the concentration, whereby a polishing composition of Example 1 was obtained. The mass ratio of each component was adjusted so that the polishing composition would have a composition and a pH indicated in Table 2. The contents of the water-soluble polymers and polishing particles indicated in Tables 2–4 are values with respect to a total 100 mass% of the water-soluble polymer and the polishing particles and the aqueous medium (ion-exchanged water).

[0066] [Preparation Example 2 of polishing composition]

Polishing compositions of Examples 2–31 and Comparative Examples 1–6 were prepared in the same manner as in [Preparation Example 1 of polishing

composition], except that the amount of each component was adjusted so that the polishing compositions would have a composition and a pH indicated in Tables 2–4. As the pH adjuster, 1 mol/L hydrochloric acid was used to lower pH, and 1 mass% ammonia water was used to increase pH.

[0067] [Production method of ceria-coated silica particles]

<Production method 1 of ceria-coated silica particles>

The following describes the production method of ceria-coated silica particles used to prepare the polishing compositions of Examples 1–7, 14–24, 27–31, and Comparative Example 6. First, a 20 mass% aqueous dispersion of spherical silica particles having an average primary particle diameter of 80 nm (manufactured by JGC Catalysts and Chemicals Ltd., Cataloid SI–80PW) was prepared. To the aqueous dispersion of spherical silica particles, an aqueous solution of cerium nitrate (CeO_2 material) was dropped while a 3 mass% ammonia aqueous solution was dropped separately, and the pH was kept at about 8 so as to deposit cerium on the spherical silica particles. During the dropping, the aqueous dispersion of spherical silica particles was kept at 50°C by heating. After the dropping was completed, the reaction liquid was heated for aging to 100°C for 4 hours to crystalize the ceria deposited on the particles. Thereafter, the obtained particles were filtered, washed thoroughly with water, and dried at 100°C with a dryer. Although the dry powder in this state also can be used for preparation of the polishing compositions, it was further baked at 1000°C for 2 hours in this case. The baked powder thus obtained was loosened to separate the particles sticking together by baking. Thus, ceria-coated silica particles B1 having an average primary particle diameter of 110 nm were obtained. The ceria-coated silica particles B1 was observed with TEM (transmission electron microscope), and confirmed that the surfaces of the silica particles were coated with granular ceria.

[0068] <Production method 2 of ceria-coated silica particles>

The following describes the production method of ceria-coated silica particles used to prepare the polishing compositions of Examples 8 and 9.

Ceria-coated silica particles B2 having an average primary particle diameter of 110 nm were obtained in the same manner as in <Production method 1 of ceria-coated silica particles>, except that the amount of cerium nitrate used as a CeO_2

material was reduced to one third of that in <Production method 1 of ceria-coated silica particles>. The ceria-coated silica particles B2 was observed with TEM (transmission electron microscope), and confirmed that the surfaces of the silica particles were coated with granular ceria.

[0069] <Production method 3 of ceria-coated silica particles>

The following describes the production method of ceria-coated silica particles used to prepare the polishing compositions of Examples 10, 11 and 25.

Ceria-coated silica particles B3 having an average primary particle diameter of 65 nm were obtained in the same manner as in <Production method 1 of ceria-coated silica particles>, except that a 20 mass% aqueous dispersion of spherical silica particles having an average primary particle diameter of 45 nm (manufactured by JGC Catalysts and Chemicals Ltd., Cataloid SI–45P) was used instead of the 20 mass% aqueous dispersion of spherical silica particles having an average primary particle diameter of 80 nm (manufactured by JGC Catalysts and Chemicals Ltd., Cataloid SI–80PW). The ceria-coated silica particles B3 was observed with TEM (transmission electron microscope), and confirmed that the surfaces of the silica particles were coated with granular ceria.

[0070] <Production method 4 of ceria-coated silica particles>

The following describes the production method of ceria-coated silica particles used to prepare the polishing compositions of Examples 12, 13 and 26.

Ceria-coated silica particles B4 having an average primary particle diameter of 160 nm were obtained in the same manner as in <Production method 1 of ceria-coated silica particles>, except that a 20 mass% aqueous dispersion of spherical silica particles having an average primary particle diameter of 120 nm (manufactured by JGC Catalysts and Chemicals Ltd., Cataloid SI–120P) was used instead of the 20 mass% aqueous dispersion of spherical silica particles having an average primary particle diameter of 80 nm (manufactured by JGC Catalysts and Chemicals Ltd., Cataloid SI–80PW).

[0071] In the production methods 1–4 of ceria-coated silica particles, the ceria-coated silica particles were produced under a condition to precipitate all of the charged ceria source. Because of this, the mass ratio of the charged silica to the charged ceria (silica/ceria) is considered to be almost the same as the mass ratio (silica/ceria)

calculated from the mass of silica and the mass of ceria in the dissolved substance of the ceria-coated silica particles.

[0072] In the preparation of the polishing compositions of Comparative Examples 1–5, "GPL–C1010" manufactured by SHOWA DENKO K.K. (the concentration of ceria particles: 10 mass%) was used as a dispersion of ceria particles. The ceria particles included in the dispersion are defined as ceria particles B51.

[0073] Table 1 shows the zeta potentials of the ceria-coated silica particles B1–B4 and the ceria particles B51.

[0074] [Table 1]

ζ potential (unit: mV)		pH 4.0	pH 6.0	pH 8.0
Ceria-coated silica particles	B1	−31.7	−44.0	−47.5
	B2	−41.0	−48.5	−53.2
	B3	−34.1	−45.8	−48.4
	B4	−30.7	−43.4	−45.6
Ceria particles B51		−13.4	−22.4	−23.8

[0075] [Monomethoxypolyethyleneglycol monomethacrylate (PEGMA)]

In [Synthesis method or details of water-soluble polymer] described below, PEGMA (EO average number of added moles: 120) was synthesized via esterification reaction in accordance with the method described in JP 3874917. Methacrylic acid remaining as an unreacted substance in the synthesized PEGMA was removed by distillation to be less than 1 wt% for use. PEGMAs having EO average number of added moles of 9 and 23 are marketed products (manufactured by KYOEISHA CHEMICAL CO., LTD.).

[0076] [Synthesis method or details of water-soluble polymer]

<Details of water-soluble polymers (1)–(6)>

Marketed products (manufactured by Wako Pure Chemical Industries, Ltd.) were used as polyethylene glycols (1)–(6) having a weight average molecular weight of 300, 600, 2000, 6000, 20000, or 100000.

[0077] <Synthesis method of water-soluble polymers (7) and (8)>

A water-soluble polymer (7) and a water-soluble polymer (8) were synthesized with reference to the description of JP 2012–167053 A. The weight average molecular weight was adjusted by controlling the concentration of a polymerization

initiator.

[0078] <Synthesis method of water-soluble polymer (9)>

A reactor equipped with a thermometer, an agitator, a dropping device, a nitrogen introducing pipe, and a cooling pipe was charged with 281.4 g of distilled water, and subjected to a nitrogen substitution while stirring the distilled water. The water was then heated to 80°C in a nitrogen atmosphere. A solution in which 336.5 g of PEGMA (the EO average number of added moles: 120), 22.2 g of methacrylic acid, 1.89 g of 2-mercaptoethanol was dissolved in 238.2 g of water and a solution in which 3.68 g of ammonium persulfate was dissolved in 45 g of water were each dropped into the reactor for 1.5 hours. Subsequently, a solution in which 1.47 g of ammonium persulfate was dissolved in 15 g of water was dropped into the reactor for 30 minutes and aged for 1 hour at the same temperature (80°C). After aging was completed, it was neutralized with 18.7 g of 48% sodium hydroxide to obtain a copolymer of methacrylic acid (MAA) and monomethoxypolyethyleneglycol monomethacrylate (PEGMA) (the molar ratio: 80/20) having a weight average molecular weight of 56000. Then, the resultant was adjusted with water to obtain a polymer solution having a solid content concentration of 10 mass%.

[0079] <Synthesis method of water-soluble polymer (10)>

A copolymer of MAA and PEGMA (the weight average molecular weight: 62000, the molar ratio: 65/35) was obtained in the same manner as in <Synthesis method of water-soluble polymer (9)>, except that the amounts of PEGMA (EO average number of added moles: 120) and methacrylic acid (monomers) were changed to 3588.3 g and 17.2 g, respectively. The resultant was adjusted with water to obtain a polymer solution having a solid content concentration of 10 mass%.

[0080] <Synthesis method of water-soluble polymer (11)>

A copolymer of MAA and PEGMA (the weight average molecular weight: 46000, the molar ratio: 90/10) was obtained in the same manner as in <Synthesis method of water-soluble polymer (9)>, except that the amounts of PEGMA (EO average number of added moles: 120) and methacrylic acid (monomers) were changed to 165.8 g and 24.0 g, respectively. The resultant was adjusted with water to obtain a polymer solution having a solid content concentration of 10 mass%.

[0081] <Synthesis method of water-soluble polymer (12)>

A copolymer of MAA and PEGMA (the weight average molecular weight: 40000, the molar ratio: 65/35) was obtained in the same manner as in <Synthesis method of water-soluble polymer (9)>, except that the amounts of PEGMA (EO average number of added moles: 23) and methacrylic acid (monomers) were changed to 117.2 g and 17.2 g, respectively. The resultant was adjusted with water to obtain a polymer solution having a solid content concentration of 10 mass%.

[0082] <Synthesis method of water-soluble polymer (13)>

A glass reaction vessel (four-neck flask) with an agitator was charged with 157.4 g of PEGMA (EO average number of added moles: 120) and 0.39 g of lauryl methacrylate, to which 0.075 g of azobisisobutyronitrile was added. A polymerization reaction was performed at 80°C for 20 hours in 180.0 g of ethyl acetate (polymerization solvent). After the polymerization reaction was completed, the reaction liquid thus obtained was dropped and precipitated in methanol to isolate a product. A step of dissolving the product in tetrahydrofuran (THF), dropping it into methanol, and isolating the product was repeated two more times to purify the product. The purified product thus obtained was dried under reduced pressure at 60°C for a whole day and night to obtain a polymer (the weight average molecular weight 76000, the molar ratio 5/95). The polymer was dissolved in water to prepare a polymer solution having a solid content concentration of 2 mass%.

[0083] <Synthesis method of water-soluble polymer (14)>

A glass reaction vessel (four-neck flask) with an agitator was charged with 366 g of water, and subjected to a nitrogen substitution while stirring the water. The water was then heated to 80°C in a nitrogen atmosphere. A solution in which 270 g of PEGMA (the EO average number of added moles: 23), 32.5 g of 2-hydroxyethyl methacrylate, and 4.5 g of 3-mercaptopropionic acid were mixed and a solution in which 8.4 g of ammonium persulfate was dissolved in 48 g of water were each dropped into the reaction vessel for 1.5 hours. After aging for one hour, a solution in which 1.8 g of ammonium persulfate was dissolved in 10 g of water was dropped into the reaction vessel for 30 minutes and aged for 1.5 hours at the same temperature (80°C). After aging was completed, the resultant was neutralized with 44.4 g of a 32 mass% sodium hydroxide aqueous solution to obtain a polymer having a weight average molecular weight (Mw) of 58000 and a molar ratio of 50/50, and the polymer was

adjusted with water to obtain a polymer solution having a solid content concentration of 10 mass%.

[0084] <Synthesis method of water-soluble polymer (15)>

A glass reaction vessel (four-neck flask) with an agitator was charged with 366 g of water, and subjected to a nitrogen substitution while stirring the water. The water was then heated to 80°C in a nitrogen atmosphere. A solution in which 270 g of PEGMA (the EO average number of added moles: 23), 52.4 g of phosphoric mono-(2-hydroxyethyl) methacrylate, and 4.5 g of 3-mercaptopropionic acid were mixed and a solution in which 8.4 g of ammonium persulfate was dissolved in 48 g of water were each dropped into the reaction vessel for 1.5 hours. After aging for one hour, a solution in which 1.8 g of ammonium persulfate was dissolved in 10 g of water was dropped into the reaction vessel for 30 minutes and aged for 1.5 hours at the same temperature (80°C). After aging was completed, the resultant was neutralized with 44.4 g of a 32 mass% sodium hydroxide aqueous solution to obtain a polymer having a weight average molecular weight (Mw) of 64000 and a molar ratio of 50/50, and the polymer was adjusted with water to obtain a polymer solution having a solid content concentration of 10 mass%.

[0085] <Water-soluble polymer (16)>

A copolymer of polivinyl alcohol and polyethylene glycol (product name: Kollicoat (registred trademark), manufactured by BASF SE) was used as the water-soluble polymer (16).

[0086] <Water-soluble polymer (17)>

A copolymer of MAA and PEGMA (the weight average molecular weight: 40000, the molar ratio: 80/20) was obtained in the same manner as in <Synthesis method of water-soluble polymer (9)>, except that the amounts of PEGMA (EO average number of added moles: 9) and methacrylic acid (monomers) were changed to 30.2 g and 22.2 g, respectively. The resultant was adjusted with water to obtain a polymer solution having a solid content concentration of 10 mass%.

[0087] 2. Various measurement methods

(a) pH measurement of polishing composition

The pH of the polishing composition at 25°C was measured with a pH meter (HM-30G, DKK-TOA CORPORATION) and is read on the pH meter 1 minute after

dipping an electrode into the polishing composition.

[0088] (b–1) Average secondary particle diameter of polishing particles measured by dynamic light scattering (DLS)

The average secondary particle diameter of the polishing particles was determined in the following manner. A polishing particle slurry having a solid content concentration of 0.1 mass% was prepared, and the volume average particle diameter of the slurry was measured by a Zetasizer Nano ZS (dynamic light scattering) manufactured by Malvern Instruments Ltd. The volume average particle diameter thus obtained was determined as an average secondary particle diameter and expressed as a DLS particle diameter in Tables 2–4.

[0089] (b–2) Average primary particle diameter of silica particles

The average primary particle diameters of the silica particles before and after ceria coating were determined by measuring the diameters of 50 silica particles using images obtained by TEM (transmission electron microscope) and averaging the measured diameters (Tables 2–4). There was no difference in the average primary particle diameters of the silica particles before and after ceria coating.

[0090] (b–3) Average primary particle diameter of granular ceria

The average primary particle diameter of the granular ceria on the silica particles was determined by measuring the diameters of 100 granular ceria particles on the silica particles using images obtained by TEM (transmission electron microscope) and averaging the measured diameters (Tables 2–4). Alternatively, the average primary particle diameter of the granular ceria thereon may be obtained by subjecting a powder of the ceria-coated silica particles to a powder X-ray diffraction measurement, calculating a crystallite diameter from the Scherrer equation using the half-width and diffraction angle of the peak in the (1, 1, 1) plane of the ceria appearing near 29 ° to 30°, and determining the crystallite diameter as an average primary particle diameter of the granular ceria.

Scherrer equation: crystallite diameter (Å) = $K \times \lambda / (\beta \times \cos\theta)$

K: Scherrer's constant, λ: wavelength of X-ray = 1.54056 Å, β: half-width, θ: diffraction angle $2\theta/\theta$

[0091] (b–4) Average primary particle diameter of polishing particles

The average primary particle diameter of the polishing particles was

determined by measuring the diameters of 50 polishing particles using images obtained by TEM (transmission electron microscope) and averaging the measured diameters. The average primary particle diameters of the ceria-coated silica particles B1–B4 used for preparation of the polishing compositions of Examples 1–31 and Comparative Example 6 were as indicated above, and the average primary particle diameter of the ceria particles B51 used for preparation of the polishing compositions of Comparative Examples 1–5 was 120 nm.

[0092] (b–5) ζ potential of polishing particles

100 g of an ion-exchanged water suspension containing 1 mass% of polishing particles was prepared, which was then subjected to an ultrasonic treatment for 10 minutes to obtain a dispersion. 1 g of the dispersion, 40 g or more of ion-exchanged water, and a hydrochloric acid aqueous solution and ammonia water (pH adjusters) were mixed to obtain measurement samples containing 0.02 mass% of polishing particles and at a pH of 4.0, 6.0, or 8.0. The ζ potentials of the polishing particles were measured by "Zetasizer Nano ZS" manufactured by Malvern Instruments Ltd using the obtained measurement samples.

[0093] (c) Measurement method of weight average molecular weight of polymer

The following describes the measurement method of the weight average molecular weights of the water-soluble polymers (1)–(17) and the weight average molecular weights of the PEG chains used for preparation of the polishing compositions of the examples and comparative examples.

The weight average molecular weights of the water-soluble polymers (1)–(17) and the weight average molecular weights of the PEG chains were measured by gel permeation chromatography (GPC) under the conditions described below.

[GPC conditions]

Detector: Shodex (registered trademark) RISE-61, differential refractometer

Columns: G4000PWXL and G2500PWXL (manufactured by TOSOH CORPORATION) connected in series

Eluent: The concentration was adjusted at 0.5 g/100 mL using 0.2M phosphate buffer/acetonitrile = 90/10 (capacity ratio), and 20 μL of the resultant was used.

Column temperature: 40 °C

Flow rate: 1.0 mL/min

Standard polymer: monodisperse polyethylene glycol with known molecular weight

[0094] 3. Evaluation of polishing compositions

[Production of specimen]

An oxide film specimen was prepared by forming a 2000-nm-thick silicon oxide film (oxide film) on one side of a silicon wafer by a TEOS-plasma CVD method and cutting out a 40 mm x 40 mm square piece therefrom. Similarly, a polysilicon film specimen was prepared by forming a 100-nm-thick thermal oxide film on one side of a silicon wafer, forming a 500-nm-thick polysilicon film (Poly-Si film) thereon by a CVD method, and cutting out a 40 mm x 40 mm square piece therefrom.

[0095] [Measurement of polishing rate for oxide film]

"MA-300" manufactured by Musashino Denshi Co., Ltd. (platen diameter: 300 mm) was used as a polishing device. A rigid urethane pad "IC-1000/Sub400" manufactured by Nitta Haas Incorporated was used as a polishing pad. The polishing pad was attached onto the platen of the polishing device. The specimen was set in a holder having a diameter of 120 mm, and the holder was then placed on the polishing pad so that the surface of the specimen on which the silicon oxide film was formed would face downward (so that the oxide film would face the polishing pad). Further, a weight was placed on the holder so that a load to be applied to the specimen would be 300 g weight/cm^2. The oxide film specimen was polished by rotating both of the platen and the holder in the same rotation direction at 90 r/min for two minutes while dropping the polishing composition at a rate of 50 mL/min onto the center of the platen, on which the polishing pad was attached. The oxide film specimen after polishing was washed with ultrapure water, dried, and measured by a spectroscopic reflectometer described below.

[0096] The thicknesses of the oxide film before and after polishing were measured with a spectroscopic reflectometer ("Lambda Ace VM−1000" manufactured by SCREEN Semiconductor Solutions Co., Ltd.). The polishing rate for the oxide film was calculated from the formula below. Tables 2–4 below show the polishing rate for the oxide film (SiO_2).

Polishing rate (nm/min) for oxide film (SiO_2)

= [Thickness of oxide film before polishing (nm) – Thickness of oxide film after polishing (nm)] / Polishing time (min)

[0097] [Measurement of polishing rate for polysilicon film]

The polishing of the polysilicon film, the measurement of the film thickness, and the calculation of the polishing rate were performed in the same manner as in the above [Measurement of polishing rate for oxide film], except that the polysilicon film specimen was used instead of the oxide film specimen as a specimen. Tables 2–4 below show the polishing rate for the polysilicon film (Poly-Si).

[0098] [Polishing rate ratio]

The ratio of the polishing rate for the silicon oxide film to the polishing rate for the polysilicon film (SiO_2/Poly-Si) was determined as a polishing rate ratio, and calculated from the formula below. The polishing selectivity improves as the polishing rate ratio increases, thereby exhibiting a high ability in eliminating a step height. Tables 2–4 below show the results.

Polishing rate ratio (SiO_2/Poly-Si)

= Polishing rate for silicon oxide film (nm/min) / Polishing rate for polysilicon film (nm/min)

[0099] [Measurement method of polishing flaws (the number of scratches)]

Measurement instrument: Optical microscope (VMX–3100, manufactured by VisionTech Inc.)

Evaluation: To measure polishing flaws, the polysilicon film specimen that had been washed and dried after polishing was attached to a flat substrate, and irradiated with a light source for observation under dark field condition. In the present disclosure, "polishing flaws" refer to flaws having a length of 1 μm or more based on the detection by an optical microscope.

[0100]

[Table 2]

Table 2		Water-soluble polymer (polymer)					Polishing particles (abrasive grain)					Mass ratio	Polishing composition		Polishing rate (nm/min)		Polishing rate ratio	Poly-Si polishing flaws (number)
							Ceria-coated silica particles												
		No.	Kind	Molecular weight[1]	Molecular weight of PEG part[2]	Content (mass%)		Diameter of silica particles[3] (nm)	Diameter of granular ceria[4] (nm)	Mass ratio of silica/ceria	Content (mass%)	Polymer/Abrasive grain	pH (25°C)	DLS particle diameter[5] (nm)	SiO_2	Poly-Si	SiO_2/Poly-Si	
Ex.	1	(1)	Polyethylene glycol	6000	6000	0.05	B1	80	15	1	1	0.05	6.0	180	720	10	72.0	14
	2					0.25						0.25	5.9	185	700	8	87.5	—
	3					0.5						0.5	6.0	189	700	7	100.0	—
	4					1						1	6.0	185	600	7	85.7	—
	5	(2)	Polyethylene glycol	2000	2000	0.5	B1	80	15	1	1	0.5	6.0	180	725	8	90.6	—
	6	(3)	Polyethylene glycol	20000	20000	0.05	B1	80	15	1	1	0.05	6.0	181	597	6	99.5	—
	7	(4)	Polyethylene glycol	100000	100000	0.01	B1	80	15	1	1	0.01	6.0	185	500	5	100.0	—
	8	(1)	Polyethylene glycol	6000	6000	0.05	B2	80	15	3	1	0.05	6.0	180	395	7	56.4	—
	9					0.5						0.5	5.9	181	370	6	61.7	—
	10					0.05	B3	45	10	1	1	0.05	6.1	175	370	5	74.0	11
	11					0.25						0.25	6.0	174	350	5	70.0	—
	12					0.05	B4	120	20	1	1	0.05	6.1	202	815	10	81.5	17
	13					0.25						0.25	6.0	205	800	9	88.9	—
	14					0.05	B1	80	15	1	0.5	0.1	6.0	181	487	4	121.8	—
	15										0.25	0.2	5.9	185	300	4	75.0	—
	16	(7)	Copolymer of monomethoxypolyethyleneglycol monomethacrylate (EO average number of added moles: 90)	61000	4000	0.05	B1	80	15	1	1	0.05	6.0	180	700	7	100.0	—
	17	(8)	Copolymer of monomethoxypolyethyleneglycol monomethacrylate (EO average number of added moles: 90)	261000	4000	0.05	B1	80	15	1	1	0.05	6.0	179	720	7	102.9	—
	18	(5)	Polyethylene glycol	600	600	0.5	B1	80	15	1	1	0.5	6.0	178	700	25	28.0	—
	19	(6)	Polyethylene glycol	300	300	0.5	B1	80	15	1	1	0.5	6.0	180	700	30	23.3	—
Comp. Ex.	1	(1)	Polyethylene glycol	6000	6000	0.05	Ceria particles B51				1	0.05	6.0	183	380	8	47.5	87
	2	(6)	Polyethylene glycol	300	300	0.5	Ceria particles B51				1	0.5	6.1	180	390	15	26.0	—
	3		None	—	—	—	Ceria particles B51				1	—	6.0	185	390	30	13	90

1) Weight average molecular weight of water-soluble polymer
2) Weight average molecular weight of PEG chain in water-soluble polymer
3) Average primary particle diameter of silica particles
4) Average primary particle diameter of granular ceria
5) Average secondary particle diameter of polishing particles measured by dynamic light scattering (DLS)

[0101] [Table 3]

Table 3		Water-soluble polymer (polymer)									Polishing particles (abrasive grain)					Mass ratio	Polishing composition		Polishing rate (nm/min)		Polishing rate ratio	Poly-Si polishing flaws (number)
		No.	Kind	Kind of monomer A	Kind of monomer B	Molar ratio of monomers A	Molar ratio of monomers B	Molecular weight[1]	Molecular weight of PEG part[2]	Content (mass%)	Ceria-coated silica particles	Diameter of silica particles[3] (nm)	Diameter of granular ceria[4] (nm)	Mass ratio of silica/ceria	Content (mass%)	Polymer/Abrasive grain	pH (25°C)	DLS particle diameter[5] (nm)	SiO_2	Poly-Si	SiO_2/Poly-Si	
Ex.	20	(9)	Methacrylic acid/Monomethoxypolyethyleneglycol monomethacrylate (EO number of added moles: 120)	Methacrylic acid	Monomethoxy-polyethyleneglycol monomethacrylate	80	20	56000	5300	0.05	B1	80	15	1	1	0.05	6.1	183	718	8	89.8	16
	21									0.5						0.5	6.0	183	695	6	115.8	—
	22	(10)	Methacrylic acid/Monomethoxypolyethyleneglycol monomethacrylate (EO number of added moles: 120)	Methacrylic acid	Monomethoxy-polyethyleneglycol monomethacrylate	65	35	62000	5300	0.05	B1	80	15	1	1	0.05	6.0	179	720	9	80.0	—
	23	(11)	Methacrylic acid/Monomethoxypolyethyleneglycol monomethacrylate (EO number of added moles: 120)	Methacrylic acid	Monomethoxy-polyethyleneglycol monomethacrylate	90	10	46000	5300	0.05	B1	80	15	1	1	0.05	6.1	180	720	8	90.0	—
	24	(12)	Methacrylic acid/Monomethoxypolyethyleneglycol monomethacrylate (EO number of added moles: 23)	Methacrylic acid	Monomethoxy-polyethyleneglycol monomethacrylate	65	35	40000	1000	0.5	B1	80	15	1	1	0.5	6.0	184	620	10	62.0	—
	25	(9)	Methacrylic acid/Monomethoxypolyethyleneglycol monomethacrylate (EO number of added moles: 120)	Methacrylic acid	Monomethoxy-polyethyleneglycol monomethacrylate	80	20	56000	5300	0.05	B3	45	10	1	1	0.05	6.0	173	350	6	58.3	17
	26										B4	120	20				6.1	200	820	8	102.5	22
	27	(13)	Lauryl methacrylate/Monomethoxypolyethyleneglycol monomethacrylate (EO number of added moles: 120)	Lauryl methacrylate	Monomethoxy-polyethyleneglycol monomethacrylate	5	95	76000	5300	0.05	B1	80	15	1	1	0.05	6.0	178	720	10	72.0	—
	28	(14)	2-Hydroxyethyl methacrylate/Monomethoxypolyethyleneglycol monomethacrylate (EO number of added moles: 23)	2-Hydroxyethyl methacrylate	Monomethoxy-polyethyleneglycol monomethacrylate	50	50	58000	1000	0.5	B1	80	15	1	1	0.5	5.9	180	700	10	70.0	—
	29	(15)	Phosphoric mono-(2-hydroxyethyl) methacrylate/Monomethoxypolyethyleneglycol monomethacrylate (EO number of added moles: 23)	Phosphoric mono-(2-hydroxyethyl) methacrylate	Monomethoxy-polyethyleneglycol monomethacrylate	50	50	64000	1000	0.5	B1	80	15	1	1	0.5	5.9	182	710	8	88.8	—
	30	(16)	Polyvinyl alcohol/Polyethylene glycol (product name: Kollicoat (registred trademark))	Vinyl alcohol	Polyethylene glycol	75	25	19000	6000	0.75	B1	80	15	1	1	0.75	6.0	180	693	7	99.0	—

1) Weight average molecular weight of water-soluble polymer
2) Weight average molecular weight of PEG chain in water-soluble polymer
3) Average primary particle diameter of silica particles
4) Average primary particle diameter of granular ceria
5) Average secondary particle diameter of polishing particles measured by dynamic light scattering (DLS)

[0102] [Table 4]

Table 4		Water-soluble polymer (polymer)									Polishing particles (abrasive grain)					Mass ratio	Polishing composition		Polishing rate (nm/min)		Polishing rate ratio	Poly-Si polishing flaws (number)
		No.	Kind	Kind of monomer A	Kind of monomer B	Molar ratio of monomers A	Molar ratio of monomers B	Molecular weight[1]	Molecular weight of PEG part[2]	Content (mass%)	Ceria-coated silica particles	Particle diameter of silica[3] (nm)	Particle diameter of ceria[4] (nm)	Mass ratio of silica/ceria	Content (mass%)	Polymer/Abrasive grain	pH (25°C)	DLS particle diameter[5] (nm)	SiO_2	Poly-Si	SiO_2/Poly-Si	
Ex.	31	(17)	Methacrylic acid/Monomethoxypolyethyleneglycol monomethacrylate (EO number of added moles: 9)	Methacrylic acid	Monomethoxy-polyethyleneglycol monomethacrylate	80	20	40000	400	0.5	B1	80	15	1	1	0.5	6.0	180	700	20	35.0	—
Comp. Ex.	4	(9)	Methacrylic acid/Monomethoxypolyethyleneglycol monomethacrylate (EO number of added moles: 120)	Methacrylic acid	Monomethoxy-polyethyleneglycol monomethacrylate	80	20	56000	5300	0.05	Ceria particles B51				1	0.05	6.0	181	300	5	60.0	90
	5	(17)	Methacrylic acid/Monomethoxypolyethyleneglycol monomethacrylate (EO number of added moles: 9)	Methacrylic acid	Monomethoxy-polyethyleneglycol monomethacrylate	80	20	40000	400	0.5	Ceria particles B51				1	0.5	6.0	183	370	18	20.6	—
	6		None								B1	80	15	1	1	—	6.0	182	730	45	16.2	—

1) Weight average molecular weight of water-soluble polymer
2) Weight average molecular weight of PEG chain in water-soluble polymer
3) Average primary particle diameter of silica particles
4) Average primary particle diameter of granular ceria
5) Average secondary particle diameter of polishing particles measured by dynamic light scattering (DLS)

[0103] As can be seen from the measurement results of the polishing flaws as to the polishing composition of Example 1 and that of Comparative Example 1, when the polishing compositions containing the ceria-coated silica particles (polishing particles) were used, the polishing flaws were significantly reduced, as compared with the case of using the polishing compositions of comparative examples containing ceria particles as the polishing particles. Therefore, as shown in Tables 2–4, the polishing compositions of Examples 1–31, which contain the ceria-coated silica particles (component B) as the polishing particles and the water-soluble polymer containing a PEG chain (component A) as the polishing aid, achieved more excellent polishing selectivity and fewer polishing flaws on the surface of the polysilicon film than the polishing compositions of the comparative examples.

Industrial Applicability

[0104] The polishing composition of the present invention exhibits high polishing selectivity that enables high-rate polishing of a silicon oxide film while minimizing polishing of a polysilicon film (polishing stop film), and reduces polishing flaws, and thus is suitable for, e.g., a method for manufacturing semiconductor substrates for high density or high integration purpose.

CLAIMS

[1] A silicon oxide film polishing composition for polishing a silicon oxide film on a polysilicon film, comprising components A–C below:

component A: a water-soluble polymer containing a polyethylene glycol chain;

component B: ceria-coated silica particles in which surfaces of silica particles are at least partially coated with granular ceria; and

component C: an aqueous medium.

[2] The silicon oxide film polishing composition according to claim 1, wherein a weight average molecular weight of the polyethylene glycol chain contained in the component A is 1000 or more and 200000 or less.

[3] The silicon oxide film polishing composition according to claim 1 or 2,

wherein the component B represents ceria-coated silica particles in which silica particles that have an average primary particle diameter of 15 nm or more and 300 nm or less are coated with granular ceria that has an average primary particle diameter of 5 nm or more and 40 nm or less, and

a mass ratio of silica to ceria (silica/ceria) is 0.5 or more and 4.0 or less.

[4] The silicon oxide film polishing composition according to any one of claims 1 to 3, wherein the water-soluble polymer further contains an anionic group.

[5] The silicon oxide film polishing composition according to any one of claims 1 to 4, wherein the component A is at least one water-soluble polymer selected from the group consisting of polyethylene glycol, a homopolymer of monomethoxypolyethyleneglycol mono(meth)acrylate, a copolymer of (meth)acrylate and monomethoxypolyethyleneglycol mono(meth)acrylate, a copolymer of alkyl (meth)acrylate and (meth)acrylic acid and monomethoxypolyethyleneglycol mono(meth)acrylate, alkali metal salts of these, and ammonium salts of these.

[6] The silicon oxide film polishing composition according to any one of claims 1 to 5, wherein a content of the component A in the silicon oxide film polishing

composition is 0.05 mass% or more and 5 mass% or less, when a total mass of the water-soluble polymer (component A), the ceria-coated silica particles (component B), and the aqueous medium (component C) is 100 mass%.

[7] The silicon oxide film polishing composition according to any one of claims 1 to 6, wherein a ratio of a polishing rate for the silicon oxide film to a polishing rate for the polysilicon film (a polishing rate for the silicon oxide film / a polishing rate for the polysilicon film) is 50 or more.

[8] A method for manufacturing a semiconductor substrate, comprising polishing a silicon oxide film on a polysilicon film of a substrate to be polished using a polishing composition until the silicon oxide film is removed, the substrate to be polished comprising the silicon oxide film and the polysilicon film arranged under and in contact with the silicon oxide film,

wherein the silicon oxide film polishing composition according to any one of claims 1 to 7 is used as the polishing composition.

[9] A method for polishing a semiconductor substrate, comprising polishing a silicon oxide film on a polysilicon film of a substrate to be polished using a polishing composition until the silicon oxide film is removed, the substrate to be polished comprising the silicon oxide film and the polysilicon film arranged under and in contact with the silicon oxide film,

wherein the silicon oxide film polishing composition according to any one of claims 1 to 7 is used as the polishing composition.

[10] A use of the silicon oxide film polishing composition according to any one of claims 1 to 7 for polishing a silicon oxide film on a polysilicon film.

[11] A use of the silicon oxide film polishing composition according to any one of claims 1 to 7 for polishing, in a step of manufacturing a semiconductor substrate, a silicon oxide film on a polysilicon film of a substrate to be polished until the silicon oxide film is removed, the substrate to be polished comprising the silicon oxide film

and the polysilicon film arranged under and in contact with the silicon oxide film.