

POLISHING COMPOSITION

TECHNICAL FIELD

[0001] The present invention relates to a polishing composition.

BACKGROUND ART

[0002] During polishing of a semiconductor wafer by CMP, a polishing process with multiple stages, e.g., three or four stages, is performed to achieve smoothening and planarization with high precision. The finish-polishing step, which is performed at the last stage, mainly aims at reducing small defects and/or haze (i.e., surface haze).

[0003] Polishing compositions used in the finish-polishing step for a semiconductor wafer generally contain a water-soluble polymer such as hydroxyethyl cellulose (HEC). Water-soluble polymer works to hydrophilize the surface of the semiconductor wafer, thereby preventing, for example, adherence of abrasive grains on the surface, excess chemical etching, and/or aggregation of abrasive grains to prevent damage to the semiconductor wafer. It is known that all this can reduce small defects and/or haze.

[0004] The raw material from which HEC is made is natural cellulose, and thus HEC may contain water-insoluble impurities derived from cellulose. As such, a polishing composition containing HEC may cause small defects due to the effects of such impurities. Further, HEC that is mainly used has a molecular weight ranging from hundreds of thousands to millions; the larger the molecular weight, the more likely the filter is to be clogged, and thus it is difficult for a filter with a small aperture size to allow liquid to pass therethrough. As such, when a water-soluble polymer with a large molecular weight is used, coarse particles will be difficult to remove. Further, since aggregation of abrasive grains can easily occur, there are concerns about the long-term stability of the polishing composition.

[0005] JP 2012-216723 A discloses a polishing composition containing at least one water-soluble polymer selected from a vinyl alcohol-based resins having 1,2-diol structural unit.

[0006] Japanese Patent No. 6245939 discloses a silicon wafer polishing solution composition containing a modified polyvinyl alcohol-based polymer having a polyalkylene-oxy group in a side chain.

[0007] JP 2016-56220 A discloses a slurry composition containing a

water-soluble polymer in which a polyalkylene oxide structural unit and a polyvinyl alcohol structural unit form a stem or a side chain.

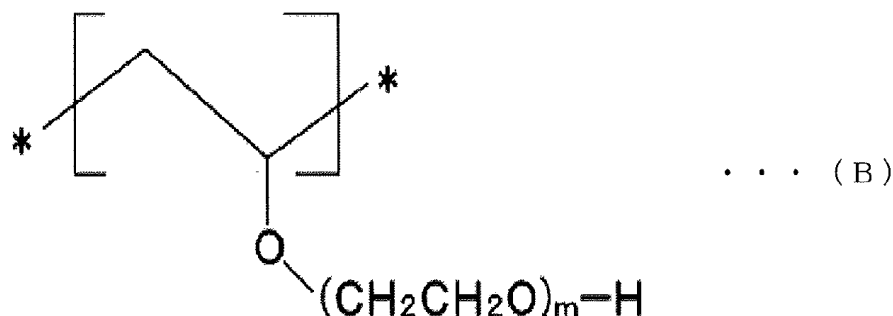
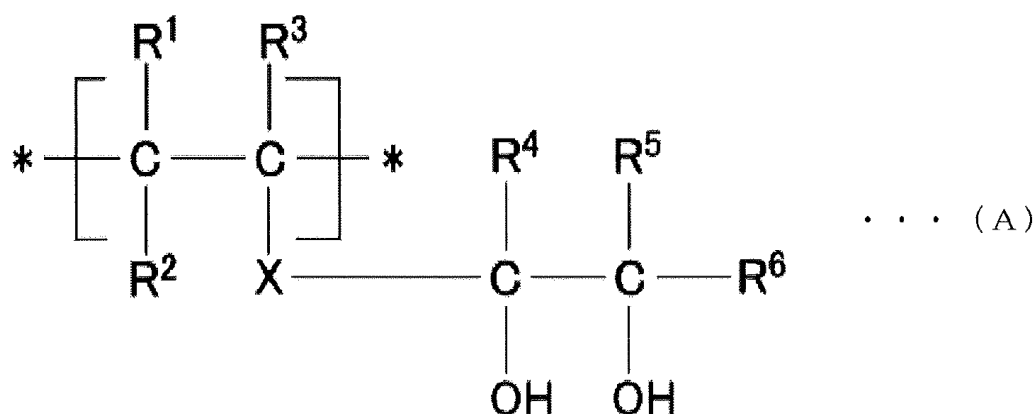
DISCLOSURE OF THE INVENTION

[0008] Design rules for semiconductor devices have become finer and finer in recent years, which requires stricter control of small defects and/or haze on the surface of a semiconductor wafer.

[0009] An object of the present invention is to provide a polishing composition that can further reduce small defects and haze on a semiconductor wafer after polishing.

[0010] A polishing composition according to an embodiment of the present invention includes: an abrasive; a basic compound; a vinyl alcohol-based resin having a 1,2-diol structural unit represented by the following general formula, (A); and a vinyl alcohol-based resin having a polyoxyethylene structural unit represented by the following general formula, (B):

[Chem. 1]



Here, each of R¹, R² and R³ independently indicates a hydrogen atom or an organic group, X indicates a single bond or a joining chain, and each of R⁴, R⁵ and R⁶ independently indicates a hydrogen atom or an organic group. m is

an integer ranging from 1 to 1,000.

[0011] The present invention reduces small defects and haze on a semiconductor wafer after polishing compared with conventional techniques.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] [FIG. 1] FIG. 1 is a graph for comparing polishing properties for different contents of PEG-added PVA.

[FIG. 2] FIG. 2 is a graph for comparing polishing properties for different contents of PEG-added PVA.

[FIG. 3] FIG. 3 is a graph for comparing polishing properties for different contents of PEG-added PVA.

[FIG. 4] FIG. 4 is a graph for comparing polishing properties for different contents of PEG-added PVA.

[FIG. 5] FIG. 5 is a graph for comparing polishing properties for different contents of PEG-added PVA.

[FIG. 6] FIG. 6 is a graph for comparing polishing properties for different contents of diol-modified PVA.

[FIG. 7] FIG. 7 is a graph for comparing the polishing properties of polishing compositions having the same total amount of polymers with different polymer breakdowns.

[FIG. 8] FIG. 8 is a graph for comparing the polishing properties of polishing compositions using a diol-modified PVA and the polishing properties of a polishing composition using normal PVA which is not diol-modified PVA.

[FIG. 9] FIG. 9 is a graph for comparing the polishing properties of polishing compositions using both diol-modified PVA and a polymer other than PEG-added PVA.

[FIG. 10] FIG. 10 is a graph for comparing polishing properties for different contents of PEG-added PVA.

[FIG. 11] FIG. 11 is a group for comparing polishing properties for different contents of PEG-added PVA.

EMBODIMENTS FOR CARRYING OUT THE INVENTION

[0013] To solve the above-stated problems, the present inventors conducted various investigations, and found that using both a vinyl alcohol-based resin having a 1,2-diol structural unit and a vinyl alcohol-based resin having, in a

side chain, a polyoxyethylene group will reduce small defects and haze compared with conventional techniques. Although the mechanism therefor is unknown, it is thought that these two resins have different adherences with respect to a wafer, and that these two act complementarily to reduce small defects and, in addition, increase the effect of etching prevention and increase the ability to remove steps, thereby reducing haze.

[0014] The present invention was made based on these findings. A polishing composition according to an embodiment of the present invention will now be described in detail.

[0015] A polishing composition according to an embodiment of the present invention includes: an abrasive; a basic compound; a vinyl alcohol-based resin having a 1,2-diol structural unit (hereinafter referred to as “diol-modified PVA”); and a vinyl alcohol-based resin having, in a side chain, a polyoxyethylene group (hereinafter referred to as “PEG-added PVA”).

[0016] The abrasive used may be an abrasive that is commonly used in this field, and may be, for example, colloidal silica, fumed silica, colloidal alumina, fumed alumina or ceria; colloidal silica and fumed silica are particularly suitable. The abrasive is not limited to any particular grain size, and may be an abrasive with a mean secondary particle size of 30 to 100 nm, for example.

[0017] The content of the abrasive is not limited to any particular value, and may be 0.10 to 20 % by mass of the entire polishing composition, for example. Prior to use, the polishing composition is diluted by a factor of 10 to 40 for polishing. The polishing composition of the present embodiment is preferably diluted, prior to use, such that the concentration of the abrasive is 100 to 5000 ppm (ppm by mass; the same applies hereinafter). There is a tendency that the higher the concentration of the abrasive, the less small defects and/or haze. A lower limit for the concentration of the abrasive after dilution is preferably 1000 ppm, and more preferably 2000 ppm. An upper limit for the concentration of the abrasive after dilution is preferably 4000 ppm, and more preferably 3000 ppm.

[0018] The basic compound efficiently reacts with the wafer surface and contributes to polishing properties in chemical mechanical polishing (CMP). The basic compound may be, for example, an amine compound or an inorganic alkali compound.

[0019] Examples of amine compounds include primary amines, secondary

amines, tertiary amines, quaternary ammonium and hydroxides thereof, heterocyclic amines and the like. Specific examples include ammonia, tetramethylammonium hydroxide (TMAH), tetraethylammonium hydroxide (TEAH), tetrabutylammonium hydroxide (TBAH), methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, hexylamine, cyclohexylamine, ethylenediamine, hexamethylenediamine, diethylenetriamine (DETA), triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, monoethanolamine, diethanolamine, triethanolamine, N-(β -aminoethyl)ethanolamine, anhydrous piperazine, piperazine hexahydrate, 1-(2-aminoethyl)piperazine, N-methylpiperazine, piperazine hydrochloride, guanidine carbonate, and the like.

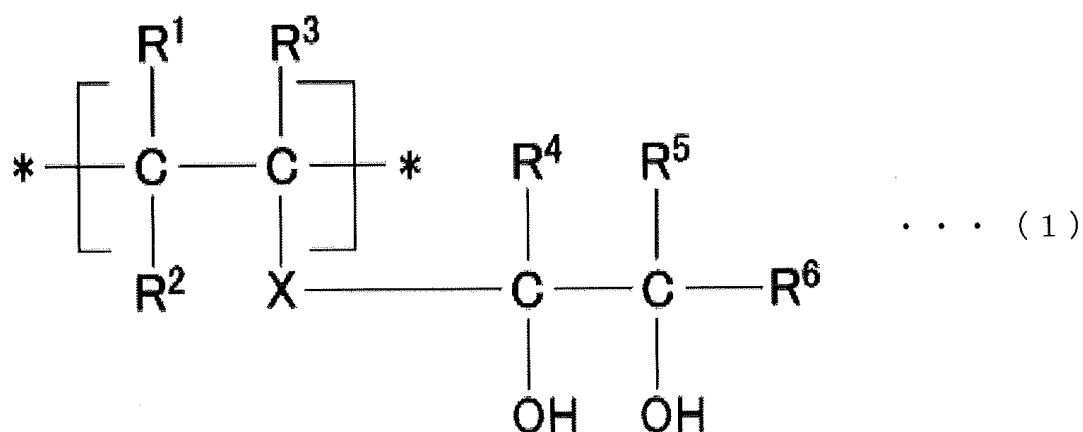
[0020] Examples of inorganic alkali compounds include alkali metal hydroxides, alkali metal salts, alkaline earth metal hydroxides, alkaline earth metal salts, and the like. Specific examples of inorganic alkali compounds include potassium hydroxide, sodium hydroxide, potassium hydrogencarbonate, potassium carbonate, sodium hydrogencarbonate, sodium carbonate, and the like.

[0021] One of the above-listed basic compounds may be used alone, or two or more thereof may be mixed and used. Particularly preferable ones of the above-listed basic compounds are alkali metal hydroxides, alkali metal salts, ammonia, amines, ammonium salts, and quaternary ammonium hydroxides.

[0022] The content of the basic compound (when two or more basic compounds are contained, their total amount) is not limited to a particular value, and may be such that the mass ratio between the abrasive and the basic compound is in a range of 1:0.001 to 1:0.10, for example. Prior to use, the polishing composition according to the present embodiment is preferably diluted such that the concentration of the basic compound is in a range of 5 to 200 ppm.

[0023] The diol-modified PVA is a vinyl alcohol-based resin having a 1,2-diol structural unit represented by the following general formula, (1):

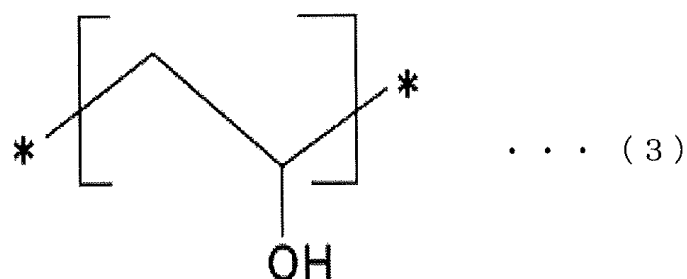
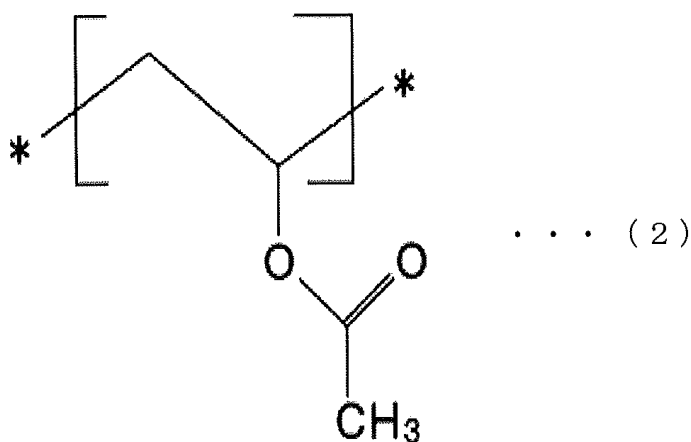
[Chem. 2]



Here, each of R¹, R² and R³ independently indicates a hydrogen atom or an organic group, X indicates a single bond or a joining chain, and each of R⁴, R⁵ and R⁶ independently indicates a hydrogen atom or an organic group.

[0024] “Vinyl alcohol-based resin” means a water-soluble polymer including a structural unit represented by the following formulas, (2) and (3).

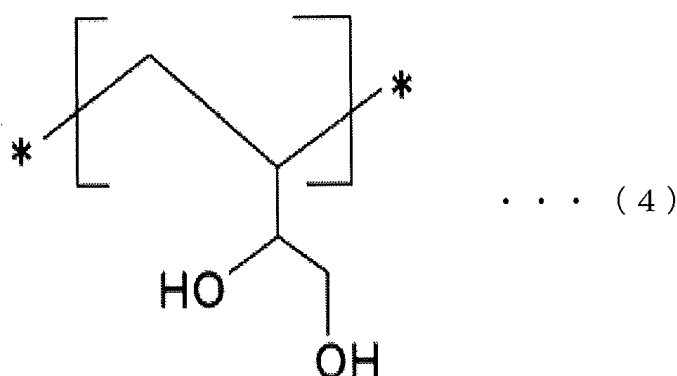
[0025] [Chem. 3]



[0026] The diol-modified PVA has a 1,2-diol structural unit represented by formula (1), in addition to the structural unit represented by formulas (2) and (3). This reduces crystallization of polyvinyl alcohol and further

reduces small defects and/or haze on the semiconductor wafer after polishing. The amount of modification of the 1,2-diol structural unit in the polymer is not limited to any particular value, and may be 1 to 20 mol %, for example. [0027] It is particularly preferable that, in the diol-modified PVA, every one of R¹ to R⁶ in the 1,2-diol structural unit represented by general formula (1) is a hydrogen atom and X is a single bond. That is, a diol-modified PVA having a structural unit represented by the following formula, (4), is particularly preferable:

[Chem. 4]



[0028] The average degree of polymerization of the diol-modified PVA is not limited to any particular value, and may be 200 to 3000, for example. The average degree of polymerization of the diol-modified PVA may be measured in accordance with JIS K 6726.

[0029] Preferably, the diol-modified PVA has a degree of saponification of 80 to 95 mol %. Typically, a polyvinyl alcohol-based resin used in a polishing composition is a completely saponified product (with a degree of saponification of 98 mol % or above); however, in a diol-modified PVA, using a partially saponified product, rather than a completely saponified one, results in a larger reduction in small defects and/or haze. Although the mechanism therefor is unknown, one possible reason is that using a partially saponified product reduces hydrogen bonding between hydroxyl groups, which weakens the bonding between molecules and makes it easier for polymers to dissolve in water, thus preventing production of undissolved matters and/or gelatinous foreign matters. Another possible reason is that the increased content of vinyl acetate groups, which are hydrophobic groups, strengthens hydrophobic interaction with the semiconductor wafer, thus increasing the ability to protect the semiconductor wafer.

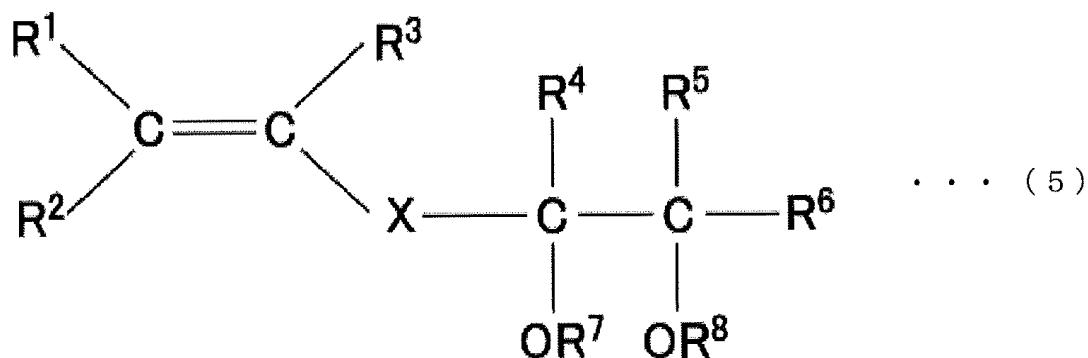
[0030] The degree of saponification of the diol-modified PVA is more preferably 85 to 90 mol %. The degree of saponification of the diol-modified PVA is measured in accordance with JIS K 6726, as is the case with normal polyvinyl alcohol.

[0031] The content of the diol-modified PVA (when two or more such PVAs are contained, their total amount) is not limited to any particular value, and may be such that the mass ratio between the abrasive and the diol-modified PVA is 1:0.001 to 1:0.40. A lower limit for the mass ratio of the diol-modified PVA to the abrasive is preferably 0.004, and more preferably 0.008.

[0032] Prior to use, the polishing composition according to the present embodiment is preferably diluted such that the concentration of the diol-modified PVA is 10 to 200 ppm. There is a tendency that the higher the concentration of the diol-modified PVA after dilution, the less small defects and/or haze. A lower limit for the concentration of the modified PVA after dilution is preferably 10 ppm, and more preferably 20 ppm.

[0033] The diol-modified PVA may be produced by, for example, saponifying a copolymer of a vinyl ester-based monomer and a compound represented by the following general formula, (5).

[0034] [Chem. 5]

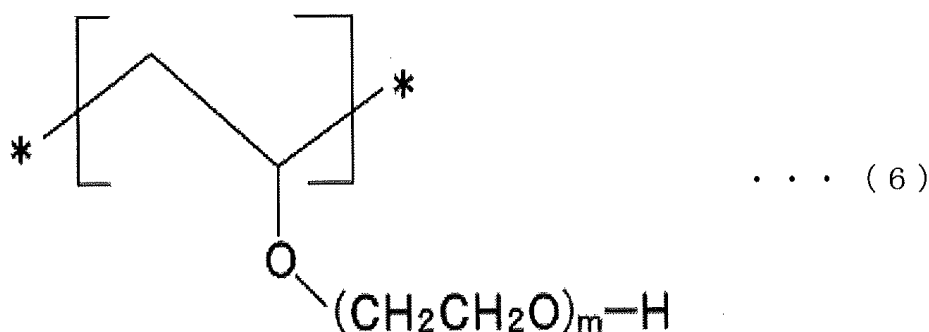


Here, each of R¹, R² and R³ independently indicates a hydrogen atom or an organic group, X indicates a single bond or a joining chain, each of R⁴, R⁵ and R⁶ independently indicates a hydrogen atom or an organic group, and each of R⁷ and R⁸ independently indicates a hydrogen atom or R⁹-CO- (R⁹ is an alkyl group with one to nine carbon atoms).

[0035] The polishing composition according to the present embodiment further includes a PEG-added PVA, in addition to the above-described diol-modified PVA. The PEG-added PVA is a vinyl alcohol-based resin

having a polyoxyethylene structural unit represented by the general formula shown below, (6). The PEG-added PVA includes, in addition to the structural unit represented by formulas (2) and (3), a polyoxyethylene structural unit represented by formula (6).

[0036] [Chem. 6]



Here, m is an integer of 1 to 1000.

[0037] Using both the diol-modified PVA and PEG-added PVA reduces small defects and haze compared with conventional techniques. Although the mechanism therefor is unknown, it is thought that these two resins have different adherences with respect to a wafer, and that these two act complementarily to reduce small defects and, in addition, increase the effect of etching prevention and increase the ability to remove steps, thereby reducing haze.

[0038] The average degree of polymerization of the PEG-added PVA is not limited to any particular value, and may be 200 to 3000, for example. The average degree of polymerization of the PEG-added PVA may be measured in accordance with JIS K 6726.

[0039] Although not limiting, the presence ratio between the polyoxyethylene backbone and the polyvinyl alcohol backbone in the PEG-added PVA may be, for example, in mol %, 5:95 to 40:60, and preferably 10:90 to 30:70. m is preferably 2 to 300, and more preferably 3 to 200.

[0040] The content of the PEG-added PVA (when two or more such PVAs are contained, their total amount) is not limited to any particular value, and may be such that, for example, the mass ratio between the abrasive and the PEG-added PVA is 1:0.001 to 1:0.40, for example. A lower limit for the mass ratio of the PEG-added PVA to the abrasive is preferably 0.004, and more preferably 0.008.

[0041] Prior to use, the polishing composition according to the present

embodiment is preferably diluted such that the concentration of the PEG-added PVA is 3 to 200 ppm. There is a tendency that the higher the concentration of the PEG-added PVA after dilution, the less small defects and/or haze. A lower limit for the concentration of the PEG-added PVA after dilution is preferably 10 ppm, and more preferably 20 ppm.

[0042] A lower limit for the ratio of the content of the PEG-added PVA to the content of the diol-modified PVA is preferably 3 parts by mass of PEG-added PVA to 20 parts by mass of diol-modified PVA, more preferably 1 part by mass of PEG-added PVA to 2 parts by mass of diol-modified PVA, still more preferably 3 parts by mass of PEG-added PVA to 5 parts by mass of diol-modified PVA. An upper limit for the ratio of the content of the PEG-added PVA to the content of the diol-modified PVA is preferably 5 parts by mass of PEG-added PVA to 1 part by mass of diol-modified PVA, more preferably 2 parts by mass of PEG-added PVA to 1 part by mass of diol-modified PVA, and still more preferably 3 parts by mass of PEG-added PVA to 2 parts by mass of diol-modified PVA.

[0043] The polishing composition according to the present embodiment may further include a non-ionic surfactant. The inclusion of the non-ionic surfactant further reduces small defects and/or haze.

[0044] Examples of non-ionic surfactants suitable for the polishing composition of the present embodiment include ethylenediamine tetrapolyoxyethylene polyoxypropylene (poloxamine), poloxamer, polyoxyalkylene alkyl ethers, polyoxyalkylene fatty acid esters, polyoxyalkylene alkylamines, polyoxyalkylene methylglucoside, and the like.

[0045] Examples of polyoxyalkylene alkyl ethers include polyoxyethylene lauryl ethers, polyoxyethylene cetyl ethers, polyoxyethylene stearyl ethers, and the like. Examples of polyoxyalkylene fatty acid esters include polyoxyethylene monolaurate and polyoxyethylene monostearate. Examples of polyoxyalkylene alkylamines include polyoxyethylene laurylamines and polyoxyethylene oleylamines. Examples of the polyoxyalkylene methyl glucoside include polyoxyethylene methylglucoside and polyoxypropylene methylglucoside.

[0046] The content of the non-ionic surfactant (when two or more non-ionic surfactants are contained, their total amount) is not limited to any particular value, and may be such that the mass ratio between the abrasive and the non-ionic surfactant is 1:0.0001 to 1:0.015, for example. Prior to use, the

polishing composition according to the present embodiment is preferably diluted such that the concentration of the non-ionic surfactant is 0.5 to 30 ppm.

[0047] The polishing composition according to the present embodiment may further include a pH controller. The pH of the polishing composition according to the present embodiment is preferably 8.0 to 12.0.

[0048] The polishing composition according to the present embodiment may include, in addition to the above, any ingredient(s) that is/are generally known in the field of polishing compositions.

[0049] The polishing composition according to the present embodiment is prepared by appropriately mixing the abrasive, basic compound, diol-modified PVA, PEG-added PVA, and other ingredients and then adding water. Alternatively, the polishing composition according to the present embodiment may be prepared by successively mixing with water the abrasive, basic compound, diol-modified PVA, PEG-added PVA, and other ingredients. These ingredients may be mixed by a means that is typically used in the technical field of polishing compositions, such as a homogenizer or ultrasonics.

[0050] The polishing composition described above is diluted with water to an appropriate concentration before being used to polish a semiconductor wafer.

[0051] The polishing composition according to the present embodiment is particularly suitable for finish-polishing of a silicon wafer.

EXAMPLES

[0052] The present invention will now be described more specifically with reference to examples. The present invention is not limited to these examples.

[0053] [Polishing Example 1]

Polishing compositions labeled inventive examples 1 to 11 and comparative examples 1 to 15 shown in Table 1 were prepared.

[0054] [Table 1]

	Abrasive	NH ₄ OH	Diol-modified PVA		PEG-added PVA	Other polymers	Defects (number of defects)	Haze
	Content (ppm)	Content (ppm)	Type	Content (ppm)	Content (ppm)			
Inv. ex. 1	2300	20	A	20	3	—	2362	144
Inv. ex. 2	2300	20	A	20	10	—	1130	134
Inv. ex. 3	2300	20	A	20	20	—	615	134
Inv. ex. 4	1100	20	A	20	3	—	1859	143
Inv. ex. 5	1100	20	A	20	20	—	648	133
Inv. ex. 6	2300	20	B	20	3	—	433	137
Inv. ex. 7	2300	20	B	20	10	—	220	134
Inv. ex. 8	2300	20	B	20	20	—	178	133
Inv. ex. 9	1100	20	B	20	3	—	571	137
Inv. ex. 10	1100	20	B	20	20	—	174	132
Inv. ex. 11	1100	20	C	20	10	—	519	134
Comp. ex. 1	2300	20	A	20	—	—	2454	152
Comp. ex. 2	1100	20	A	20	—	—	2828	150
Comp. ex. 3	2300	20	B	20	—	—	541	142
Comp. ex. 4	1100	20	B	20	—	—	1215	144
Comp. ex. 5	1100	20	C	20	—	—	776	141
Comp. ex. 6	1100	20	—	—	20	—	3875	131
Comp. ex. 7	2300	20	A	40	—	—	2067	151
Comp. ex. 8	1100	20	A	40	—	—	1844	150
Comp. ex. 9	2300	20	—	—	3	PVA: 20 ppm	5853	168
Comp. ex. 10	2300	20	—	—	20	PVA: 20 ppm	2956	145
Comp. ex. 11	2300	20	—	—	3	HEC: 20 ppm	above 50000	141
Comp. ex. 12	2300	20	—	—	20	HEC: 20 ppm	above 50000	137
Comp. ex. 13	2300	20	A	20	—	HEC: 3 ppm	5645	162
Comp. ex. 14	2300	20	A	20	—	HEC: 20 ppm	8304	161
Comp. ex. 15	2300	20	A	20	—	PVP: 3 ppm	3387	156

[0055] All the values of contents in Table 1 represent contents after dilution. The abrasive used was a colloidal silica with a mean secondary particle size of 65 nm. “NH₄OH” means ammonia aqueous solution.

[0056] Three diol-modified PVAs were used. “A” in the column for “Type” indicates butenediol vinyl alcohol polymer with a degree of polymerization of 450 and a degree of saponification of 99.0 mol % or higher. “B” indicates butenediol vinyl alcohol polymer with a degree of polymerization of 450 and a degree of saponification of 86.0 mol %. “C” indicates butenediol vinyl alcohol polymer with a degree of polymerization of 300 and a degree of saponification of 89.0 mol %.

[0057] The PEG-added PVA used was a polyvinyl alcohol with polyethylene glycol introduced therein, with a degree of polymerization of 500 and a degree of saponification of 98.5 mol % or higher (EF-05 from Japan Vam & Poval Co., Ltd.).

[0058] “PVA” in the column for “Other polymers” indicates polyvinyl alcohol

with a degree of polymerization of 500 and a degree of saponification of 98.5 mol %. “HEC” indicates hydroxyethyl cellulose with a weight-average molecular weight of 800,000. “PVP” indicates polyvinylpyrrolidone with a weight-average molecular weight of 2500.

[0059] These inventive- and comparative-example polishing compositions were used to polish a 12-inch silicon wafer. The silicon wafer used had p-type conductivity and had a resistivity not lower than 0.1 Ωcm and lower than 100 Ωcm . The surface being polished was plane <100>. The polishing equipment used was an SPP800S single-side polisher from Okamoto Machine Tool Works, Ltd. The polishing pad used was a suede pad. Each polishing composition was diluted by a factor of 31, and was supplied at a supply rate of 1 liter/min. Polishing was performed for two minutes, where the rate of rotation of the surface plate was 40 rpm, the rate of rotation of the carrier 39 rpm, and the polishing load 100 gf/cm². Prior to polishing with the inventive- and comparative-example polishing compositions, preliminary polishing was performed for three minutes using polishing slurry Nanopure (registered trademark) NP7050S (from Nitta Haas Incorporated).

[0060] Small defects and haze on the silicon wafer after polishing were measured. Small defects were measured by a wafer surface tester MAGICS M5640 (from Lasertec Corporation). Haze was measured by a wafer surface tester LS6600 (from HITACHI Engineering Co., Ltd.). The results are shown in the columns for “Defects” and “Haze” in Table 1 above.

[0061] FIGS. 1 to 5 are graphs for comparing polishing properties for different contents of PEG-added PVA.

[0062] Specifically, FIG. 1 is a graph for comparing polishing properties for the following fixed conditions: the abrasive content was 2300 ppm, the NH₄OH content was 20 ppm, the type of the diol-modified PVA was “A” and the diol-modified PVA content was 20 ppm, and the following varying condition: the PEG-added PVA content was zero (comparative example 1), 3 ppm (inventive example 1), 10ppm (inventive example 2), or 20 ppm (inventive example 3).

[0063] FIG. 2 is a graph for comparing polishing properties for the following fixed conditions: the abrasive content was 1100 ppm, the NH₄OH content was 20 ppm, the type of the diol-modified PVA was “A” and the diol-modified PVA content was 20 ppm, and the following varying condition: the

PEG-added PVA content was zero (comparative example 2), 3 ppm (inventive example 4), or 20ppm (inventive example 5).

[0064] FIG. 3 is a graph for comparing polishing properties for the following fixed conditions: the abrasive content was 2300 ppm, the NH_4OH content was 20 ppm, the type of the diol-modified PVA was “B” and the diol-modified PVA content was 20 ppm, and the following varying condition: the PEG-added PVA content was zero (comparative example 3), 3 ppm (inventive example 6), 10 ppm (inventive example 7) or 20 ppm (inventive example 8).

[0065] FIG. 4 is a graph for comparing polishing properties for the following fixed conditions: the abrasive content was 1100 ppm, the NH_4OH content was 20 ppm, the type of the diol-modified PVA was “B” and the diol-modified PVA content was 20 ppm, and the following varying condition: the PEG-added PVA content was zero (comparative example 4), 3 ppm (inventive example 9), or 20 ppm (inventive example 10).

[0066] FIG. 5 is a graph for comparing polishing properties for the following fixed conditions: the abrasive content was 1100 ppm, the NH_4OH content was 20 ppm, the type of the diol-modified PVA was “C” and the diol-modified PVA content was 20 ppm, and the following varying condition: the PEG-added PVA content was zero (comparative example 5) or 10 ppm (inventive example 11).

[0067] FIGS. 1 to 5 show that every one of the diol-modified PVAs used here, used together with the PEG-added PVA, reduced small defects and haze. Further, FIGS. 1 to 4 show a tendency that the higher the PEG-added PVA content, the less small defects and haze.

[0068] FIG. 6 is a graph for comparing the polishing properties for different types of diol-modified PVAs. Specifically, it is a graph for comparing polishing properties for the following varying condition: the diol-modified PVA was zero (comparative example 6), “A” in 20 ppm (inventive example 5), “B” in 20 ppm (inventive example 10), or “C” in 20 ppm (inventive example 11). The PEG-added PVA content was 10 ppm for the example with the type-C diol-modified PVA (i.e., inventive example 11), and 20 ppm for all the other examples.

[0069] FIG. 6, too, shows that using both diol-modified PVA and PEG-added PVA reduced small defects and haze. Further, among the diol-modified PVAs used here, “B” and “C” with low degrees of saponification had better polishing properties than “A”.

[0070] FIG. 7 is a graph for comparing the polishing properties of polishing compositions having the same total amount of polymers with different polymer breakdowns. Specifically, it is a graph for comparing the polishing properties of polishing compositions containing diol-modified PVA in 40 ppm and no other polymers (comparative examples 7 and 8) and the polishing properties of polishing compositions containing diol-modified PVA and PEG-added PVA, each in 20 ppm (inventive examples 3 and 5). FIG. 7, too, shows that using both diol-modified PVA and PEG-added PVA reduced small defects and haze.

[0071] FIG. 8 is a graph for comparing the polishing properties of polishing compositions using diol-modified PVA (inventive examples 3 and 8) and the polishing properties of a polishing composition using normal PVA which is not diol-modified PVA (comparative example 10). FIG. 8 shows that the improvement in polishing properties resulting from the PEG-added PVA being also used is an effect specific to the diol-modified PVA, and normal PVA does not provide such an effect.

[0072] Further, although now shown, the polishing compositions using both PEG-added PVA and HEC (comparative examples 11 and 12) had numbers of small defects exceeding the detection limit. This, too, shows that the improvement in polishing properties resulting from the PEG-added PVA being also used is an effect specific to the diol-modified PVA.

[0073] FIG. 9 is a graph for comparing the polishing properties of polishing compositions using both diol-modified PVA and a polymer other than PEG-added PVA. Specifically, it is a graph for comparing the polishing properties of a polishing composition using diol-modified PVA and no other polymers (comparative example 1), a polishing composition with 3 ppm HEC in addition to diol-modified PVA (comparative example 13), a polishing composition with 20 ppm HEC in addition to diol-modified PVA (comparative example 14), and a polishing composition with 3 ppm PVP in addition to diol-modified PVA (comparative example 15). It shows that adding polymers other than PEG-added PVA to diol-modified PVA deteriorated, instead of improved, the polishing properties.

[0074] [Polishing Example 2]

The polishing compositions labeled inventive examples 12 and 13 and comparative examples 16 and 17 shown in Table 2 were prepared. Again, all the values of contents in Table 2 represent contents after dilution. The

compositions in Polishing Example 2 contained, in addition to the ingredients shown in Table 2, a non-ionic surfactant constituted by ethylenediamine tetrapolyoxyethylene polyoxypropylene with a weight-average molecular weight of 7240 and polyoxypropylene methylglucoside with a weight-average molecular weight of 775, where their contents after dilution were 2.9 ppm and 2.4 ppm, respectively. The details about the abrasive, NH_4OH , diol-modified PVA, and PEG-added PVA are the same as in Polishing Example 1.

[0075] [Table 2]

	Silica	NH_4OH	Diol-modified PVA		PEG-added PVA	Defects (number of defects)	Haze
	Content (ppm)	Content (ppm)	Type	Content (ppm)	Content (ppm)		
Inv. ex. 12	1100	20	A	20	20	70	130
Inv. ex. 13	1100	20	C	20	10	77	127
Comp. ex. 16	1100	20	A	20	—	149	129
Comp. ex. 17	1100	20	C	20	—	126	127

[0076] The polishing compositions labeled inventive examples 12 and 13 and comparative examples 16 and 17 were used to polish a silicon wafer in the same manner as in Polishing Example 1, and small defects and haze were measured. The results are shown in Table 2.

[0077] A comparison with Polishing Example 1 shows that the compositions containing a non-ionic surfactant had significantly reduced small defects and haze.

[0078] FIG. 10 is a graph for comparing polishing properties for the following fixed conditions: the abrasive content was 1100 ppm, the NH_4OH content was 20 ppm, the type of the diol-modified PVA was “A” and the diol-modified PVA content was 20 ppm, and the following varying condition: the PEG-added PVA content was zero (comparative example 16) or 20 ppm (inventive example 12).

[0079] FIG. 11 is a graph for comparing polishing properties for the following fixed conditions: the abrasive content was 1100 ppm, the NH_4OH content was 20 ppm, the type of the diol-modified PVA was “C” and the diol-modified PVA content was 20 ppm, and the following varying condition: the PEG-added PVA content was zero (comparative example 17) or 10 ppm

(inventive example 13).

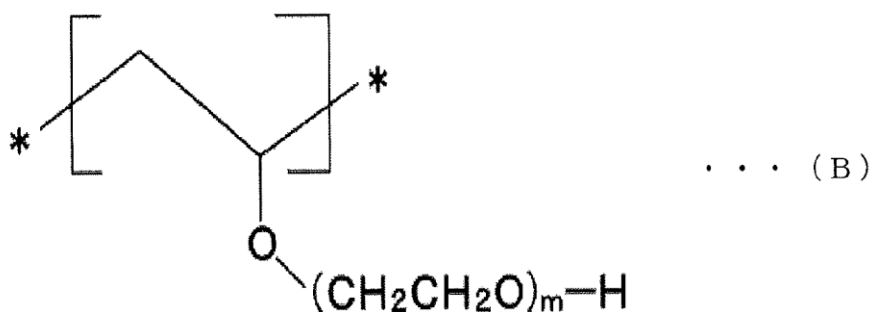
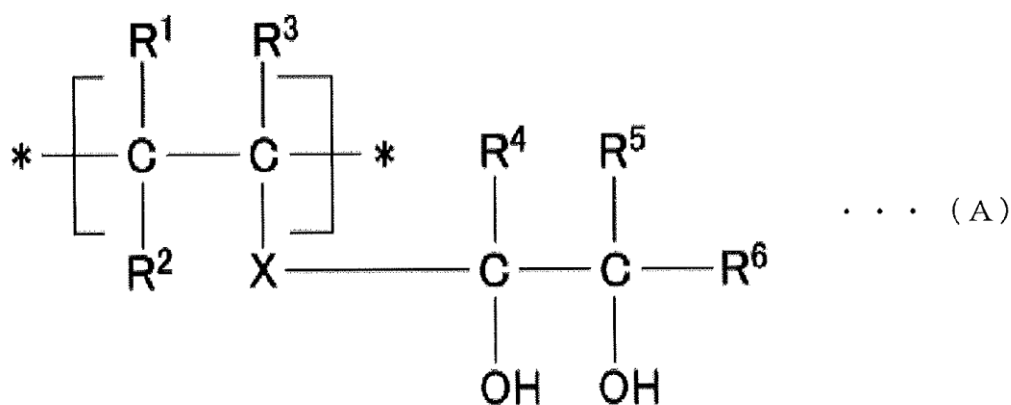
[0080] FIGS. 10 and 11 show that, in polishing compositions containing a non-ionic surfactant, too, using both diol-modified PVA and PEG-added PVA improved polishing properties. Specifically, small defects were further reduced, while haze was kept below acceptable levels.

[0081] Embodiments of the present invention have been described. The above-described embodiments are exemplary only, intended to allow the present invention to be carried out. Accordingly, the present invention is not limited to the above-described embodiments, and the above-described embodiments, when carried out, may be modified as appropriate without departing from the spirit of the invention.

CLAIMS

1. A polishing composition, comprising:
an abrasive;
a basic compound;
a vinyl alcohol-based resin having a 1,2-diol structural unit represented by the following general formula, (A); and
a vinyl alcohol-based resin having a polyoxyethylene structural unit represented by the following general formula, (B):

[Chem. 1]



where each of R¹, R² and R³ independently indicates a hydrogen atom or an organic group, X indicates a single bond or a joining chain, and each of R⁴, R⁵ and R⁶ independently indicates a hydrogen atom or an organic group, and where m is an integer ranging from 1 to 1,000.

2. The polishing composition according to claim 1, further comprising: a non-ionic surfactant.
3. The polishing composition according to claim 1 or 2, wherein the basic compound is one or more selected from the group consisting of alkali

metal hydroxides, alkali metal salts, ammonia, amines, ammonium salts, and quaternary ammonium hydroxides.