DESCRIPTION

Title of Invention: ETCHING FLUID FOR FORMING TEXTURE AND TEXTURE-FORMING METHOD USING SAME

Technical Field

[0001]

The present invention relates to an etching fluid and an etching method for forming an irregular structure, called a texture, on a surface of a silicon substrate.

Background Art

[0002]

Crystalline silicon substrates used for solar cells are subjected to a surface structure treatment, or texturing as it is also called, to reduce the reflectance of light at a substrate surface for efficient absorption of light.

[0003]

In one conventional approach, a method is used that forms, for example, a pyramidal texture structure by dipping and etching a monocrystalline silicon substrate in an alkaline solution such as sodium hydroxide and potassium hydroxide. It is known that a texture structure of a uniform size or shape can be formed with the use of additives other than the alkali component in the etching fluid.

[0004]

For example, a mixture of a sodium hydroxide or potassium hydroxide aqueous solution and isopropyl alcohol (IPA) is used as an etching fluid for forming such a texture. A texture can be formed by dipping a silicon substrate in such an etching fluid for 10 to 30 minutes under 60 to 95°C heated conditions.

[0005]

IPA is used with the intent to moderately facilitate alkali etching of silicon, and form a pyramidal texture on a silicon substrate. IPA is the most widely known material for

achieving this goal. A problem of IPA, however, is that its boiling point of about 82°C, nearly the same as the etching temperature, which causes IPA to vaporize during the treatment, and easily changes the composition of the etching fluid. Methods using IPA are also not desirable considering the reported low yield of the substrate treatment, and the difficulty in handling due to the low flash point of IPA. For these and other reasons, it has become difficult with the IPA-based etching fluid to meet the increasing demands for improved performance of the increasing popular solar-cell silicon substrates. Among such requirements are control of texture size or shape, high yield in mass production, ease of handling, and high safety.

[0006]

Aside from IPA, a variety of components have been proposed for an etching fluid intended for texture formation. However, as it currently stands, no etching fluids or additives are available that are satisfactory in all respects, including texture formation, and quality management such as management of concentration during use (PTLs 1 to 6).

[0007]

For slicing of a silicon substrate, the trend has been shifting from the conventional loose-abrasive grain method to the more current fixed-abrasive grain method. These methods produce different substrate surface states after the slicing, and an etching fluid usable for a silicon substrate produced by using the conventional loose-abrasive grain method is not always directly applicable to a silicon substrate produced by using the fixed-abrasive grain method.

Citation List

Patent Literature

[0008]

PTL 1: JP-A-2000-183378

PTL 2: WO2007/129555

PTL 3: JP-A-2009-123811

PTL 4: JP-A-2002-57139

PTL 5: JP-A-2007-258656

PTL 6: JP-A-2010-141139

Summary of Invention

Technical Problem

[0009]

The present invention has been made in view of the foregoing problems, and it is an object of the present invention to provide a silicon substrate etching fluid for forming texture with which a desirable low-reflectance texture can be uniformly and stably formed on a substrate surface without causing the components of the etching fluid composition to vaporize in the common working temperature range of 60°C to 95°C, and that is applicable to both a silicon substrate produced by using the loose-abrasive grain method, and a silicon substrate produced by using the fixed-abrasive grain method.

Solution to Problem

[0010]

The etching fluid of the present invention is an etching fluid for forming irregularities on a silicon substrate surface. In order to solve the foregoing problems, the etching fluid contains:

(A) an alkali component;

(B)a phosphonic acid derivative or a salt thereof; and

(C) a compound that contains at least one selected from the group consisting of a carboxy group, a sulfo group, a carboxy or sulfo group forming a salt, and a carboxymethyl group within the molecule.

[0011]

In the etching fluid, the alkali component (A) may preferably be sodium hydroxide or potassium hydroxide.

[0012]

The phosphonic acid derivative or a salt thereof (B) may preferably be 1-hydroxyethylidene-1,1-diphosphonic acid or a salt thereof.

[0013]

The compound (C) may be at least one selected from the group consisting of carboxylic acid, a salt of carboxylic acid, sulfonic acid, and a salt of sulfonic acid.

[0014]

More specifically, the compound (C) may be a compound represented by the following general formula (I);

[0015]

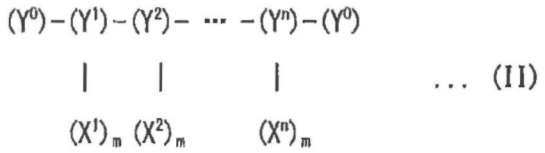
R^1-X ... (I)

wherein R^1 is any of an alkyl group of 4 to 12 carbon atoms, an alkenyl group, an alkoxy group, and an aryl group, and X is a carboxy group or a sulfo group. The compound of the general formula (I) is preferably a compound in which R^1 is an alkyl group having a branched structure, an alkenyl group having a branched structure, an alkoxy group having a branched structure, or an aryl group.

[0016]

The compound (C) may be a compound represented by the following general formula (II) or a salt thereof

[Chem. 1]



... (II)

[0017]

wherein n is an integer of 2 or more, and m is an integer of 1 to 5, and may have the same or different values,

Y^0 represents a hydrogen atom, and Y^1 to Y^n each represent a hydrocarbon group of 1 to 30 carbon atoms, and may be the same or different from each other,

X^1 to X^n each represent a sulfo group, a carboxy group, or a hydrogen atom, and may be the same or different from each other, provided that at least one of X^1 to X^n is a sulfo group or a carboxy group.

[0018]

The compound represented by the general formula (II) or a salt thereof may be at least one selected from the group consisting of polycarboxylic acid, a salt of polycarboxylic acid, polysulfonic acid, and a salt of polysulfonic acid. The compound represented by the general formula (II) or a salt thereof may be at least one selected from the group consisting of polyacrylic acid, a salt of polyacrylic acid, a naphthalenesulfonic acid formalin condensation product, a salt of a naphthalenesulfonic acid formalin condensation product, polystyrene sulfonic acid, and a salt of polystyrene sulfonic acid.

[0019]

The compound (C) may be a compound having a carboxymethyl group within the molecule. The compound having a carboxymethyl group within the molecule may preferably be a compound that contains a monosaccharide as a basic constituting unit. For example, a carboxymethyl cellulose salt may be used.

[0020]

The alkali component (A), the phosphonic acid derivative or a salt thereof (B), and the compound (C) are preferably mixed in a mass ratio A/(B + C) of 0.1 to 10.

[0021]

Preferably, the concentration of the alkali component (A) is 0.3 mass% to 25 mass%, the concentration of the phosphonic acid derivative or a salt thereof (B) is 0.1 mass% to 25 mass%, and the concentration of the compound (C) is 0.0001 mass% to 25 mass%.

[0022]

A method for treating a surface of a silicon substrate according to the present invention includes dipping the silicon substrate in the etching fluid of the present invention to form an irregular structure on the substrate surface.

Advantageous Effects of Invention

[0023]

The etching fluid of the present invention can form a uniform pyramidal texture

structure on a silicon substrate surface. The etching fluid can be used to stably mass produce a low-reflectance silicon substrate, and produce a high-quality silicon substrate that can improve the performance of solar cells. The components of the etching fluid do not vaporize in the working temperature range of 60°C to 95°C, and enable forming a stable texture with high safety. The etching fluid of the present invention is equally effective for silicon substrates formed by using the loose-abrasive grain method and the fixed-abrasive grain method.

Description of Embodiments

[0024]

An embodiment of the present invention is described below in detail.

[0025]

The alkali component (A) used in the present invention is not particularly limited, and conventional components used for silicon substrate etching fluids may be used as appropriate. Examples include hydroxides of alkali metals or alkali earth metals such as sodium hydroxide and potassium hydroxide, and salts thereof. Typically preferred for ease of availability is sodium hydroxide. The alkali components may be used in a combination of two or more, as required.

[0026]

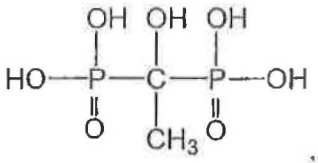
The phosphonic acid derivative or salts thereof (hereinafter, also referred to simply as "phosphonic acid derivatives or the like") (B) used in the present invention are not particularly limited, provided that they are ones typically used as sequestering agents.

[0027]

Preferred examples of the phosphonic acid derivatives include 1-hydroxyethylidene-1,1-diphosphonic acid represented by the formula (1) below, nitrilotris(methylenephosphonic acid) represented by the formula (2) below, phosphonobutane tricarboxylic acid represented by the formula (3) below, alkylenediaminetetra(methylenephosphonic acid) represented by the general formula (4) below (for example, ethylenediaminetetra(methylenephosphonic acid) of formula (4) with n

= 2, and hexamethylenediaminetetra(methylenephosphonic acid) of formula (4) with n = 6), dialkylenetriaminepenta(methylenephosphonic acid) represented by the general formula (5) below (for example, diethylenetriaminepenta(methylenephosphonic acid) of formula (5) with n = 2), and/or salts thereof. Examples of the salts include alkali metal salts, alkali-earth metal salts, amine salts, and ammonium salts. Alkali metal salts such as sodium salts and potassium salts are preferred because these are generally easily available. The phosphonic acid derivatives may be used in a combination of two or more, as required.

[Chem. 2]



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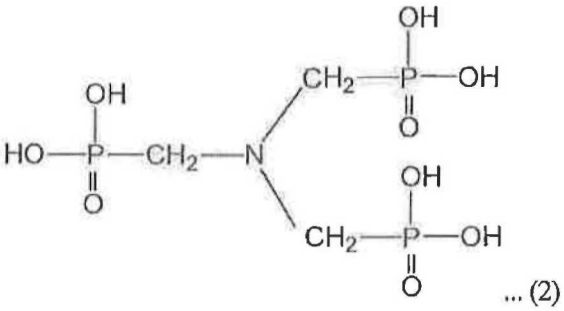
[Chem. 3]



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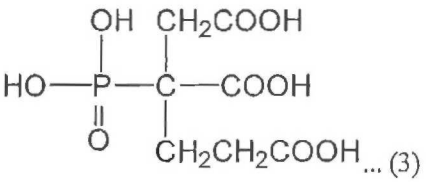
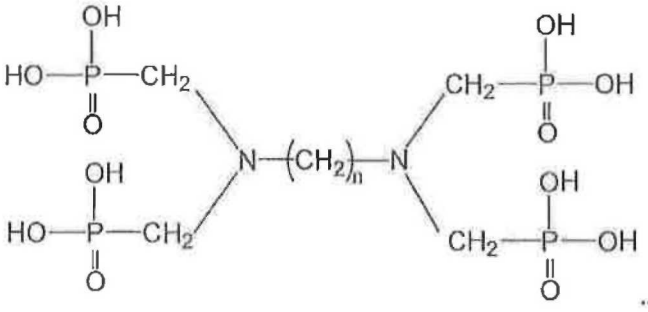
[Chem. 4]



... (3)

[Chem. 5]



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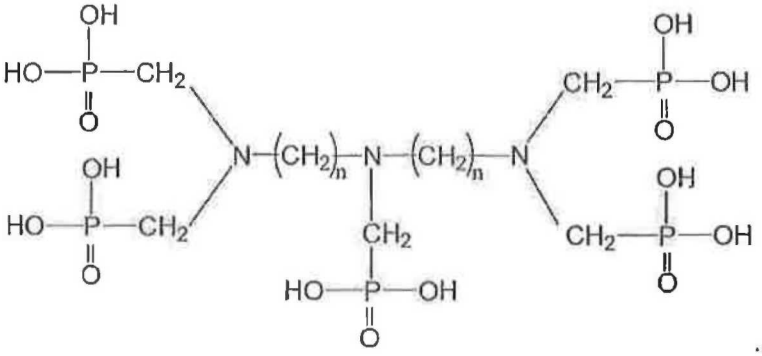
[Chem. 6]



... (5)

[0028]

Particularly preferred as the phosphonic acid derivatives are 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilotris(methylenephosphonic acid), and phosphonobutane tricarboxylic acid, because these improve the uniformity of the resulting texture structure, and tend to produce a high purity product with few impurities, which should be avoided for purposes of the invention.

[0029]

The following describes the compound (C) of the present invention that includes at least one selected from the group consisting of a carboxy group, a sulfo group, a carboxy or sulfo group forming a salt, and a carboxymethyl group.

[0030]

The compound (C) may be one or more selected from sulfonic acid, a salt of sulfonic acid, carboxylic acid, and a salt of carboxylic acid. Sulfonic acid is a compound with at least one sulfo group contained within the molecule. A salt of sulfonic acid is a

compound in the form of a salt with at least one sulfonate group contained within the molecule. Carboxylic acid is a compound with at least one carboxy group contained within the molecule. A salt of carboxylic acid is a compound in the form of a salt with at least one carboxylate group contained within the molecule.

[0031]

More specifically, preferred as the compound (C) are, for example, compounds represented by the following general formula (I), and salts thereof.

[0032]

R^1-X ... (I)

R^1 is an alkyl group of 4 to 12 carbon atoms, an alkenyl group, an alkoxy group, or an aryl group, and may have a branched structure in the carbon backbone. X is a carboxy group or a sulfo group.

[0033]

The compounds represented by general formula (I) are not particularly limited. Specific examples of the carboxy group-containing substance include carboxylic acids with a linear carbon backbone, such as butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, and dodecanoic acid, and carboxylic acids with a branched structure in the carbon backbone, such as 2-ethylhexanoic acid, 2,3-dimethylnonanoic acid, 2-ethyl-3-methylnonanoic acid, and 3,5,5-trimethylhexanoic acid. Also usable are carboxylic acids having an aromatic ring structure such as a benzene ring, and a naphthalene ring.

[0034]

Specific examples of the sulfo group-containing substance include butanesulfonic acid, pentanesulfonic acid, hexanesulfonic acid, heptanesulfonic acid, octanesulfonic acid, nonanesulfonic acid, decanesulfonic acid, undecanesulfonic acid, and dodecanesulfonic acid. Also usable as the sulfo group-containing substance are sulfonic acids with a branched structure in the carbon backbone, and sulfonic acids with an aromatic ring structure, as with the case of the carboxy group-containing substance. These, including mixtures of

carboxylic acid and sulfonic acid, may be used either alone or in a combination of two or more. The carboxylic acids and sulfonic acids may be used in the forms of alkali metal salts, alkali-earth metal salts, amine salts, or ammonium salts.

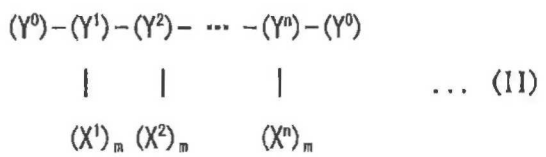
[0035]

Preferred as the compounds of the general formula (I) are carboxylic acids having 6 to 8 carbon atoms in the longest carbon chain with 1 to 3 branched methyl or ethyl side chains (for example, 3,5,5-trimethylhexanoic acid), because such carboxylic acids tend to produce synergy with the phosphonic acid.

[0036]

Also preferred for use as compound (C) are compounds of the structure represented by the following general formula (II), or salts thereof.

[Chem. 7]



... (II)

[0037]

In formula (II), n is an integer of 2 or more, and m is an integer of 1 to 5, and may have the same or different values when m is 2 or more. Y^0 represents a hydrogen atom, Y^1 to Y^n each represent a hydrocarbon group of 1 to 30 carbon atoms. The hydrocarbon group may have a structure with a single bond, a double bond, or a triple bond, and may be an aliphatic hydrocarbon group or an aromatic hydrocarbon group, and may be the same or different from each other. X^1 to X^n each represent a sulfo group, a carboxy group, or a hydrogen atom, and may be the same or different from each other, provided that at least one of X^1 to X^n is a sulfo group or a carboxy group.

[0038]

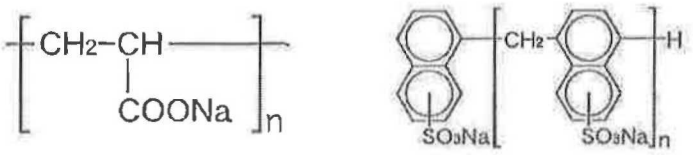
Preferred are polysulfonic acids and salts thereof in which at least two or more of X^1 to X^n in the general formula (II) (n being the number of X) are sulfonic acid groups and/or salts thereof, and polycarboxylic acids and salts thereof in which at least two or more

of X^1 to X^n in the general formula (II) (n being the number of X) are carboxy groups and/or salts thereof. These are preferred for their high ability to provide a desirable etching fluid when used with the phosphonic acid derivatives, as described above. The salts are not particularly limited, and may be, for example, sodium salts or potassium salts.

[0039]

Preferred as the compounds represented by the general formula (II) are polyacrylic acids produced after the polymerization of the acrylic acid represented by the formula below, naphthalenesulfonic acid formalin condensation products produced after the condensation polymerization of naphthalenesulfonic acid and formalin, and polystyrene sulfonic acids. Particularly preferred are naphthalenesulfonic acid formalin condensation products and salts thereof because these can greatly improve the synergy with the phosphonic acid.

[Chem. 8]



[0040]

The compounds that can be used are not limited to polymers obtained after the polymerization of monomers, and the type of monomer, and the number of repeating units in the polymers are not limited either. The polymers may be block polymers formed from a repeating single type of monomer, or random polymers in which more than one type of monomer is randomly polymerized. The number of repeating units (n) is not particularly limited, provided that n is 2 or more. In the case of polyacrylic acids, it is possible to use a polyacrylic acid with a molecular weight of about 10,000 resulting from the polymerization of about 130 molecules of acrylic acid, and a polyacrylic acid with a molecular weight of about 3,000 resulting from the polymerization of about 40 molecules of acrylic acid.

[0041]

Also preferred for use as compound (C) are compounds having a carboxymethyl

group within the molecule. Examples of compounds having a carboxymethyl group within the molecule include carboxymethyl cellulose salts, carboxymethyl starch, carboxymethyl sucrose, carboxymethyl inulin, carboxymethyl chitin, carboxymethyl chitosan, carboxymethyl dextran, carboxymethyl lignin, and carboxymethyl guar gum. Aside from the existing compounds having a carboxymethyl group within the molecule, novel compounds that have had a carboxymethyl group introduced into the molecule also may be used for purposes of the present invention. These may be used either alone or in a combination of two or more.

[0042]

For obtaining synergy with the phosphonic acid, compounds composed of monosaccharide basic constituting units such as glucose and fructose are preferred as the compounds having a carboxymethyl group within the molecule for use as a component of the etching fluid for forming texture. Specifically, carboxymethyl cellulose salts, and carboxymethyl starch are preferred, and carboxymethyl cellulose salts are particularly preferred. The salts are preferably alkali metal salts, more preferably lithium salts, sodium salts, and potassium salts.

[0043]

The carboxymethyl group-containing compounds preferred for use in the present invention are described below in detail, taking carboxymethyl cellulose salts as an example. A cellulose produced after the polymerization of glucose contains three hydroxy groups per constituting glucose unit. Carboxymethyl cellulose is a cellulose in which these hydroxy groups are substituted with carboxymethyl groups. The extent of the hydroxy group for carboxymethyl substitution is described in terms of the degree of etherification. The degree of etherification can theoretically take a value up to 3.

[0044]

The carboxymethyl cellulose salts used may have any degree of etherification, and have a degree of etherification of preferably 0.4 to 2.0, particularly preferably 0.7 to 1.5. The molecular weights of the carboxymethyl cellulose salts are not particularly limited, and

the carboxymethyl cellulose salts preferably have an average degree of polymerization of 1,000 or less, and an average molecular weight of 220,000 or less, further preferably an average degree of polymerization of 250 or less, and an average molecular weight of 54,000 or less.

[0045]

The compound (C) usable in the present invention is not limited to the existing compounds, and is not particularly limited, as long as it has a structure that can dissolve in a high-temperature alkaline aqueous solution used in the present invention. Undissolvable compounds make the etching fluid heterogeneous, and may have adverse effects on uniformity of the substrate treatment. The compounds may be used either alone or in a combination of two or more.

[0046]

With the etching fluid of the present invention, the phosphonic acid derivatives or the like (B) are orderly arranged and adsorbed on a silicon substrate surface. It is believed that this inhibits the alkali component (A) from overly etching the substrate, and allows for formation of a texture on the substrate surface. In contrast, an etching fluid containing only an alkali and a phosphonic acid derivative often results in nonuniformly etching a silicon substrate surface, and such nonuniformity is believed to be the result of hydrogen bubbles formed in the course of etching, and nonuniformly adhering to the silicon substrate surface while the reaction proceeds. It is believed that the use of various compounds such as above for compound (C) with the phosphonic acid derivatives or the like (B) reduces such bubbles, and enables more uniform etching.

[0047]

The etching fluid of the present invention may be used in the form of an aqueous solution of the alkali component (A), the phosphonic acid derivatives or the like (B), and the compound (C). The water used is preferably water with no impurities, such as ion-exchange water, and distilled water. When the etching fluid contains an insoluble component, the etching fluid should preferably be used after removing such an insoluble

component by using a known fractionation procedure such as filtration.

[0048]

The concentration of the alkali component (A) in the aqueous solution is preferably 0.3 to 25 mass%, more preferably 1 to 15 mass%. When the alkali component concentration is 0.3 mass% or more, a texture can be efficiently formed in a short time period. The etching effect remains intact also in concentrations above 25 mass%. However, such a concentration range has the cost disadvantage as it increases the required amount of an etching inhibitor used as an additive.

[0049]

The content of the phosphonic acid derivative (B) in the etching fluid is preferably 0.1 to 25 mass%, more preferably 0.3 to 15 mass%, particularly preferably 0.5 to 15 mass%. With the phosphonic acid derivative content falling in these ranges, a moderate alkali etching inhibiting effect can be obtained, and a uniform texture can be formed in a short time period.

[0050]

For uniform and efficient etching, the content of the compound (C) is preferably 0.0001 to 25 mass%. The preferred content depends on the type of compound (C). When compound (C) is a compound represented by formula (I), the content of compound (C) is more preferably 0.1 to 25 mass%, particularly preferably 0.3 to 15 mass%. When compound (C) is a compound represented by formula (II), the content of compound (C) is more preferably 0.0001 to 10 mass%, particularly preferably 0.01 to 5 mass%. When compound (C) is a compound having a carboxymethyl group, the content of compound (C) is more preferably 0.001 to 10 mass%, particularly preferably 0.01 to 3 mass%.

[0051]

It is preferable to control the content proportions of the phosphonic acid derivatives or the like (B) and compound (C) (such as sulfonic acid/carboxylic acid) with respect to the content of alkali component (A) such that the mixture ratio (A/(B + C) by mass) of alkali component (A), phosphonic acid derivative (B), and compound (C) falls in a range of preferably 0.1 to 10, more preferably 0.2 to 5. It is believed that the phosphonic acid

derivatives or the like (B) and the compound (C) in these content ranges appropriately can inhibit the anisotropic etching of silicon by the alkali component, and contribute to forming a desirable texture. With excessively small amounts of phosphonic acid derivatives or the like (B) and compound (C) with respect to the alkali component (A), etching inhibiting effect becomes deficient, and the etching rate increases. This makes it difficult to control the shape and size of the texture structure, and tends to make a nonuniform surface. On the other hand, when the amounts of phosphonic acid derivatives or the like (B) and compound (C) with respect to the alkali component (A) are too large, the etching inhibiting effect becomes excessive, and the excessive slow etching rate makes it difficult to form a texture structure.

[0052]

The etching fluid of the present invention may contain additives such as isopropyl alcohol, fatty acid, and silicate commonly used for etching fluids used to form a texture on a silicon substrate, as required, provided that it is not contrary to the objects of the present invention.

[0053]

An etching fluid prepared to obtain the desired performance may be able to form a suitable texture on a silicon substrate produced by using the conventional loose-abrasive grain method. However, it is not necessarily the case that such an etching fluid is directly applicable to a silicon substrate produced by using the fixed-abrasive grain method, and can form a suitable texture on such a silicon substrate. Possible reasons for this include, for example, different marks left on the sliced substrate surface, and the adverse effect of a coolant residue resulting from different coolants used for slicing when the washing in the subsequent washing step fails to sufficiently remove these coolants. There is a demand for an etching fluid that can exhibit excellent etching performance for silicon substrates produced by using the loose-abrasive grain method and the fixed-abrasive grain method. In this regard, the etching fluid of the present invention is desirable for its applicability to both silicon substrates. The etching fluid of the present invention is also applicable to both a

monocrystalline silicon substrate and a polycrystalline silicon substrate, and can be used for all silicon substrates regardless of the slicing method, whether it is a loose-abrasive grain method or a fixed-abrasive grain method. The etching fluid of the present invention is particularly preferable for monocrystalline silicon substrates with a substrate surface lying on a (100) plane.

[0054]

The etching method used for the etching fluid of the present invention is not particularly limited, and may be a method in which the etching fluid is heated to about 60°C to 95°C, and a silicon substrate is dipped in the heated etching fluid for 10 to 30 minutes as conventionally performed.

Examples

[0055]

The following describes the present invention in greater detail using Examples. Note, however, that the present invention is not limited by the following examples.

[0056]

[Examples and Comparative Examples]

Aqueous solutions of alkali component (A), phosphonic acid derivatives or the like (B), and compound (C) were prepared as etching fluids in the mixed proportions given in the tables below. Ion-exchange water was used for the preparation of the etching fluids.

[0057]

Each etching fluid was heated to 80°C, and a monocrystalline silicon substrate wafer (hereinafter, "wafer") sliced by using either a loose-abrasive grain method or a fixed-abrasive grain method as shown in the tables was dipped in the heated etching fluid for 20 minutes to etch the substrate. The substrate was water washed, dried, and evaluated for texture structure and measured for reflectance in the manner described below. The results are presented in the tables.

[0058]

(1) Evaluation of texture structure appearance, and reflectance measurement were performed

as follows.

[0059]

The texture structure was observed with an electron scanning microscope (JSM-6380LV, JEOL). The substrate was observed at a magnification of 1,000 times and considered excellent ("A" in the tables) when 5% or less of the whole area of the substrate surface was a flat region with no texture structure, and poor ("F" in the tables) when such a flat region occurred in more than 5% of the whole area of the substrate surface.

[0060]

(2) Wafer Reflectance Measurement

Wafer reflectance was measured with a UV-visible spectrophotometer (U-3900H, Hitachi High-Technologies). The measurement used light of 600 nm wavelength for evaluation.

[Table 1]

[1900]

		(A) Alkali component		(B) Phosphonic acid derivative		(C) Compound with carboxy group or sulfo group within the molecule		Wafer slicing method	Evaluation results	
		Name	Concentration (Mass%)	Name	Concentration (Mass%)	Name	Concentration (Mass%)		Evaluation of texture structure appearance	Evaluation of wafer reflectance
Example	1-1	Sodium hydroxide	0.5	1-Hydroxyethylidene -1,1-diphosphonic acid	0.3	Heptanoic acid	0.1	Loose-abrasive grain method	A	11.2%
	1-2		1		0.9		0.3	Loose-abrasive grain method	A	11.1%
	1-3		5		4		1	Loose-abrasive grain method	A	11.5%
	1-4		10		6		4	Fixed-abrasive grain method	A	11.6%
	1-5		15		10		5	Loose-abrasive grain method	A	11.7%
	1-6	Sodium hydroxide	0.5	1-Hydroxyethylidene -1,1-diphosphonic acid	0.3	Octanoic acid	0.2	Loose-abrasive grain method	A	11.8%
	1-7		1		0.9		0.4	Loose-abrasive grain method	A	11.6%
	1-8		5		4		0.5	Loose-abrasive grain method	A	11.4%
	1-9		10		8		1	Fixed-abrasive grain method	A	11.7%
	1-10	Sodium hydroxide	0.5	1-Hydroxyethylidene -1,1-diphosphonic acid	0.3	2-Ethylhexanoic acid	0.1	Loose-abrasive grain method	A	10.7%
	1-11		1		0.9		0.5	Loose-abrasive grain method	A	10.6%
	1-12		5		4		1	Loose-abrasive grain method	A	10.6%
	1-13		10		8		2	Fixed-abrasive grain method	A	10.9%
	1-14	Sodium hydroxide	0.5	1-Hydroxyethylidene -1,1-diphosphonic acid	0.3	3,5,5-Trimethylhexanoic acid	0.1	Loose-abrasive grain method	A	10.2%
	1-15		1		0.9		0.5	Loose-abrasive grain method	A	10.3%
	1-16		5		4		1.2	Loose-abrasive grain method	A	10.2%
	1-17		10		8		2	Fixed-abrasive grain method	A	10.6%
	1-18	Sodium hydroxide	0.5	1-Hydroxyethylidene -1,1-diphosphonic acid	0.3	Heptanesulfonic acid	0.3	Loose-abrasive grain method	A	11.9%
	1-19		1		1		0.8	Loose-abrasive grain method	A	11.8%
	1-20		5		4		2	Loose-abrasive grain method	A	11.4%
	1-21		10		5		5	Fixed-abrasive grain method	A	11.3%
	1-22	Sodium hydroxide	0.5	1-Hydroxyethylidene -1,1-diphosphonic acid	0.3	Octanesulfonic acid	0.1	Loose-abrasive grain method	A	11.8%
	1-23		1		0.9		0.4	Loose-abrasive grain method	A	11.6%
	1-24		5		4		2	Loose-abrasive grain method	A	11.5%
	1-25		10		8		3	Fixed-abrasive grain method	A	11.4%
	1-26	Sodium hydroxide	0.5	1-Hydroxyethylidene -1,1-diphosphonic acid	0.3	Naphthalenesulfonic acid	0.1	Loose-abrasive grain method	A	11.8%
	1-27		1		0.9		0.2	Loose-abrasive grain method	A	11.9%
	1-28		5		3		3	Loose-abrasive grain method	A	11.6%
	1-29		10		8		2	Fixed-abrasive grain method	A	11.8%

[Table 2]

		(A) Alkali component		(B) Phosphonic acid derivative		(C) Compound with carboxy group or sulfo group within the molecule		Wafer slicing method	Evaluation results	
		Name	Concentration (Mass%)	Name	Concentration (Mass%)	Name	Concentration (Mass%)		Evaluation of texture structure appearance	Evaluation of wafer reflectance
Example	1-30	Sodium hydroxide	5	Nitrilotris (methylenephosphonic acid)	4	Heptanoic acid	1	Loose-abrasive grain method	A	11.9%
	1-31		5		4	Octanoic acid	1	Loose-abrasive grain method	A	11.5%
	1-32		5		4	2-Ethylhexanoic acid	1	Loose-abrasive grain method	A	10.8%
	1-33		5		4	3,5,5-Trimethylhexanoic acid	1	Loose-abrasive grain method	A	10.5%
	1-34		5		4	Heptanesulfonic acid	1	Loose-abrasive grain method	A	11.8%
	1-35		5		4	Octanesulfonic acid	1	Loose-abrasive grain method	A	11.9%
	1-36		5		4	Naphthalenesulfonic acid	1	Loose-abrasive grain method	A	11.9%
	1-37	Sodium hydroxide	5	Phosphonobutane tricarboxylic acid	4	Heptanoic acid	1	Loose-abrasive grain method	A	11.4%
	1-38		5		4	Octanoic acid	1	Loose-abrasive grain method	A	11.5%
	1-39		5		4	2-Ethylhexanoic acid	1	Loose-abrasive grain method	A	11.1%
	1-40		5		4	3,5,5-Trimethylhexanoic acid	1	Loose-abrasive grain method	A	10.4%
	1-41		5		4	Heptanesulfonic acid	1	Loose-abrasive grain method	A	11.4%
	1-42		5		4	Octanesulfonic acid	1	Loose-abrasive grain method	A	11.5%
	1-43		5		4	Naphthalenesulfonic acid	1	Loose-abrasive grain method	A	11.6%
	1-44	Potassium hydroxide	5	1-Hydroxyethylidene -1,1-diphosphonic acid	4	Octanoic acid	1	Loose-abrasive grain method	A	11.6%
	1-45		5		4	3,5,5-Trimethylhexanoic acid	1	Fixed-abrasive grain method	A	10.7%

[0062]

[Table 3]

		(A) Alkali component		(B) Phosphonic acid derivative		(C) Compound with carboxy group or sulfo group within the molecule		Wafer slicing method	Evaluation results	
		Name	Concentration (Mass%)	Name	Concentration (Mass%)	Name	Concentration (Mass%)		Evaluation of texture structure appearance	Evaluation of wafer reflectance
Example	2-1	Sodium hydroxide	0.5	1-Hydroxyethylidene -1,1-diphosphonic acid	0.3	Sodium polyacrylate (Molecular weight 3000)	0.1	Loose-abrasive grain method	A	11.5%
	2-2		1		0.9		0.3	Loose-abrasive grain method	A	11.0%
	2-3		5		4		1	Fixed-abrasive grain method	A	11.2%
	2-4		15		10		5	Loose-abrasive grain method	A	11.3%
	2-5	Sodium hydroxide	0.5	1-Hydroxyethylidene -1,1-diphosphonic acid	0.3	Sodium polyacrylate (Molecular weight 5000)	0.1	Loose-abrasive grain method	A	11.2%
	2-6		1		0.9		0.3	Loose-abrasive grain method	A	11.3%
	2-7		5		4		1	Loose-abrasive grain method	A	11.3%
	2-8		15		10		5	Fixed-abrasive grain method	A	11.4%
	2-9	Sodium hydroxide	0.5	1-Hydroxyethylidene -1,1-diphosphonic acid	0.3	Sodium polyacrylate (Molecular weight 10000)	0.1	Loose-abrasive grain method	A	11.2%
	2-10		1		0.9		0.3	Fixed-abrasive grain method	A	11.1%
	2-11		5		4		1	Loose-abrasive grain method	A	11.1%
	2-12		15		10		5	Loose-abrasive grain method	A	11.0%

[0063]

[Table 4]

		(A) Alkali component		(B) Phosphonic acid derivative		(C) Compound with carboxy group or sulfo group within the molecule		Wafer slicing method	Evaluation results	
		Name	Concentration (Mass%)	Name	Concentration (Mass%)	Name	Concentration (Mass%)		Evaluation of texture structure appearance	Evaluation of wafer reflectance
Example	2-13	Sodium hydroxide	8	1-Hydroxyethylidene -1,1-diphosphonic acid	1	Sodium naphthalenesulfonate formalin condensate (Molecular weight 1200)	0.02	Loose-abrasive grain method	A	10.3%
	2-14		10		3		0.1	Loose-abrasive grain method	A	10.3%
	2-15		10		3		0.15	Fixed-abrasive grain method	A	10.4%
	2-16	Sodium hydroxide	8	1-Hydroxyethylidene -1,1-diphosphonic acid	1	Sodium naphthalenesulfonate formalin condensate (Molecular weight 2600)	0.02	Fixed-abrasive grain method	A	10.3%
	2-17		10		3		0.1	Fixed-abrasive grain method	A	10.5%
	2-18		10		3		0.15	Fixed-abrasive grain method	A	10.5%
	2-19		10		3		0.4	Fixed-abrasive grain method	A	10.5%
	2-20	Sodium hydroxide	8	1-Hydroxyethylidene -1,1-diphosphonic acid	1	Sodium naphthalenesulfonate formalin condensate (Molecular weight 5000)	0.02	Fixed-abrasive grain method	A	10.3%
	2-21		10		3		0.1	Fixed-abrasive grain method	A	10.4%
	2-22		10		3		0.15	Fixed-abrasive grain method	A	10.3%
	2-23		10		3		0.4	Fixed-abrasive grain method	A	10.5%

[0064]

[Table 5]

		(A) Alkali component		(B) Phosphonic acid derivative		(C) Compound with carboxy group or sulfo group within the molecule		Wafer slicing method	Evaluation results	
		Name	Concentration (Mass%)	Name	Concentration (Mass%)	Name	Concentration (Mass%)		Evaluation of texture structure appearance	Evaluation of wafer reflectance
Example	2-24	Sodium hydroxide	8	1-Hydroxyethylidene -1,1-diphosphonic acid	1	Sodium polystyrene sulfonate (Molecular weight 20000)	0.02	Fixed-abrasive grain method	A	10.6%
	2-25		10		3		0.1	Fixed-abrasive grain method	A	10.6%
	2-26		10		3		0.15	Fixed-abrasive grain method	A	10.7%
	2-27		10		3		0.4	Fixed-abrasive grain method	A	10.7%
	2-28	Sodium hydroxide	0.5	1-Hydroxyethylidene -1,1-diphosphonic acid	0.3	Sodium polystyrene sulfonate (Molecular weight 75000)	0.1	Loose-abrasive grain method	A	10.8%
	2-29		1		0.9		0.5	Fixed-abrasive grain method	A	10.8%
	2-30		5		4		1	Loose-abrasive grain method	A	10.9%
	2-31		10		8		2	Fixed-abrasive grain method	A	11.0%
	2-32	Sodium hydroxide	5	Nitrilotris (methylenephosphonic acid)	4	Sodium polyacrylate (Molecular weight 10000)	1	Loose-abrasive grain method	A	11.6%
	2-33		8		1	Sodium naphthalenesulfonate formalin condensate (Molecular weight 1200)	0.02	Fixed-abrasive grain method	A	11.5%
	2-34	Sodium hydroxide	5	Phosphonobutane tricarboxylic acid	4	Sodium polyacrylate (Molecular weight 10000)	1	Fixed-abrasive grain method	A	11.4%
	2-35		8		1	Sodium naphthalenesulfonate formalin condensate (Molecular weight 1200)	0.02	Fixed-abrasive grain method	A	11.5%
	2-36	Potassium hydroxide	8	1-Hydroxyethylidene -1,1-diphosphonic acid	1	Sodium naphthalenesulfonate formalin condensate (Molecular weight 1200)	0.02	Fixed-abrasive grain method	A	11.6%

[0065]

[0066]

[Table 6]

		(A) Alkali component		(B) Phosphonic acid derivative		(C) Compound with carboxymethyl group within the molecule		Water rubbing method	Evaluation results	
		Name	Concentration (Mass%)	Name	Concentration (Mass%)	Name	Concentration (Mass%)		Evaluation of texture structure appearance	Evaluation of water retentance
Example	3-1	Sodium hydroxide	0.5	1-Hydroxyethylidene -1,1-diphosphonic acid	0.3	Carboxymethylcellulose sodium (Degree of etherification 0.40/Average molecular weight 30000)	0.05	Loose-abrasive grain method	A	12.4%
	3-2		1		0.9		0.05	Loose-abrasive grain method	A	12.5%
	3-3		5		4		0.2	Loose-abrasive grain method	A	12.7%
	3-4		10		8		0.5	Fixed-abrasive grain method	A	12.6%
	3-5		15		12		3	Loose-abrasive grain method	A	12.7%
	3-6	Sodium hydroxide	0.5	1-Hydroxyethylidene -1,1-diphosphonic acid	0.3	Carboxymethylcellulose sodium (Degree of etherification 0.70/Average molecular weight 30000)	0.05	Loose-abrasive grain method	A	11.4%
	3-7		1		0.9		0.05	Loose-abrasive grain method	A	11.4%
	3-8		5		4		0.2	Loose-abrasive grain method	A	11.4%
	3-9		10		8		0.5	Fixed-abrasive grain method	A	11.5%
	3-10	Sodium hydroxide	0.5	1-Hydroxyethylidene -1,1-diphosphonic acid	0.3	Carboxymethylcellulose sodium (Degree of etherification 0.80/Average molecular weight 30000)	0.05	Loose-abrasive grain method	A	11.0%
	3-11		1		0.9		0.05	Loose-abrasive grain method	A	11.0%
	3-12		5		4		0.2	Loose-abrasive grain method	A	11.1%
	3-13		10		8		0.5	Fixed-abrasive grain method	A	11.1%
	3-14	Sodium hydroxide	0.5	1-Hydroxyethylidene -1,1-diphosphonic acid	0.3	Carboxymethylcellulose sodium (Degree of etherification 0.90/Average molecular weight 63000)	0.05	Loose-abrasive grain method	A	11.2%
	3-15		1		0.9		0.05	Loose-abrasive grain method	A	11.1%
	3-16		5		4		0.2	Loose-abrasive grain method	A	11.3%
	3-17		10		8		0.5	Fixed-abrasive grain method	A	11.2%
	3-18	Sodium hydroxide	0.5	1-Hydroxyethylidene -1,1-diphosphonic acid	0.3	Carboxymethylcellulose sodium (Degree of etherification 1.3/Average molecular weight 350000)	0.05	Loose-abrasive grain method	A	12.2%
	3-19		1		0.9		0.05	Loose-abrasive grain method	A	12.1%
	3-20		5		4		0.1	Loose-abrasive grain method	A	12.2%
	3-21		10		8		0.3	Fixed-abrasive grain method	A	12.1%

[Table 7]

		(A) Alkali component		(B) Phosphonic acid derivative		(C) Compound with carboxymethyl group within the molecule		Wafer slicing method	Evaluation results	
		Name	Concentration (Mass%)	Name	Concentration (Mass%)	Name	Concentration (Mass%)		Evaluation of texture structure appearance	Evaluation of water retentance
Example	3-22	Sodium hydroxide	5	Nitrilotris (methylenephosphonic acid)	4	Carboxymethylcellulose sodium (Degree of etherification 0.70/Average molecular weight 30000)	0.2	Loose-abrasive grain method	A	11.5%
	3-23		5		4	Carboxymethylcellulose sodium (Degree of etherification 0.90/Average molecular weight 63000)	0.5	Loose-abrasive grain method	A	12.1%
	3-24	Sodium hydroxide	5	Phosphonobutane tricarboxylic acid	4	Carboxymethylcellulose sodium (Degree of etherification 0.70/Average molecular weight 30000)	0.2	Loose-abrasive grain method	A	12.1%
	3-25		5		4	Carboxymethylcellulose sodium (Degree of etherification 0.90/Average molecular weight 63000)	0.4	Loose-abrasive grain method	A	12.3%
	3-26	Sodium hydroxide	5	1-Hydroxyethylidene -1,1-diphosphonic acid	4	Carboxymethyl starch (*1)	0.05	Loose-abrasive grain method	A	12.5%
	3-27		5		4		0.1	Loose-abrasive grain method	A	12.7%
	3-28	Sodium hydroxide	5	1-Hydroxyethylidene -1,1-diphosphonic acid	4	Carboxymethyl guar gum (*2)	0.02	Loose-abrasive grain method	A	12.8%
	3-29		5		4		0.05	Loose-abrasive grain method	A	12.9%
	3-30	Potassium hydroxide	5	1-Hydroxyethylidene -1,1-diphosphonic acid	4	Carboxymethylcellulose sodium (Degree of etherification 0.70/Average molecular weight 30000)	0.2	Loose-abrasive grain method	A	11.6%
	3-31		5		4		0.4	Fixed-abrasive grain method	A	11.8%

*1 : Nippon Starch Chemical carboxymethyl starch "Kiprogum M-800A"

*2 : Nippon Starch Chemical carboxymethyl starch "Kiprogum HH"

[0067]

[Table 8]

		(A) Alkali component		(B) Phosphoric acid derivative		(C) Compound with carboxymethyl group within the molecule		Water eluting method	Evaluation results	
		Name	Concentration (Mass%)	Name	Concentration (Mass%)	Name	Concentration (Mass%)		Evaluation of texture structure appearance	Evaluation of water reflectance
Comparative Example	1	Sodium hydroxide	5	None	-	None	-	Loose-abrasive grain method	F	25.8%
	2	Potassium hydroxide	5	None	-	None	-	Loose-abrasive grain method	F	24.5%

Industrial Applicability

[0068]

The etching fluid of the present invention can be used for, for example, etching of solar cell silicon substrates.

CLAIMS

[Claim 1]

An etching fluid for forming irregularities on a silicon substrate surface,

the etching fluid comprising:

(A) an alkali component;

(B) a phosphonic acid derivative or a salt thereof; and

(C) a compound that contains at least one selected from the group consisting of a carboxy group, a sulfo group, a carboxy or sulfo group forming a salt, and a carboxymethyl group within the molecule;

wherein the concentration of the alkali component (A) is 0.3 mass% to 15 mass%, the concentration of the phosphonic acid derivative or a salt thereof (B) is 0.3 mass% to 25 mass%, and the concentration of the compound (C) is 0.0001 mass% to 25 mass%.

[Claim 2]

The etching fluid according to claim 1, wherein the alkali component (A) is sodium hydroxide or potassium hydroxide.

[Claim 3]

The etching fluid according to claim 1 or 2, wherein the phosphonic acid derivative or a salt thereof (B) is 1-hydroxyethylidene-1,1-diphosphonic acid or a salt thereof.

[Claim 4]

The etching fluid according to any one of claims 1 to 3, wherein the compound (C) is at least one selected from the group consisting of carboxylic acid, a salt of carboxylic acid, sulfonic acid, and a salt of sulfonic acid.

[Claim 5]

The etching fluid according to claim 4, wherein the compound (C) is a compound represented by the following general formula (I);

R^1-X ... (I)

wherein R^1 is any of an alkyl group of 4 to 12 carbon atoms, an alkenyl group, an alkoxy group, and an aryl group, and X is a carboxy group or a sulfo group.

[Claim 6]

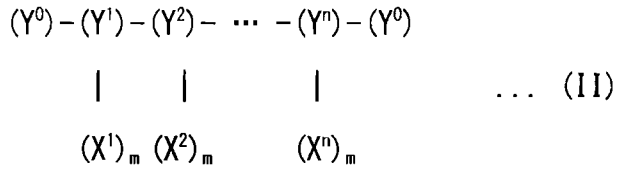
The etching fluid according to claim 5, wherein the compound (C) is a compound of the general formula (I) in which R^1 is an alkyl group having a branched structure, an

alkenyl group having a branched structure, an alkoxy group having a branched structure, or an aryl group.

[Claim 7]

The etching fluid according to claim 4, wherein the compound (C) is a compound represented by the following general formula (II) or a salt thereof.

[Chem. 1]



... (II)

wherein n is an integer of 2 or more, and m is an integer of 1 to 5, and may have the same or different values,

Y^0 represents a hydrogen atom, and Y^1 to Y^n each represent a hydrocarbon group of 1 to 30 carbon atoms, and may be the same or different from each other,

X^1 to X^n each represent a sulfo group, a carboxy group, or a hydrogen atom, and may be the same or different from each other, provided that at least one of X^1 to X^n is a sulfo group or a carboxy group.

[Claim 8]

The etching fluid according to claim 7, wherein the compound (C) is at least one selected from the group consisting of polycarboxylic acid, a salt of polycarboxylic acid, polysulfonic acid, and a salt of polysulfonic acid.

[Claim 9]

The etching fluid according to claim 7 or 8, wherein the compound (C) is at least one selected from the group consisting of polyacrylic acid, a salt of polyacrylic acid, a naphthalenesulfonic acid formalin condensation product, a salt of a naphthalenesulfonic acid formalin condensation product, polystyrene sulfonic acid, and a salt of polystyrene sulfonic acid.

[Claim 10]

The etching fluid according to any one of claims 1 to 3, wherein the compound (C)

is a compound having a carboxymethyl group within the molecule.

[Claim 11]

The etching fluid according to claim 10, wherein the compound having a carboxymethyl group within the molecule is a compound that contains a monosaccharide as a basic constituting unit.

[Claim 12]

The etching fluid according to claim 11, wherein the compound having a carboxymethyl group within the molecule is a carboxymethyl cellulose salt.

[Claim 13]

The etching fluid according to any one of claims 1 to 12, wherein the alkali component (A), the phosphonic acid derivative or a salt thereof (B), and the compound (C) are mixed in a mass ratio A/(B + C) of 0.1 to 10.

[Claim 14]

A method for treating a surface of a silicon substrate,

the method comprising dipping the silicon substrate in the etching fluid of any one of claims 1 to 13 to form an irregular structure on the substrate surface.