

DESCRIPTION

TITLE OF THE INVENTION: METHOD FOR RECYCLING ETCHING SOLUTION

5 TECHNICAL FIELD

[0001]

The present invention relates to a method that is for recycling an etching solution and in which an inorganic acid-based etching solution that is or has been used in etching of
10 a semiconductor is regenerated (or recycled) by diffusion dialysis.

BACKGROUND ART

[0002] Fabrication of a semiconductor circuit having a higher
15 integration density and higher high capacity requires a finer etching technique. In particular, in fabrication of a semiconductor having a silicon oxide film and a silicon nitride film that serves as a sacrificial layer (e.g., a 2D NAND, 3D NAND, CMOS, DRAM, 3D RAM, logic IC, etc.), it is
20 necessary to meticulously remove only the silicon nitride film. To this end, an etching solution additionally contains an etch inhibitor that reduces etching of silicon oxide in order to achieve high etch selectivity.

[0003]

25 For example, Patent Document 1 describes an etching solution that is used in a fabrication process of a three-

dimensional semiconductor, and that is a composition including a solution containing silica and an alkali, phosphoric acid, and water. Patent Document 1 indicates that the use of such an etching solution reduces etching of silicon oxide film, resulting in an improvement in etch selectivity of silicon nitride film (see paragraph [0013] in the description of Patent Document 1).

[0004]

Incidentally, etching solutions require a high disposal cost, and therefore, it is desirable to recycle etching solutions. However, an etching solution that has been used in a semiconductor etching treatment (exhausted solution) contains a large amount of Si compounds derived from a semiconductor. Therefore, recycling of the used etching solution requires removal of Si compounds from the etching solution.

[0005]

As a method for removing Si compounds from an etching solution, Patent Document 2 describes a removal method using a filter, for example. Patent Document 2 indicates that regeneration of an etching solution suitable for an industrial process can be achieved using a filtration material having a high Si compound removal rate as a filter (see paragraph [0018] in the description of Patent Document 2).

CITATION LIST

PATENT LITERATURE

[0006]

Patent Document 1: Japanese Unexamined Patent
Application Publication No. 2020-96160

5 Patent Document 2: Japanese Patent No. 4944558

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0007]

10 However, the etching solution described in Patent
Document 1 originally contains silica (silicate) as an
additive. Therefore, when a silicon nitride etching treatment
is conducted, the concentration of silicate in the solution
further increases, so that fine silica crystals are highly
15 likely to be deposited in the solution. Therefore, if the
filter described in Patent Document 2 is used for regenerating
the etching solution described in Patent Document 1, the
filter is likely to be quickly clogged.

[0008]

20 To meet a demand for higher performance from users, some
recent etching solutions are designed so as to reduce
deposition of Si compounds dissolved in the etching solution
on a semiconductor substrate in the form of silica. Such an
etching solution in which silica deposition is reduced is
25 herein referred to as a "high-performance etching solution" so
as to be distinguished from conventional etching solutions.

The high-performance etching solution contains a deposition inhibitor that reduces silica deposition. Therefore, Si compounds are present in a dissolved state in the solution. Therefore, even if a removal method using a filter such as
5 that described in Patent Document 2 is applied for regeneration of the high-performance etching solution, it is not possible to remove Si compounds from the solution.

[0009]

With the above problems in mind, the present invention
10 has been made. It is an object of the present invention to provide a method that is for recycling an etching solution, in which an etching solution (exhausted solution) that has been used in a semiconductor etching treatment is regenerated, and that is capable of regenerating not only conventional etching
15 solutions but also a high-performance etching solution that is an etching solution containing a silica deposition inhibitor.

SOLUTION TO PROBLEM

[0010]

20 A characteristic feature of a method for recycling an etching solution according to the present invention for solving the above problem is a method for recycling an etching solution, wherein an inorganic acid-based etching solution that is used or has been used in etching of a semiconductor is
25 regenerated by diffusion dialysis, and the method comprises:

an extraction step of bringing a dialysis aid-containing

etching solution into contact with water through an anion-exchange membrane and thereby extracting an inorganic acid contained in the etching solution into the water.

[0011]

5 With the thus-configured method for recycling an etching solution, diffusion dialysis using an anion-exchange membrane is employed for regenerating an inorganic acid-based etching solution that is or has been used in etching of a semiconductor, instead of filtration using a filter, which is
10 conventionally performed. Diffusion dialysis is a technique of bringing an etching solution into contact with water through an anion-exchange membrane to extract an inorganic acid contained in the etching solution into the water. Here, because the etching solution contains a dialysis aid, the
15 inorganic acid can be recovered without occurrence of clogging during diffusion dialysis. Therefore, not only conventional etching solutions but also a high-performance etching solution obtained by adding a deposition inhibitor for inhibiting silica deposition to an etching solution can be regenerated.

20 [0012]

The method for recycling an etching solution according to the present invention, preferably comprises:

an addition step of, before the extraction step, adding a dialysis aid to an etching solution to obtain the dialysis
25 aid-containing etching solution.

[0013]

With the thus-configured method for recycling an etching solution, for regeneration of an etching solution by diffusion dialysis, a dialysis aid is added to the etching solution (used solution) (addition step) before the extraction step. As
5 a result, the dialysis capability of the anion-exchange membrane is sufficiently maintained, and therefore, the inorganic acid contained in the etching solution can be efficiently extracted into water. As a result, a used solution (exhausted solution) can be regenerated not only as an etching
10 solution but also in a state in which the regenerated solution can be used in various applications other than etching solution.

[0014]

The method for recycling an etching solution according
15 to the present invention, preferably comprises:

a preparation step of adding all or a portion of a dialysis aid to an etching solution to obtain the dialysis aid-containing etching solution before etching of the semiconductor.

20 [0015]

With the thus-configured method for recycling an etching solution, for regeneration of an etching solution by diffusion dialysis, all or a portion of the dialysis aid is added to the etching solution (unused solution) (preparation step) before
25 etching of a semiconductor. As a result, the dialysis capability of the anion-exchange membrane is sufficiently

maintained, and therefore, the inorganic acid contained in the etching solution can be efficiently extracted into water. As a result, a used etching solution (exhausted solution) can be regenerated not only as an etching solution but also in a state in which the regenerated solution can be used in various applications other than etching solution. It should be noted that in the case in which a portion of the dialysis aid is added to an etching solution (unused solution), the remainder of the dialysis aid can be added to the etching solution (used solution) before the extraction step.

[0016]

In the method for recycling an etching solution according to the present invention,

the dialysis aid is preferably a heteroatom-containing compound.

[0017]

With the thus-configured method for recycling an etching solution, the use of a heteroatom-containing compound as the dialysis aid can improve dialysis efficiency, so that the inorganic acid contained in the etching solution can be efficiently extracted into water.

[0018]

In the method for recycling an etching solution according to the present invention,

the heteroatom-containing compound is preferably a silicon-containing compound, a nitrogen-containing compound,

and/or a phosphorus-containing compound.

[0019]

With the thus-configured method for recycling an etching solution, the use of a silicon-containing compound, a
5 nitrogen-containing compound, and/or a phosphorus-containing compound as the dialysis aid can improve dialysis efficiency, so that the inorganic acid contained in the etching solution can be efficiently extracted into water.

[0020]

10 In the method for recycling an etching solution according to the present invention,

the silicon-containing compound is preferably a silane compound that has, in the molecular structure, at most three of alkoxy groups, hydroxy groups, and/or functional groups
15 that are a precursor of a hydroxy group, and/or a silane compound that has, in the molecular structure, at least four of alkoxy groups, hydroxy groups, and/or functional groups that are a precursor of a hydroxy group, and/or a halogen-containing silane compound.

20 [0021]

With the thus-configured method for recycling an etching solution, the use of the silane compound as the dialysis aid can particularly result in excellent dialysis efficiency.

[0022]

25 In the method for recycling an etching solution according to the present invention,

the nitrogen-containing compound is preferably a hydrazide and/or an ammonium compound.

[0023]

With the thus-configured method for recycling an etching
5 solution, the use of a hydrazide and/or an ammonium compound as the dialysis aid can particularly result in excellent dialysis efficiency.

[0024]

In the method for recycling an etching solution
10 according to the present invention,

the phosphorus-containing compound is particularly a phosphonic acid compound.

[0025]

With the thus-configured method for recycling an etching
15 solution, the use of a phosphonic acid compound as the dialysis aid can particularly result in excellent dialysis efficiency.

[0026]

In the method for recycling an etching solution
20 according to the present invention,

the inorganic acid is preferably phosphoric acid.

[0027]

The thus-configured method for recycling an etching solution is suitable for regeneration of an etching solution
25 for a semiconductor that contains phosphoric acid as the inorganic acid.

[0028]

In the method for recycling an etching solution according to the present invention,

the etching solution preferably contains Si derived from
5 the semiconductor at a predetermined concentration or higher.

[0029]

The thus-configured method for recycling an etching solution is useful because the method can be used to regenerate an etching solution containing Si derived from a
10 semiconductor at a predetermined concentration or higher.

[0030]

In the method for recycling an etching solution according to the present invention,

the etching solution is preferably an exhausted solution
15 that has been used in etching of the semiconductor.

[0031]

The thus-configured method for recycling an etching solution is significantly beneficial for regeneration particularly in the case in which the method is applied to an
20 exhausted solution that has been used in etching of a semiconductor.

[0032]

In the method for recycling an etching solution according to the present invention,

25 the extraction step is preferably performed by counter-current contact between the etching solution and the water

through an anion-exchange membrane.

[0033]

With the thus-configured method for recycling an etching solution, the inorganic acid contained in the etching solution
5 can be efficiently extracted into water by counter-current contact.

[0034]

In the method for recycling an etching solution according to the present invention,
10 the semiconductor preferably has a silicon nitride film as a sacrificial layer.

[0035]

The thus-configured method for recycling an etching solution is suitable for regeneration of an etching solution
15 (exhausted solution) having a high concentration of Si derived from silicon nitride.

BRIEF DESCRIPTION OF DRAWINGS

[0036]

20 [FIG. 1] FIG. 1 is a schematic diagram showing a configuration of a regeneration device for regenerating an etching solution.

[FIG. 2] FIG. 2 is a flowchart representing a method for recycling an etching solution according to the present
25 invention.

[FIG. 3] FIG. 3 is a graph of the recovery rates of

phosphoric acid recovered from etching solutions of Examples 1 to 6 and Comparative Example 1.

[FIG. 4] FIG. 4 shows graphs of the results of etching tests (with no dialysis aid) in Example 7 and Comparative Example 2.

[FIG. 5] FIG. 5 shows graphs of the results of etching tests (with a dialysis aid) in Example 8 and Comparative Example 3.

[FIG. 6] FIG. 6 shows graphs of the results of etching tests (with no dialysis aid) in Example 9.

[FIG. 7] FIG. 7 shows graphs of the results of etching tests (with no dialysis aid) in Example 10.

[FIG. 8] FIG. 8 shows graphs of the results of etching tests (with no dialysis aid) in Example 11.

[FIG. 9] FIG. 9 shows graphs of the results of etching tests (with no dialysis aid) in Example 12.

[FIG. 10] FIG. 10 shows graphs of the results of etching tests (with no dialysis aid) in Example 13.

[FIG. 11] FIG. 11 shows graphs of the results of an etching test (with a dialysis aid) in Example 14 and an etching test in Comparative Example 4.

[FIG. 12] FIG. 12 shows graphs of the results of an etching test (with a dialysis aid) in Example 15 and an etching test in Comparative Example 5.

[FIG. 13] FIG. 13 shows graphs of the results of an etching test (with a dialysis aid) in Example 16 and an

etching test in Comparative Example 6.

[FIG. 14] FIG. 14 shows graphs of the results of an etching test (with a dialysis aid) in Example 17 and an etching test in Comparative Example 7.

5 [FIG. 15] FIG. 15 shows graphs of the results of an etching test (with a dialysis aid) in Example 18 and an etching test in Comparative Example 8.

DESCRIPTION OF EMBODIMENTS

10 [0037]

Embodiments related to a method for recycling an etching solution according to the present invention will be described. The present invention is not intended to be limited to the embodiments below.

15 [0038]

[Etching Solution]

In the method for recycling an etching solution according to the present invention, an etching solution to be recycled is an etching solution that is or has been used in etching of a semiconductor. Here, the etching solution that is used in etching of a semiconductor includes an etching solution that is not unused and is still usable. The etching solution that has been used in etching of a semiconductor includes an etching solution that is exhausted (referred to as an exhausted solution). The method for recycling an etching solution according to the present invention is applicable to

recycling of not only conventional etching solutions but also etching solutions having higher performance in which silica deposition is reduced (high-performance etching solutions).

[0039]

5 An etching solution (treated solution) that is subjected to the method for recycling an etching solution according to the present invention is an inorganic acid-based solution containing a dialysis aid. The dialysis aid has the function of improving the efficiency of dialysis or reducing an
10 increase in dialysis resistance in diffusion dialysis of an etching solution using an anion-exchange membrane. The inorganic acid and dialysis aid contained in the etching solution will be described below.

[0040]

15 <Inorganic Acids>

 Examples of the inorganic acid include phosphoric acid, sulfuric acid, nitric acid, hydrochloric acid, and mixtures of these inorganic acids. Of these inorganic acids, phosphoric acid is preferable. Phosphoric acid is used in the form of an
20 aqueous solution when diluted in use, and the concentration thereof is preferably 50 to 100% by weight (wt%), more preferably 70 to 95 wt%, and even more preferably 85 to 95 wt%. It should be noted that the etching solution may be used with the phosphoric acid thereof adjusted to the above
25 concentration. For example, the above appropriate concentration can be obtained by concentrating a stock

solution containing a low-concentration aqueous phosphoric acid solution during or before use, by diluting a stock solution having a phosphoric acid concentration of more than 100 wt% (polyphosphoric acid) with water during or before use,
5 or by dissolving phosphoric anhydride (P_2O_5) in water during or before use.

[0041]

<Dialysis Aids>

Examples of the dialysis aid include heteroatom-
10 containing compounds. Examples of the heteroatom-containing compounds include silicon-containing compounds, nitrogen-containing compounds, and/or phosphorus-containing compounds. It should be noted that the silicon-containing compounds can also function as an etch inhibitor that reduces etching of
15 silicon oxide. The nitrogen-containing compounds and phosphorus-containing compounds can also function as a deposition inhibitor that reduces deposition of silica on the silicon oxide surface.

[0042]

[Silicon-Containing Compounds]

Examples of the silicon-containing compounds mainly include a silane compound that has, in the molecular structure, at most three of alkoxy groups, hydroxy groups, and/or functional groups that are a precursor of a hydroxy
25 group (this is referred to as a "first silane compound"), and/or a silane compound that has, in the molecular structure,

at least four of alkoxy groups, hydroxy groups, and/or functional groups that are a precursor of a hydroxy group (this is referred to as a "second silane compound"). The first and second silane compounds that have a hydroxy group may be a
5 silane compound that can be eventually changed to have a hydroxy group in the solution. For the first silane compound, the contained amount of the silicon-containing compound in the etching solution is preferably 0.5 to 20 wt%, more preferably 1 to 20 wt%, and even more preferably 1 to 6 wt%. For the
10 second silane compound, the contained amount of the silicon-containing compound in the etching solution is preferably 0.01 to 5 wt%, more preferably 0.01 to 1 wt%, and even more preferably 0.09 to 0.6 wt%. The silicon-containing compounds will be illustrated below.

15 [0043]

Examples of the first silane compound include
methyltrimethoxysilane, dimethyldimethoxysilane,
phenyltrimethoxysilane, dimethoxydiphenylsilane,
methyltriethoxysilane, dimethyldiethoxysilane,
20 phenyltriethoxysilane, n-propyltrimethoxysilane, n-propyltriethoxysilane, hexyltrimethoxysilane,
hexyltriethoxysilane, octyltriethoxysilane, 1,6-bis(trimethoxysilyl)hexane, vinyltrimethoxysilane, 3-glycidoxypropylmethyldimethoxysilane, 3-glycidoxypropyltrimethoxysilane, p-styryltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, 3-

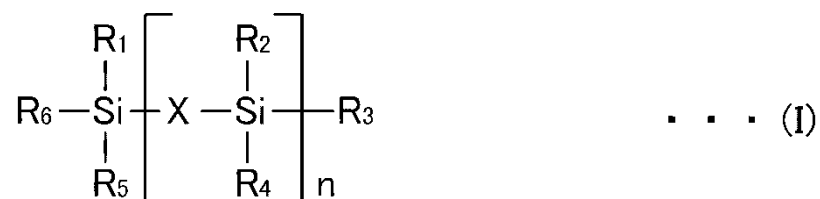
acryloxypropyltrimethoxysilane, N-2-(aminoethyl)-3-
 aminopropyltrimethoxysilane, N-2-(aminoethyl)-4-
 aminobutyltrimethoxysilane, N-2-(aminoethyl)-5-
 aminopentyltrimethoxysilane, N-2-(aminoethyl)-6-
 5 aminohexyltrimethoxysilane, N-2-(aminoethyl)-3-
 aminopropylmethyldimethoxysilane, 3-
 aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-
 triethoxysilyl-N-(1,3-dimethyl-butylidene)propylamine, N-
 phenyl-3-aminopropyltrimethoxysilane, N-(vinylbenzyl)-2-
 10 aminoethyl-3-aminopropyltrimethoxysilane, a hydrochloride of
 each of the above aminosilanes, tris-
 (trimethoxysilylpropyl)isocyanurate, 3-
 mercaptopropylmethyldimethoxysilane, 3-
 isocyanatepropyltriethoxysilane, 3-
 15 trimethoxysilylpropylsuccinic anhydride, and a hydrolysate of
 each of the above alkoxy silanes. Of these first silane
 compounds, 3-aminopropyltrimethoxysilane, 3-
 aminopropyltriethoxysilane, N-2-(aminoethyl)-3-
 aminopropyltrimethoxysilane, N-2-(aminoethyl)-3-
 20 aminopropylmethyldimethoxysilane, and hydrolysates of these
 alkoxy silanes are preferable. These first silane compounds
 may be used alone or in a mixture of two or more thereof.

[0044]

The second silane compound typically has a chemical
 25 structure represented by the following formula (I).

[0045]

[Chemical Structural Formula 1]



In formula (I), R₁ to R₆ represent a substituent. At least four of these substituents are at least one specific substituent selected from the group consisting of an alkoxy group, a hydroxy group, and chlorine. The substituents other than the specific substituent(s) are at least one substituent selected from the group consisting of an alkyl group, an aryl group, a carbonyl group, a carboxyl group, an amino group, an ethylene diamine group, and derivatives or complexes of these substituents. In formula (I), X represents "O" (oxygen atom) or "-" (single bond). In formula (I), n represents an integer of 0 to 3. Thus, the second silane compound may be not only a compound having an alkoxy group (a siloxane compound or a disilane compound, the same applies to the following) or a compound having a hydroxy group, but also a compound having chlorine. It should be noted that the compound having an alkoxy group and the compound having chlorine are a compound that does not originally have a hydroxy group, and has a hydroxy group when the compound is hydrolyzed.

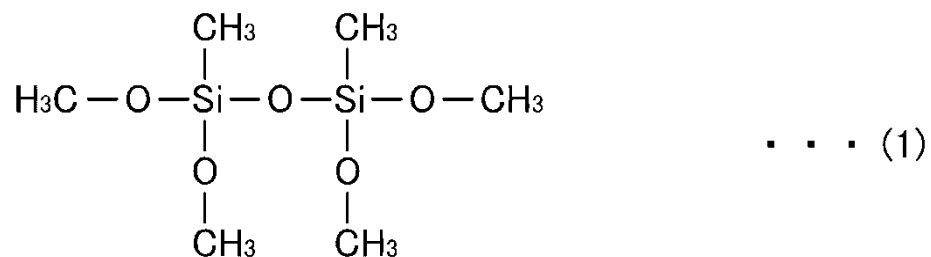
[0046]

Specific examples of the second silane compound include 1,3-dimethyltetramethoxydisiloxane, represented by the

following chemical structural formula (1):

[0047]

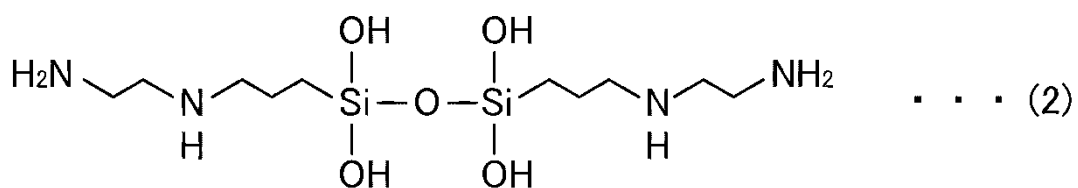
[Chemical Structural Formula 2]



5 a siloxane compound represented by the following chemical structural formula (2):

[0048]

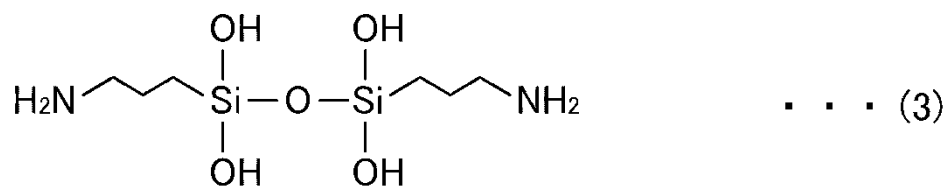
[Chemical Structural Formula 3]



10 a siloxane compound represented by the following chemical structural formula (3):

[0049]

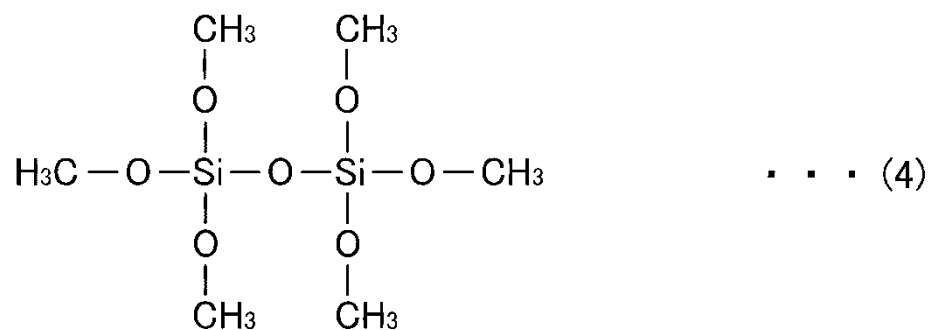
[Chemical Structural Formula 4]



15 hexamethoxydisiloxane, represented by the following chemical structural formula (4):

[0050]

[Chemical Structural Formula 5]



tetramethoxysilane, tetraethoxysilane, tetrabutoxysilane,
 hexamethoxydisilane, hexaethoxydisilane, hexabutoxydisilane,
 hexamethoxydisiloxane, hexaethoxydisiloxane,
 5 hexabutoxydisiloxane, 1,3-dimethyltetraethoxydisiloxane, 1,3-
 dimethyltetrabutoxydisiloxane, 1,3-
 diethyltetramethoxydisiloxane, 1,3-
 diethyltetraethoxydisiloxane, 1,3-
 diethyltetrabutoxydisiloxane, 1,3-
 10 divinyltetramethoxydisiloxane, 1,3-
 divinyltetraethoxydisiloxane, 1,3-
 divinyltetrabutoxydisiloxane, 1,3-bis(3-
 aminopropyl)tetramethoxydisiloxane, tetrachloride silicon,
 hexachlorodisilane, hexachlorodisiloxane, 1,3-
 15 dimethyltetrachlorodisiloxane, 1,3-
 diethyltetrachlorodisiloxane, and 1,3-
 dibutyltetrachlorodisiloxane. Incidentally, examples of the
 siloxane compound that is commercially available include the
 silane coupling agents "X-12-1098," "X-12-1135," "KBP-64," and
 20 "KBP-90," manufactured by Shin-Etsu Chemical Co., Ltd. These
 second silane compounds may be used alone or in a mixture of
 two or more thereof.

[0051]

The silicon-containing compounds may include, in addition to the first and second silane compounds, halogen-containing silane compounds. Examples of the halogen-containing silane compounds include hexafluorosilicates and salts thereof.

[0052]

[Nitrogen-Containing Compounds]

Examples of the nitrogen-containing compounds include hydrazine compounds, pyrazoles, triazoles, hydrazides, ammonium compounds, compounds having an imidazole backbone, compounds having a pyrrolidine backbone, compounds having a piperidine backbone, compounds having a morpholine backbone, compounds having a pyridine backbone, compounds having a quaternary ammonium backbone, compounds having a pyrimidine backbone, compounds having a purine backbone, and compounds having a urea backbone. Hydrazides and ammonium compounds are preferably used. These compounds and substances may be used alone or in a mixture of two or more thereof. When at least two different nitrogen-containing compounds are used, the nitrogen-containing compounds are considerably useful in terms of not only performance in the etching process but also the longer life and cost reduction of the solution. The amount of the nitrogen-containing compound(s) contained in the etching solution is preferably 0.1 to 1 wt%, more preferably 0.3 to 0.4 wt%. The nitrogen-containing compounds will be illustrated

below.

[0053]

[Hydrazine Compounds]

Examples of the hydrazine compounds include hydrazine,
5 butylhydrazine, isopropylhydrazine, benzylhydrazine, N,N-
dimethylhydrazine, 1,2-diacetylhydrazine, phenylhydrazine,
N,N-dicarbamoylhydrazine, hydrazine sulfate, hydrazine
monohydrochloride, hydrazine dihydrochloride, butylhydrazine
hydrochloride, hydrazine carbonate, and hydrazine
10 monohydrobromide. These hydrazine compounds may be used alone
or in a mixture of two or more thereof.

[0054]

[Pyrazoles]

Examples of the pyrazoles include 3,5-dimethylpyrazole
15 and 3-methyl-5pyrazon. These pyrazoles may be used alone or in
a mixture of two or more thereof.

[0055]

[Triazoles]

Examples of the triazoles include 4-amino-1,2,4-
20 triazole, 1,2,4-triazole, 1,2,3-triazole, 1-
hydroxybenzotriazole, and 3-mercapto-1,2,4-triazole. These
triazoles may be used alone or in a mixture of two or more
thereof.

[0056]

25 [Hydrazides]

Examples of the hydrazides include propionic acid

hydrazide, laurylic acid hydrazide, salicylic acid hydrazide, formohydrazide, acetohydrazide, acetohydrazide chloride, p-hydroxybenzoic acid hydrazide, naphthoic acid hydrazide, 3-hydroxy-2-naphthoic acid hydrazide, benzhydrazide, carbodihydrazide, oxalic acid dihydrazide, malonic acid dihydrazide, succinic acid dihydrazide, succinic acid 2,2-dimethylhydrazide, glutaric acid dihydrazide, adipic acid dihydrazide, azelaic acid dihydrazide, sebacic acid dihydrazide, dodecanedioic acid dihydrazide, maleic acid dihydrazide, fumaric acid dihydrazide, tartaric acid dihydrazide, malic acid dihydrazide, diglycolic acid dihydrazide, isophthalic acid dihydrazide, terephthalic acid dihydrazide, 2,6-naphthalenedicarboxylic acid dihydrazide, 2,6-naphthoic acid dihydrazide, citric acid trihydrazide, pyromellitic acid trihydrazide, 1,2,4-benzenetricarboxylic acid trihydrazide, nitrilotriacetic acid trihydrazide, 1,3,5-cyclohexanetricarboxylic acid trihydrazide, ethylenediaminetetraacetic acid tetrahydrazide, and 1,4,5,8-naphthoic acid tetrahydrazide. Of these hydrazides, adipic acid dihydrazide, succinic acid dihydrazide, acetohydrazide chloride, succinic acid 2,2-dimethylhydrazide, and azelaic acid dihydrazide are preferable. These hydrazides may be used alone or in a mixture of two or more thereof.

[0057]

25 [Ammonium Compounds]

Examples of the ammonium compounds include ammonium

phosphate, ammonium sulfate, ammonium nitrate, and ammonium chloride. Ammonium phosphate is preferable. These ammonium compounds may be used alone or in a mixture of two or more thereof.

5 [0058]

[Compounds Having Imidazole Backbone]

Examples of the compounds having an imidazole backbone include compounds such as imidazole, imidazolecarboxylic acid, imidurea, diazolidinyl urea, 3-(2-oxoimidazolidin-1-yl)benzate, and imidazolehydrochlorides, and imidazolium salts such as 1-ethyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium chloride, 1,3-dimethylimidazoliummethyl sulfate, 1-ethyl-3-methylimidazolium acetate, 1-ethyl-3-octylimidazolium tetrafluoroborate, 1,3-dimethylimidazolium dimethylphosphate, 1-ethyl-3-methylimidazolium tetrafluoroborate, and 1-ethyl-3-methylimidazolium phosphate. These compounds having an imidazole backbone may be used alone or in a mixture of two or more thereof.

[0059]

20 [Compounds Having Pyrrolidine Backbone]

Examples of the compounds having a pyrrolidine backbone include compounds such as pyrrolidine, 2-pyrrolidone, N-methylpyrrolidone, N-vinyl-2-pyrrolidone, pyroglutamic acid, and piracetam, and pyrrolidinium salts such as 1-ethyl-1-methylpyrrolidinium chloride, 1-butyl-1-methylpyrrolidinium chloride, 1-ethyl-1-methylpyrrolidinium acetate, 1-ethyl-1-

methylypyrrolidinium tetrafluoroborate, 1-butyl-1-
methylypyrrolidinium tetrafluoroborate, 1-ethyl-1-
methylypyrrolidinium hexafluorophosphate, and 1-butyl-1-
methylypyrrolidinium hexafluorophosphate. These compounds
5 having a pyrrolidine backbone may be used alone or in a
mixture of two or more thereof.

[0060]

[Compounds Having Piperidine Backbone]

Examples of the compounds having a piperidine backbone
10 include compounds such as piperidine, ethylpiperidine-4-
carboxylate, piperidin-2-ylacetate, and methylpiperidine-4-
carboxamide, and piperidinium salts such as (piperidinium-1-
ylmethyl)trifluoroborate, 1-butyl-1-methylpiperidinium
bromide, and 1-butyl-1-methylpiperidinium bisimide. These
15 compounds having a piperidine backbone may be used alone or in
a mixture of two or more thereof.

[0061]

[Compounds Having Morpholine Backbone]

Examples of the compounds having a morpholine backbone
20 include compounds such as morpholine, morpholin-2-ylmethanol,
morpholin-3-one, morpholine-4-carbothioic acid amide,
morpholin-4-ylacetate, and morpholine-4-ylethylacetate, and
morpholinium salts such as 4-ethyl-4-methylmorpholinium
bromide, and 4-(2-ethoxyethyl)-4-methylmorpholinium bisimide.
25 These compounds having a morpholine backbone may be used alone
or in a mixture of two or more thereof.

[0062]

[Compounds Having Pyridine Backbone]

Examples of the compounds having a pyridine backbone include compounds such as pyridine, N,N-dimethyl-4-aminopyridine, bipyridine, 2,6-lutidine, and pyridinium p-toluenesulfonate, and pyridinium salts such as 1-butyl-3-methylpyridinium chloride, 1-butylpyridinium tetrafluoroborate, and 1-butylpyridinium hexafluorophosphate. These compounds having a pyridine backbone may be used alone or in a mixture of two or more thereof.

[0063]

[Compounds Having Quaternary Ammonium Backbone]

Examples of the compounds having a quaternary ammonium backbone include tetramethylammonium chloride, tetrabutylammonium chloride, tetramethylammonium bromide, tetramethylammonium hydroxide, tetramethylammonium iodide, tetrabutylammonium bromide, tetrabutylammonium hydrogen sulfate, tetramethylammonium hexafluorophosphate, tetrabutylammonium hexafluorophosphate, and choline acetate. These compounds having a quaternary ammonium backbone may be used alone or in a mixture of two or more thereof.

[0064]

[Compounds Having Pyrimidine Backbone]

Examples of the compounds having a pyrimidine backbone include thymine, cytosine, uracil, and nucleosides, ribonucleosides, and deoxyribonucleosides thereof. These

compounds having a pyrimidine backbone may be used alone or in a mixture of two or more thereof.

[0065]

[Compounds Having Purine Backbone]

5 Examples of the compounds having a purine backbone include purine, adenine, guanine, uric acid, caffeine, hypoxanthine, xanthine, theophylline, theobromine, isoguanine, and nucleosides, ribonucleosides, and deoxyribonucleosides thereof. These compounds having a purine backbone may be used
10 alone or in a mixture of two or more thereof.

[0066]

[Compounds Having Urea Backbone]

 Examples of the compounds having a urea backbone include urea, hydroxyurea, N,N-diethylthiourea, N,N-dibutylthiourea,
15 biurea, biuret, and N-amidinothiourea. These compounds having a urea backbone may be used alone or in a mixture of two or more thereof.

[0067]

[Phosphorus-Containing Compounds]

20 Examples of the phosphorus-containing compounds include phosphonic acid compounds. Examples of the phosphonic acid compounds include compounds such as phosphonic acid, diphenyl phosphite, butyl phosphite, dipentyl phosphite, phosphorous acid, hypophosphorous acid, and ammonium phosphate, and
25 phosphonium salts such as tetrabutylphosphonium hexafluorophosphate, tetrabutylphosphonium bisimide, and

tetrabutylphosphonium bromide. It should be noted that the ammonium phosphate compounds are a phosphorus-containing compound and a nitrogen-containing compound. These phosphonic acid compounds may be used alone or in a mixture of two or
5 more thereof.

[0068]

[Formulation of Etching Solution Before Regeneration Treatment]

An etching solution that is subjected to a regeneration
10 treatment is formulated by adding a dialysis aid. The dialysis aid can be directly added to the etching solution. Alternatively, the dialysis aid may be dissolved or suspended in a solvent, which may then be added to the etching solution. Concerning the timing with which the dialysis aid is added to
15 the etching solution, the dialysis aid is typically added to an exhausted solution that has been used in etching of a semiconductor. Alternatively, the dialysis aid may be previously added to a brand-new etching solution before the etching solution is used in etching of a semiconductor. The
20 dialysis aid may be added to the etching solution at room temperature or while the solution is being heated.

[0069]

<Solvents>

Examples of the solvent for dissolving or suspending the
25 dialysis aid include water, alcohols such as methanol, ethanol, 2-propanol, butanol, octanol, benzyl alcohol,

ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, and 2,2,2-trifluoroethanol, ethers such as diethyl ether, diisopropyl ether, dibutyl ether, cyclopentylmethyl ether (CPME), tetrahydrofuran (THF), 2-methyltetrahydrofuran, 1,4-dioxane, and dimethoxy ethane, carbonic acid esters such as ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, ethylmethyl carbonate, and 4-fluoroethylenecarbonate, esters such as methyl formate, ethyl formate, propyl formate, methyl acetate, ethyl acetate, butyl acetate, methyl propionate, ethyl propionate, methyl butyrate, and γ -lactone, nitriles such as acetonitrile, propionitrile, valeronitrile, glutaronitrile, adiponitrile, methoxyacetonitrile, 3-methoxypropionitrile, and benzonitrile, amides such as N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), and N-methylpyrrolidone (NMP), ureas such as dimethyl sulfoxide (DMSO), hexamethylphosphoric triamide (HMPA), N,N,N',N'-tetramethylurea (TMU), and N,N'-dimethylpropyleneurea (DMPU), and ionic liquids such as imidazolium salts, pyrrolidinium salts, piperidinium salts, pyridinium salts, morpholinium salts, phosphonium salts, quaternary ammonium salts, and sulfonium salts. Concerning the ionic liquids, examples of the cation include an imidazolium backbone, pyrrolidinium backbone, piperidinium backbone, morpholinium backbone, pyridinium backbone, quaternary phosphonium backbone, quaternary ammonium backbone, and sulfonium backbone, and examples of the anion include Br⁻,

BF_4^- , PF_6^- , $(\text{CN})_2\text{N}^-$, Cl^- , I^- , $(\text{CF}_3\text{SO}_2)\text{N}^-$, $(\text{F}_2\text{SO}_2)\text{N}^-$, CH_3COO^- , HSO_4^- , $(\text{CH}_3)_2\text{PO}_4^-$, CF_3COO^- , CH_3SO_3^- , CF_3SO_3^- , and SCN^- . These solvents may be used alone or in a mixture of two or more thereof.

[0070]

5 <Surfactants>

The dialysis aid may be dissolved or suspended in the solvent in combination with a surfactant. As the surfactant, any of cationic surfactants, anionic surfactants, amphoteric surfactants, and nonionic surfactants may be used, or a
10 combination of these surfactants may be used.

[0071]

[Regeneration of Etching Solution]

When an etching solution is used in etching of a semiconductor, the component Si derived from silicon nitride
15 gradually accumulates in the solution. If the Si concentration exceeds a predetermined concentration, the etching solution can no longer be used. Meanwhile, the high-performance etching solution also contains the component Si derived from a silane coupling agent or the like. However, the high-performance
20 etching solution can be still used even when the concentration of Si derived silicon nitride in the solution reaches a concentration significantly higher than those of conventional etching solutions. This is because the silane coupling agent or the like maintains a stable structure even at any high
25 temperature in an etching solution, and is not involved with a decrease in performance of an etching solution that is caused

when the component Si derived from a silane coupling agent or the like is deposited in the form of silica.

[0072]

However, even in the high-performance etching solution,
5 when the concentration of Si derived from silicon nitride in the solution is excessively high, the component Si is likely to aggregate and settle out of the solution in the form of small silica crystals, for example. Therefore, in the present invention, a used etching solution (exhausted solution) is
10 subjected to a regeneration (or recycling) treatment so as to be recycled as an etching solution (including a high-performance etching solution) or various other products.

[0073]

Embodiments related to the the method for recycling an
15 etching solution according to the present invention will be described below. It should be noted that in the embodiments below, it is assumed that phosphoric acid (H_3PO_4) is used as an inorganic acid that serves as the base of an etching solution. It should be noted that the unit of the concentration of
20 phosphoric acid used in an etching solution is expressed as percent by weight (wt%), which is herein denoted by %. The unit of the concentration of Si derived from silicon nitride in an etching solution is expressed as weight by weight (mg/kg), which is herein denoted by ppm.

25 [0074]

<Regeneration Device>

Firstly, a regeneration device used for carrying out the method for recycling an etching solution according to the present invention will be described. FIG. 1 is a schematic diagram showing a configuration of a regeneration device 100 for regenerating (or recycling) an etching solution. FIG. 1(a) is a diagram showing an entire configuration of the regeneration device 100. FIG. 1(b) is a partially enlarged view of the regeneration device 100 surrounded by a dashed-line elliptical portion A in FIG. 1(a). The regeneration device 100 is used for regenerating an etching solution that is or has been used in etching of a semiconductor. The regeneration device 100 mainly includes an original solution reservoir tank 10 for retaining a used etching solution, a water reservoir tank 20 for retaining water, an aid reservoir tank 30 for retaining a dialysis aid, a diffusion dialysis device 40 for regenerating an etching solution, a treated solution reservoir tank 50 for retaining a treated solution (hereinafter also referred to as a "recovered acid") produced from the diffusion dialysis device 40, and a waste solution reservoir tank 60 for retaining a waste solution discharged from the diffusion dialysis device 40 (hereinafter also referred to as a "deoxidized solution"). It should be noted that all the dialysis aid may be previously added to a brand-new etching solution that is before being used in etching of a semiconductor. In that case, the aid reservoir tank 30 may not be used. A portion of the dialysis aid may be previously added

to a brand-new etching solution that is before being used in etching of a semiconductor. In that case, the remainder of the dialysis aid may be retained in the aid reservoir tank 30.

[0075]

5 The original solution reservoir tank 10 retains a phosphoric acid-based etching solution (exhausted solution) that has been used in etching of a semiconductor having a silicon nitride film as a sacrificial layer (e.g., a 2D NAND, 3D NAND, CMOS, DRAM, 3D RAM, logic IC, etc.). This etching
10 solution has already been used, and therefore, contains Si derived from silicon nitride at a predetermined concentration or higher. The concentration (predetermined concentration) of Si derived from silicon nitride is typically at least 10 ppm, but may be in the range of about 50 to 2000 ppm, or may reach
15 3000 ppm, for example.

[0076]

 The water reservoir tank 20 retains water that is used in regeneration of an etching solution. The water serves as a medium for extracting phosphoric acid from an etching solution
20 and therefore is preferably pure water.

[0077]

 The aid reservoir tank 30 retains an aqueous solution obtained by dissolving a dialysis aid in water. As the dialysis aid, the above various heteroatom-containing
25 compounds can be used. The dialysis aid is added to the original solution reservoir tank 10 by an aid addition pump

31. It should be noted that when a sufficient amount of the heteroatom-containing compound is already contained in an etching solution, the dialysis aid is considered to be already added, and a reduced amount of the dialysis aid may be added to the original solution reservoir tank 10, or the dialysis aid may not be added to the original solution reservoir tank 10.

[0078]

The diffusion dialysis device 40 mainly has a plurality of anion-exchange membranes 42. The plurality of anion-exchange membranes 42 are sandwiched by frames 41 from the opposite ends thereof. The number of anion-exchange membranes 42 can be appropriately set. The anion-exchange membranes 42 are arranged in parallel and equally spaced with a spacer (not shown) interposed between each anion-exchange membrane. As a result, spaces 43 are arranged in parallel, one being formed between each adjacent anion-exchange membrane 42. In each space 43, a flow of an etching solution delivered from the original solution reservoir tank 10 by an original solution pump 11 or water delivered from the water reservoir tank 20 by a water pump 21 is caused to pass in alternating opposite directions. As a result, the etching solution and the water are brought into counter-current contact with each other through the anion-exchange membrane 42. It should be noted that the etching solution may optionally be passed through a filtration device 12 before being introduced into the

diffusion dialysis device 40. As a result, insoluble components present in the etching solution can be removed, so that clogging of the anion-exchange membrane 42 during diffusion dialysis can be reliably prevented.

5 [0079]

The treated solution reservoir tank 50 retains a recovered acid (aqueous phosphoric acid solution) that has been treated in the diffusion dialysis device 40. The phosphoric acid aqueous solution is pumped out by a treated
10 solution pump 51, and is used again, optionally after being passed through a concentration device 52.

[0080]

The waste solution reservoir tank 60 retains a waste solution produced in the diffusion dialysis device 40
15 (deoxidized solution after extraction of phosphoric acid from the etching solution). After the waste solution is pumped out by a waste solution pump 61, the waste solution may optionally be subjected to a neutralization treatment, desiliconization treatment, or the like in waste solution treatment equipment
20 (not shown).

[0081]

<Regeneration Method>

FIG. 2 is a flowchart representing the method for recycling an etching solution according to the present
25 invention. The method for recycling an etching solution includes, as an essential step, an extraction step of

extracting an inorganic acid contained in an etching solution containing a dialysis aid into water. The method for recycling an etching solution further includes, as a preferable step, an addition step of adding a dialysis aid to an etching solution before the extraction step. The method for recycling an etching solution further includes, as optional and additional steps, a filtration step before the extraction step, and a concentration step after the extraction step. It should be noted that apart from the steps shown in FIG. 2, a preparation step of adding a dialysis aid to an etching solution before etching of a semiconductor may be performed. In the following embodiments, the method for recycling an etching solution that includes the addition step and extraction step will be described as an example.

[0082]

For example, in order to regenerate a used etching solution (exhausted solution) in which the concentration of phosphoric acid, represented by H_3PO_4 , is 80 to 100%, a dialysis aid is added to the etching solution (S1; the addition step). The dialysis aid is preferably added in the form of an aqueous solution obtained by dissolving the dialysis aid in water. Alternatively, a solid (powder) dialysis aid may be directly added to the etching solution. In the case in which a powder dialysis aid is added to the etching solution, a screw feeder may, for example, be used instead of the aid reservoir tank 30 and the aid addition pump

31 shown in FIG. 1(a).

[0083]

The etching solution to which the dialysis aid has been added is brought into contact with water through an anion-exchange membrane so that phosphoric acid contained in the etching solution is extracted into water (S3; the extraction step). Here, the extraction step will be described in greater detail. A used etching solution typically contains Si derived from silicon nitride at a predetermined concentration or higher. In general, when Si compounds accumulate in an etching solution (the Si concentration increases), the Si compounds are likely to be deposited in the form of fine silica crystals. However, in the present invention, because a dialysis aid is added to an etching solution, Si compounds are maintained in a stable state in the solution, so that silica deposition is reduced. Meanwhile, for such an etching solution in which silica deposition is reduced, the component Si cannot be removed from the solution by conventional filtration using a filter. Therefore, in the present invention, diffusion dialysis using an anion-exchange membrane is employed. In this diffusion dialysis, an etching solution is brought into contact with water through an anion-exchange membrane so that phosphoric acid contained in the etching solution is moved to the water. In the present invention, in extraction of phosphoric acid by diffusion dialysis, an etching solution is brought into counter-current contact with water through an

anion-exchange membrane. In the example shown in FIG. 1(a), of the plurality of spaces 43 formed in parallel and each positioned between adjacent anion-exchange membranes 42, a flow of an etching solution is passed through the even-
5 numbered spaces 43 from the left of the diagram, from below the anion-exchange membrane 42, and a flow of pure water is passed through the odd-numbered spaces 43 from above the anion-exchange membrane 42. As shown in FIG. 1(b), the etching solution contains a phosphoric acid ion (PO_4^{3-}) and a cation
10 including silicon (Si^+). It should be noted that silicon is less likely to become an ion by itself, and therefore, is considered to be actually present in the form of a complex ion or the like. However, in the description and FIG. 1(b), it is assumed that silicon is present as a silicon ion (Si^+) for the
15 sake of simplicity. When an etching solution is brought into counter-current contact with water through an anion-exchange membrane, phosphoric acid ions in the etching solution can move to water through the anion-exchange membrane 42, and silicon ions cannot pass through the anion-exchange membrane
20 42 and are left in the etching solution. Because the etching solution contains a dialysis aid added thereto, the dialysis capability of the anion-exchange membrane 42 is maintained during diffusion dialysis. Therefore, in the present invention, phosphoric acid contained in an etching solution
25 can be efficiently extracted (recovered) into water.

[0084]

In the method for recycling an etching solution according to the present invention, an etching solution may be subjected to filtration (S2; a filtration step), which is not essential, before the extraction step (S3) is performed. By
5 performing the filtration step (S2), insoluble components can be removed from the etching solution, and therefore, clogging of the anion-exchange membrane 42 can be reliably prevented in the extraction step (S3). In addition, after the extraction step (S3), the treated solution containing phosphoric acid
10 obtained by the extraction step (S3) may optionally be concentrated (S4; a concentration step).

[0085]

As described above, in the method for recycling an etching solution according to the present invention, an
15 etching solution is regenerated by diffusion dialysis in which the etching solution is brought into contact with water through an anion-exchange membrane so that phosphoric acid contained in the etching solution is extracted into the water. According to the present invention, a treated solution
20 (recovered acid) can be recycled not only as an etching solution but also in a state in which the treated solution can be used in various applications other than etching solution.

[0086]

Because a dialysis aid is added to an etching solution,
25 silica deposition does not occur even when the concentration of Si derived from silicon nitride in the etching solution is

in the range of about 10 ppm to about 50-2000 ppm, or is as high as about 3000 ppm, so that the dialysis capability of the anion-exchange membrane is sufficiently maintained. As a result, phosphoric acid contained in the etching solution can
5 be efficiently extracted into water.

[0087]

Thus, the method for recycling an etching solution according to the present invention can be used for regenerating not only conventional etching solutions but also
10 a high-performance etching solution obtained by adding a deposition inhibitor for inhibiting silica deposition to an etching solution.

[Examples]

[0088]

15 Examples of the method for recycling an etching solution according to the present invention will be described below. It should be noted that the symbol % as which the added amount of each component (contained amount in an etching solution) is expressed in the examples is an abbreviation of wt% unless
20 otherwise specified.

[0089]

<Formulation of Etching Solution (Exhausted Solution)>

[Example 1]

Silicon nitride film was dissolved in phosphoric acid
25 having a concentration of 85% (manufactured by Rasa Industries, Ltd.) to adjust the concentration of Si to 200

ppm. This solution was heated at 80 to 100°C to evaporate water and thereby adjust the concentration of phosphoric acid to 87%. To the solution, 3-aminopropyltrimethoxysilane (2%) and adipic acid dihydrazide (0.2%) were added as a dialysis
5 aid. Thus, the etching solution (simulated solution) of Example 1 was prepared. The use of the etching solution of Example 1 corresponds to the situation in which the addition step of adding a dialysis aid to an etching solution has been performed before the extraction step.

10 [0090]

[Example 2]

A procedure similar to that described in Example 1, except that only 3-aminopropyltriethoxysilane (3%) was added as a dialysis aid, was used to prepare the etching solution of
15 Example 2.

[0091]

[Example 3]

A procedure similar to that described in Example 1, except that 3-aminopropyltriethoxysilane (3%) and
20 hexafluorosilicate (0.001%) were added as a dialysis aid, was used to prepare the etching solution of Example 3.

[0092]

[Example 4]

A procedure similar to that described in Example 1, except that a hydrolysate of 3-aminopropyltriethoxysilane
25 (1.2%) and ammonium phosphate (0.1%) were added as a dialysis

aid, was used to prepare the etching solution of Example 4.

[0093]

[Example 5]

A procedure similar to that described in Example 1,
5 except that a hydrolysate of 3-aminopropyltriethoxysilane
(1.2%) and phosphorous acid (0.1%) were added as a dialysis
aid, was used to prepare the etching solution of Example 5.

[0094]

[Example 6]

10 A hydrolysate of 3-aminopropyltrimethoxysilane (10.2%),
a siloxane compound represented by chemical structure formula
(2) (0.34%), and adipic acid dihydrazide (0.3%) were added to
phosphoric acid having a concentration of 85% (manufactured by
Rasa Industries, Ltd.). Then, silicon nitride film was
15 dissolved in the solution to adjust the concentration of Si to
2000 ppm. This solution was heated at 80 to 100°C to evaporate
water and thereby adjust the concentration of phosphoric acid
to 87%. Thus, the etching solution of Example 6 was prepared.
The use of the etching solution of Example 6 corresponds to
20 the situation in which the addition step of adding a dialysis
aid to an etching solution has been performed before a
semiconductor is etched.

[0095]

[Comparative Example 1]

25 A procedure similar to that described in Example 1,
except that a dialysis aid was not added (i.e., no dialysis

aid was contained), was used to prepare the etching solution of Comparative Example 1.

[0096]

<Regeneration Test>

5 Diffusion dialysis was performed on the etching solutions of Examples 1 to 6 and Comparative Example 1 using the regeneration device 100 of FIG. 1.

[0097]

FIG. 3 is a graph of the recovery rates of phosphoric acid recovered from the etching solutions of Examples 1 to 6 and Comparative Example 1. The phosphoric acid recovery rate of the etching solution of Example 1 was maintained at about 90% for 30 days, and clogging of the anion-exchange membrane did not occur. For the etching solutions of Examples 2 to 5, 15 the phosphoric acid recovery rate of at least about 90% was maintained for at least 7 days. It should be noted that for Examples 2 to 5, the regeneration test was not conducted on day 8 or later. This is because according to the tendency observed in Example 1, it was predicted that the phosphoric acid recovery rates of Examples 2 to 5 could be similarly 20 maintained for at least about 30 days. For the etching solution of Example 6, the phosphoric acid recovery rate was about 73 to 74% from the first day (day 1) to day 7, but clogging of the anion-exchange membrane did not occur. In 25 contrast to this, the phosphoric acid recovery rate of the etching solution of Comparative Example 1, which does not

contain a dialysis aid, was as low as about 60% from the first day (day 1), and subsequently, the regeneration test was not able to be continued due to clogging of the anion-exchange membrane.

5 [0098]

<Performance Confirmation Test 1 on Regenerated Etching Solution>

For an etching solution regenerated by the method for recycling an etching solution according to the present invention, a performance confirmation test was conducted in order to check if the etching performance decreased compared to a brand-new etching solution. The performance confirmation test was firstly conducted on a "dialysis aid-free system" in which a dialysis aid was not added to an etching solution (Example 7 and Comparative Example 2) and a "dialysis aid-added system" in which a dialysis aid was added to an etching solution (Example 8 and Comparative Example 3) for each of a regenerated etching solution obtained by subjecting the etching solution of Example 1 to the regeneration device 100, and a brand-new etching solution.

[0099]

[Dialysis Aid-Free System: Example 7 and Comparative Example 2]

An etching test on silicon oxide film (Example 7-1) and and an etching test on silicon nitride film (Example 7-2) were conducted using a regenerated etching solution having an

adjusted phosphoric acid concentration (87%) and an adjusted Si concentration in the solution (0 to 100 ppm). Likewise, an etching test on silicon oxide film (Comparative Example 2-1) and an etching test on silicon nitride film (Comparative Example 2-2) were conducted using a brand-new etching solution.

[0100]

FIG. 4 shows graphs of the results of the etching tests (with no dialysis aid) in Example 7 and Comparative Example 2.

FIG. 4(a) shows the results of the etching test on silicon oxide in Example 7-1 and Comparative Example 2-1. FIG. 4(b) shows the results of the etching test on silicon nitride in Example 7-2 and Comparative Example 2-2. In fabrication of a semiconductor having a silicon oxide film and a silicon nitride film that serves as a sacrificial layer, it is desirable to maintain the etch rate of silicon oxide at a low level, and maintain the etch rate of silicon nitride at a high level. For etching characteristics with respect to silicon oxide, it was confirmed that the regenerated etching solution has an etching inhibition effect on silicon oxide that is as good as or better than that of the brand-new etching solution when the Si concentration is in the range of 0 to 100 ppm. For etching characteristics with respect to silicon nitride, it was confirmed that the regenerated etching solution has an etching effect on silicon nitride that is as good as or better than that of the brand-new etching solution when the Si

concentration is in the range of 0 to 100 ppm. In particular, in a region where the Si concentration is low, the regenerated etching solution had an excellent etching inhibition effect on silicon oxide compared to the brand-new etching solution. This
5 may be because the regenerated etching solution contains a small amount of Si compounds that are not derived from silicon nitride (e.g., Si compounds derived from an etch inhibitor or dialysis aid), and the Si compounds act on silicon oxide so as to inhibit etching of silicon oxide.

10 [0101]

[Dialysis Aid-Added System: Example 8 and Comparative Example 3]

An etching test on silicon oxide film (Example 8-1) and an etching test on silicon nitride film (Example 8-2) were
15 conducted using a regenerated etching solution that had an adjusted phosphoric acid concentration (87%) and an adjusted Si concentration in the solution (0 to 200 ppm) and to which 3-aminopropyltrimethoxysilane (2%) and adipic acid dihydrazide (0.2%) were added as a dialysis aid. Likewise, an etching test
20 on silicon oxide film (Comparative Example 3-1) and an etching test on silicon nitride film (Comparative Example 3-2) were conducted using a brand-new etching solution to which 3-aminopropyltrimethoxysilane (2%) and adipic acid dihydrazide (0.2%) were added as a dialysis aid.

25 [0102]

FIG. 5 shows graphs of the results of the etching tests

(with a dialysis aid) in Example 8 and Comparative Example 3. FIG. 5(a) shows the results of the etching test on silicon oxide in Example 8-1 and Comparative Example 3-1. FIG. 5(b) shows the results of the etching test on silicon nitride in Example 8-2 and Comparative Example 3-2. For etching characteristics with respect to silicon oxide, it was confirmed that the regenerated etching solution has an etching inhibition effect on silicon oxide that is as good as that of the brand-new etching solution when the Si concentration is in the range of 0 to 200 ppm. For etching characteristics with respect to silicon nitride, it was confirmed that the regenerated etching solution has an etching effect on silicon nitride that is as good as that of the brand-new etching solution when the Si concentration is in the range of 0 to 200 ppm. Because the regenerated etching solution contains a small amount of Si compounds that are not derived from silicon nitride, the regenerated etching solution had a more excellent function than that of the brand-new etching solution (the etch rate of silicon nitride was high, and the etch rate of silicon oxide was low) in Example 7 and Comparative Example 2. However, in Example 8 and Comparative Example 3, 3-aminopropyltrimethoxysilane (2%) and adipic acid dihydrazide (0.2%) were added as a dialysis aid, so that the brand-new etching solution also contained Si compounds that are not derived from silicon nitride. It is considered that as a result, the gap in performance between the regenerated etching

solution and the brand-new etching solution was narrowed.

[0103]

[Selectivity Ratio]

In Examples 7 and 8 and Comparative Examples 2 and 3,
5 the selectivity ratio (R_1/R_2) of the etch rate (R_1) of silicon
nitride to the etch rate (R_2) of silicon oxide is shown in
Table 1 below. As the absolute value of the selectivity ratio
(R_1/R_2) increases, a higher level of etching performance with
respect to silicon nitride is obtained while etching of
10 silicon oxide is reduced. Therefore, an etching solution
having a higher selectivity ratio (R_1/R_2) can be rated as
having excellent etch selectivity. The regenerated etching
solutions of Examples 7 and 8 had a selectivity ratio (R_1/R_2)
that is equal to or higher than those of the brand-new etching
15 solutions of Comparative Examples 2 and 3, and were able to be
effectively used.

[0104]

[Table 1]

	Concentration of Si derived from SiN (ppm)	SiN etch rate [R ₁] (nm/min)	SiO etch rate [R ₂] (nm/min)	Selectivity ratio [R ₁ /R ₂]
Example 7	0	6.07	0.108	56
	50	5.93	0.018	329
	100	5.83	-0.007	-833
Example 8	0	4.89	0.045	109
	50	4.65	0.015	310
	100	4.83	0.003	1610
	150	4.84	0.001	4840
	200	4.71	0.000	∞
Comparative example 2	0	5.61	0.228	25
	50	5.57	0.047	119
	100	5.25	-0.005	-1050
Comparative example 3	0	4.89	0.044	111
	50	4.65	0.021	221
	100	4.83	0.005	966
	150	4.84	0.000	∞
	200	4.71	0.000	∞

[0105]

<Performance Confirmation Test 2 on Regenerated Etching Solution>

5 Furthermore, for regenerated etching solutions obtained by subjecting the etching solutions of Examples 2 to 6 to the regeneration device 100, a performance confirmation test was also conducted on a "dialysis aid-free system" (Examples 9 to 13) and a "dialysis aid-added system" (Examples 14 to 18). For
10 comparison, a similar performance confirmation test was conducted on the etching solutions of Examples 2 to 6, which were obtained by adding a dialysis aid to a brand-new etching solution, and which were not subjected to regeneration (Comparative Examples 4 to 8).

15 [0106]

[Examples 9 to 13: Dialysis Aid-Free System]

An etching test on silicon oxide film (Examples 9-1 to 13-1) and an etching test on silicon nitride film (Examples 9-2 to 13-2) were conducted using a regenerated etching solution that had an adjusted phosphoric acid concentration (87%) and an adjusted Si concentration in the solution (0 to 100 ppm). FIGS. 6 to 10 show graphs of the results of the etching tests (with no dialysis aid) in Examples 9 to 13.

[0107]

[Examples 14 to 18: Dialysis Aid-Added System]

An etching test on silicon oxide film (Examples 14-1 to 18-1) and an etching test on silicon nitride film (Examples 14-2 to 18-2) were conducted using a regenerated etching solution that had an adjusted phosphoric acid concentration (87%) and an adjusted Si concentration in the solution (0 to 2000 ppm) and to which the same dialysis aid(s) as those used in Examples 2 to 6 were added. FIGS. 11 to 15 show graphs of the results of the etching tests (with a dialysis aid) in Examples 14 to 18.

[0108]

[Comparative Examples 4 to 8]

An etching test on silicon oxide film (Comparative Examples 4-1 to 8-1) and an etching test on silicon nitride film (Comparative Examples 4-2 to 8-2) were conducted using the etching solutions of Examples 2 to 6, which were obtained by adding a dialysis aid to a brand-new etching solution. The results of the etching tests in Comparative Examples 4 to 8

are shown in FIGS. 11 to 15.

[0109]

[Selectivity Ratio]

For Examples 9 to 13, the selectivity ratio (R_1/R_2) of the etch rate (R_1) of silicon nitride to the etch rate (R_2) of silicon oxide is shown in Table 2 below. The regenerated etching solutions of Examples 9 to 13 had a selectivity ratio (R_1/R_2) whose absolute value is sufficiently high, and were able to be effectively used.

10 [0110]

[Table 2]

	Concentration of Si derived from SiN (ppm)	SiN etch rate [R_1] (nm/min)	SiO etch rate [R_2] (nm/min)	Selectivity ratio [R_1/R_2]
Example 9	0	4.01	0.093	43
	50	4.28	0.002	2140
	100	3.95	-0.012	-329
Example 10	0	4.79	0.099	48
	50	4.09	0.002	2045
	100	3.75	-0.011	-341
Example 11	0	4.54	0.091	50
	50	4.09	-0.002	-2045
	100	4.01	-0.010	-401
Example 12	0	4.67	0.098	48
	50	4.40	0.001	4400
	100	3.97	-0.016	-248
Example 13	0	5.57	0.134	42
	50	5.31	0.030	177
	100	4.92	-0.003	-1640

[0111]

For Examples 14 to 18, the selectivity ratio (R_1/R_2) of the etch rate (R_1) of silicon nitride to the etch rate (R_2) of silicon oxide is shown in Table 3 below. Furthermore, for Comparative Examples 4 to 8, the selectivity ratio (R_1/R_2) of

the etch rate (R_1) of silicon nitride to the etch rate (R_2) of silicon oxide is shown in Table 4 below.

[0112]

[Table 3]

	Concentration of Si derived from SiN (ppm)	SiN etch rate [R_1] (nm/min)	SiO etch rate [R_2] (nm/min)	Selectivity ratio [R_1/R_2]
Example 14	0	4.24	0.021	202
	100	3.60	0.002	1800
	200	3.26	0.000	∞
Example 15	0	3.75	0.018	208
	100	3.33	0.000	∞
	200	3.24	0.000	∞
Example 16	0	3.80	0.021	181
	100	3.42	0.002	1710
	200	3.16	0.000	∞
Example 17	0	3.79	0.020	190
	100	3.52	0.000	∞
	200	3.17	0.000	∞
Example 18	0	4.57	0.008	571
	200	4.15	0.005	830
	1000	4.03	0.000	∞
	2000	3.71	0.000	∞

5

[0113]

[Table 4]

	Concentration of Si derived from SiN (ppm)	SiN etch rate [R ₁] (nm/min)	SiO etch rate [R ₂] (nm/min)	Selectivity ratio [R ₁ /R ₂]
Comparative example 4	0	4.23	0.033	128
	100	3.93	0.002	1965
	200	3.50	0.000	∞
Comparative example 5	0	4.18	0.029	144
	100	3.82	0.004	955
	200	3.42	0.000	∞
Comparative example 6	0	4.16	0.028	149
	100	3.92	0.004	980
	200	3.52	0.000	∞
Comparative example 7	0	4.43	0.030	148
	100	3.95	0.000	∞
	200	3.71	0.000	∞
Comparative example 8	0	4.11	0.005	822
	200	4.10	0.005	820
	1000	4.10	0.000	∞
	2000	3.34	0.000	∞

[0114]

The regenerated etching solutions of Examples 14 to 18 had a selectivity ratio (R₁/R₂) that is equal to or higher than those of the etching solutions of Comparative Examples 4 to 8, which were obtained by adding a dialysis aid to a brand-new etching solution, and were able to be effectively used.

INDUSTRIAL APPLICABILITY

10 [0115]

The method for recycling an etching solution according to the present invention is for regenerating an etching solution that has been used in fabrication of a semiconductor having a silicon oxide film and a silicon nitride film that serves as a sacrificial layer, and can be used in regeneration of an etching solution that has been used in fabrication of, for example, a 2D NAND, 3D NAND, CMOS, DRAM, 3D RAM, logic IC,

or the like.

CLAIMS

1. A method for recycling an etching solution,
wherein an inorganic acid-based etching solution that is used
5 or has been used in etching of a semiconductor is regenerated
by diffusion dialysis, and the method comprises:

an extraction step of bringing a dialysis aid-containing
etching solution into contact with water through an anion-
exchange membrane and thereby extracting an inorganic acid
10 contained in the etching solution into the water.

2. The method for recycling an etching solution
according to claim 1, comprising:

an addition step of, before the extraction step, adding
15 a dialysis aid to an etching solution to obtain the dialysis
aid-containing etching solution.

3. The method for recycling an etching solution
according to claim 1, comprising:

20 a preparation step of adding all or a portion of a
dialysis aid to an etching solution to obtain the dialysis
aid-containing etching solution before etching of the
semiconductor.

25 4. The method for recycling an etching solution
according to claim 2 or 3, wherein

the dialysis aid is a heteroatom-containing compound.

5. The method for recycling an etching solution according to claim 4, wherein

5 the heteroatom-containing compound is a silicon-containing compound, a nitrogen-containing compound, and/or a phosphorus-containing compound.

6. The method for recycling an etching solution
10 according to claim 5, wherein

the silicon-containing compound is a silane compound that has, in the molecular structure, at most three of alkoxy groups, hydroxy groups, and/or functional groups that are a precursor of a hydroxy group, and/or a silane compound that
15 has, in the molecular structure, at least four of alkoxy groups, hydroxy groups, and/or functional groups that are a precursor of a hydroxy group, and/or a halogen-containing silane compound.

20 7. The method for recycling an etching solution according to claim 5, wherein

the nitrogen-containing compound is a hydrazide and/or an ammonium compound.

25 8. The method for recycling an etching solution according to claim 5, wherein

the phosphorus-containing compound is a phosphonic acid compound.

9. The method for recycling an etching solution
5 according to any one of claims 1 to 3, wherein
the inorganic acid is phosphoric acid.

10. The method for recycling an etching solution
according to any one of claims 1 to 3, wherein
10 the etching solution contains Si derived from the
semiconductor at a predetermined concentration or higher.

11. The method for recycling an etching solution
according to any one of claims 1 to 3, wherein
15 the etching solution is an exhausted solution that has
been used in etching of the semiconductor.

12. The method for recycling an etching solution
according to any one of claims 1 to 3, wherein
20 the extraction step is performed by counter-current
contact between the etching solution and the water through an
anion-exchange membrane.

13. The method for recycling an etching solution
25 according to any one of claims 1 to 3, wherein
the semiconductor has a silicon nitride film as a

sacrificial layer.