

DESCRIPTION

Title of Invention: METHOD FOR REMOVING LANTHANUM
COMPOUND AND TREATMENT LIQUID FOR LANTHANUM COMPOUND
5 REMOVAL

Technical Field

[0001]

The present invention relates to a method for
10 removing a lanthanum compound and a treatment liquid for
lanthanum compound removal.

Background Art

[0002]

15 In electronic devices, such as semiconductor
devices, a plurality of types of metal oxides is
sometimes used as a gate material. Therefore, the
microfabrication of the metal oxides requires a technique
of selectively etching a specific type of metal oxide.

20 As the technique of selectively etching metal oxide,
a method is known which includes removing metal oxide by
bringing a treatment liquid into contact with the metal
oxide. For example, PTL 1 discloses a removal treatment
liquid for removing a High-k film from a silicon
25 substrate. The removal treatment liquid contains a
fluoride ion.

Citation List

Patent Literature

[0003]

PTL 1: JP 4221601 B

5 Summary of Invention

Technical Problem

[0004]

However, when the removal treatment liquid disclosed in PTL 1 is used for removing a lanthanum compound, a
10 reaction between the fluoride ion and the lanthanum compound generates insoluble fluoride lanthanum (LaF_3). Therefore, the removal treatment liquid has posed a risk that the lanthanum compound cannot be removed from electronic devices. Further, the removal treatment
15 liquid disclosed in PTL 1 has posed a risk of removing a substance other than the lanthanum compound, and therefore has posed a risk that a portion not to be removed (non-removal object not serving as a target to be removed by the removal treatment liquid) is also removed.

20 It is an object of the present invention to provide a method for removing a lanthanum compound and a treatment liquid for lanthanum compound removal capable of selectively removing the lanthanum compound over the non-removal object.

25

Solution to Problem

[0005]

To achieve the above-described object, one aspect of

the present invention is as described in [1] to [11]
below.

[1] A method for removing a lanthanum compound
includes: a removal step of removing, from an object to
5 be treated having a lanthanum compound serving as a
target to be removed and a non-removal object not serving
as the target to be removed, the lanthanum compound by
bringing a treatment liquid for lanthanum compound
removal into contact with the object to be treated, in
10 which

the treatment liquid for lanthanum compound removal
is an aqueous solution containing an α -hydroxycarboxylic
acid salt and having a pH of 5 or more and 10 or less.

[0006]

15 [2] The method for removing a lanthanum compound
according to [1], in which the α -hydroxycarboxylic acid
salt is an α -hydroxycarboxylic acid ammonium salt.

[3] The method for removing a lanthanum compound
according to [1] or [2], in which the α -hydroxycarboxylic
20 acid is at least one selected from citric acid, tartaric
acid, malic acid, lactic acid, and glycolic acid.

[0007]

[4] The method for removing a lanthanum compound
according to any one of [1] to [3], in which the non-
25 removal object contains at least one selected from
polysilicon, silicon oxide, silicon nitride, aluminum
oxide, hafnium oxide, zirconium oxide, and titanium
nitride.

[5] The method for removing a lanthanum compound according to any one of [1] to [4], in which a ratio of the removal rate of the lanthanum compound to the removal rate of the non-removal object is 10 or more.

5 [0008]

[6] The method for removing a lanthanum compound according to any one of [1] to [5], in which the fluoride ion concentration in the treatment liquid for lanthanum compound removal is 0.5 mass% or less.

10 [7] The method for removing a lanthanum compound according to any one of [1] to [6], in which the hydrogen peroxide concentration in the treatment liquid for lanthanum compound removal is 5 mass% or less.

[0009]

15 [8] A treatment liquid for lanthanum compound removal, in which

the treatment liquid for lanthanum compound removal is used for lanthanum compound removal removing, from an object to be treated having a lanthanum compound serving as a target to be removed and a non-removal object not serving as the target to be removed, by being brought into contact with the object to be treated, in which

the treatment liquid for lanthanum compound removal is an aqueous solution containing an α -hydroxycarboxylic acid salt and having a pH of 5 or more and 10 or less, and has a content of the α -hydroxycarboxylic acid salt of 0.1 mass% or more and 60 mass% or less.

[0010]

[9] The treatment liquid for lanthanum compound removal according to [8], in which the α -hydroxycarboxylic acid salt is an α -hydroxycarboxylic acid ammonium salt.

[10] The treatment liquid for lanthanum compound removal according to [8] or [9], in which the fluoride ion concentration is 0.5 mass% or less.

[11] The treatment liquid for lanthanum compound removal according to any one of [8] to [10], in which the hydrogen peroxide concentration is 5 mass% or less.

Advantageous Effects of Invention

[0011]

The present invention can selectively remove the lanthanum compound over the non-removal object.

Description of Embodiments

[0012]

Hereinafter, one embodiment of the present invention is described. This embodiment illustrates one example of the present invention, and the present invention is not limited to this embodiment. This embodiment can be variously altered or improved, and such altered or improved aspects may also be included in the present invention.

[0013]

A method for removing a lanthanum compound according to this embodiment includes a removal step of removing, from an object to be treated having a lanthanum compound serving as a target to be removed and a non-removal
5 object not serving as the target to be removed, the lanthanum compound by bringing a treatment liquid for lanthanum compound removal into contact with the object to be treated. The treatment liquid for lanthanum compound removal is an aqueous solution containing an α -
10 hydroxycarboxylic acid salt and having a pH of 5 or more and 10 or less.

[0014]

The treatment liquid for lanthanum compound removal according to this embodiment is a treatment liquid that
15 removes, from an object to be treated having a lanthanum compound serving as a target to be removed and a non-removal object not serving as the target to be removed, the lanthanum compound by being brought into contact with the object to be treated. The treatment liquid for
20 lanthanum compound removal according to this embodiment is an aqueous solution containing an α -hydroxycarboxylic acid salt and having a pH of 5 or more and 10 or less, and has a content of the α -hydroxycarboxylic acid salt of 0.1 mass% or more and 60 mass% or less.

25 [0015]

The α -hydroxycarboxylic acid salt has a chelating action on lanthanum. Therefore, when the treatment liquid for lanthanum compound removal is brought into

contact with the object to be treated, the lanthanum compound forms a chelate with the α -hydroxycarboxylic acid salt in the treatment liquid for lanthanum compound removal and is removed from the object to be treated.

5 [0016]

On the other hand, some substances other than the lanthanum compound hardly form a chelate with the α -hydroxycarboxylic acid salt. Therefore, a portion formed of the substances hardly forming a chelate with the α -hydroxycarboxylic acid salt serves as the non-removal
10 object. Even when the treatment liquid for lanthanum compound removal is brought into contact with the object to be treated, the non-removal object is hardly removed from the object to be treated.

15 [0017]

Thus, the method for removing a lanthanum compound according to this embodiment can selectively remove the lanthanum compound serving as the removal object over the non-removal object. Therefore, the method for removing a
20 lanthanum compound according to this embodiment is applicable to the manufacture of electronic devices, such as semiconductor devices.

[0018]

For example, when the method for removing a
25 lanthanum compound according to this embodiment is applied to a substrate (corresponding to the "object to be treated", which is a constituent requirement of the present invention) to which the lanthanum compound has

been attached in the manufacture of electronic devices,
such as liquid crystal displays and semiconductor
devices, the α -hydroxycarboxylic acid salt in the
treatment liquid for lanthanum compound removal forms a
5 complex with the lanthanum compound by the chelating
action. Therefore, the lanthanum compound is removed
from the substrate and the surface of the substrate is
cleaned.

[0019]

10 Hereinafter, the method for removing a lanthanum
compound and the treatment liquid for lanthanum compound
removal according to this embodiment are described in
more detail.

[Lanthanum compound]

15 The lanthanum compound is the removal object serving
as the target to be removed by the treatment liquid for
lanthanum compound removal. The lanthanum compound
includes lanthanum oxides, lanthanum nitrides, and
lanthanum oxynitrides, for example. The lanthanum oxides
20 mean compounds having lanthanum (La) and oxygen atoms (O)
in their structures. The lanthanum nitrides mean
compounds having lanthanum and nitrogen atoms (N) in
their structures. The lanthanum oxynitrides mean
compounds having lanthanum, oxygen atoms, and nitrogen
25 atoms in their structures. The lanthanum compounds may
be used alone or in combination of two or more types
thereof.

[0020]

Specifically, the lanthanum oxides include lanthanum oxide (La_2O_3), lanthanum aluminate (LaAlO_3), lanthanum hafnate ($\text{La}_2\text{Hf}_2\text{O}_7$), and the like. The lanthanum nitrides include lanthanum nitride (LaN) and the like. The
5 lanthanum oxynitrides include lanthanum titanate oxynitride (LaTiO_2N) and the like.

[0021]

Even when the lanthanum compound contains metals other than lanthanum, such as hafnium (Hf), zirconium
10 (Zr), aluminum (Al), titanium (Ti), and silicon (Si), for example, the lanthanum compound can also serve as the removal object. From the viewpoint of ease of removal (e.g., which means the etching rate when the lanthanum compound is etched and removed by the treatment liquid
15 for lanthanum compound removal), the content of the lanthanum atoms contained in the lanthanum compound is preferably 1 mol% or more, more preferably 10 mol% or more, and still more preferably 15 mol% or more.

The forms of the lanthanum oxides, the lanthanum
20 nitrides, and the lanthanum oxynitrides are not particularly limited, and a film shape, a foil shape, a powder shape, a particle shape, and a lump shape may be acceptable, for example.

[0022] [Non-removal object]

25 The non-removal object not serving the target to be removed by the treatment liquid for lanthanum compound removal is not particularly limited insofar as it is a substance hardly forming a chelate with the α -

hydroxycarboxylic acid salt, and includes silicon materials, simple substances of metals other than lanthanum, oxides of metals other than lanthanum, nitrides of metals other than lanthanum, oxynitrides of metals other than lanthanum, and the like, for example.
[0023]

These substances hardly form a chelate with the α -hydroxycarboxylic acid salts or take a longer time to form a chelate than the lanthanum compound. Thus, even when the treatment liquid for lanthanum compound removal is brought into contact with the object to be treated, the non-removal object is hardly removed from the object to be treated.
[0024]

Examples of the silicon materials include polysilicon (Si), amorphous silicon, silicon oxide, and silicon nitride. The silicon oxide refers to a compound having silicon and oxygen in optional proportions. Examples of the silicon oxide include silicon dioxide (SiO_2). The silicon nitride refers to a compound having silicon and nitrogen in optional proportions. Examples of the silicon nitride include Si_3N_4 .
[0025]

Examples of the simple substances of metals other than lanthanum include aluminum, hafnium, zirconium, and titanium. Examples of the oxides of metals other than lanthanum include aluminum oxide (Al_2O_3), hafnium oxide (HfO_2), and zirconium oxide (ZrO_2). Examples of the

nitrides of metals other than lanthanum include titanium nitride (TiN). The non-removal object may contain one of the substances above or may contain two or more types of the substances above.

5 [0026]

The non-removal object may also contain the lanthanum compound. However, to make it hard for the non-removal object to be removed by the treatment liquid for lanthanum compound removal, the content of the
10 lanthanum compound is preferably less than 1 mass%, more preferably 0.5 mass% or less, and still more preferably less than 0.1 mass%.

[0027]

When the non-removal object has a film shape or a
15 foil shape, the thickness is preferably 0.1 nm or more, more preferably 1 nm or more, and still more preferably 5 nm or more. When the non-removal object has a lump shape, the short diameter is preferably 1 nm or more, more preferably 10 nm or more, and still more preferably
20 100 nm or more. When the non-removal object has the size in the ranges above, the non-removal object is hardly removed by the treatment liquid for lanthanum compound removal.

[0028]

25 The non-removal object is a substance constituting electronic devices, for example, and is a substance used as a wiring material, a channel material, a gate material, or barrier metal, for example, in electronic

devices. A ratio of the removal rate of the lanthanum compound to the removal rate of the non-removal object is preferably 10 or more, more preferably 20 or more, and still more preferably 30 or more. When the removal rate ratio above is 10 or more, the lanthanum compound can be selectively removed while the removal of the non-removal object is suppressed.

[0029] [Treatment liquid for lanthanum compound removal]

The treatment liquid for lanthanum compound removal is an aqueous solution containing the α -hydroxycarboxylic acid salt and having a pH of 5 or more and 10 or less.

The pH of the treatment liquid for lanthanum compound removal is 5 or more and 10 or less, and is preferably 5 or more and 9 or less, more preferably 7 or more and 9 or less, and still more preferably 7 or more and 8 or less. When the pH of the treatment liquid for lanthanum compound removal is in the numerical ranges above, the removal of the lanthanum compound is likely to proceed.

[0030]

The pH of the treatment liquid for lanthanum compound removal can be adjusted by compounding a basic aqueous solution, such as ammonia water. The pH of the treatment liquid for lanthanum compound removal in the present invention is the pH at the temperature of the treatment liquid for lanthanum compound removal when the treatment liquid for lanthanum compound removal is in

contact with the object to be treated in the removal step.

[0031]

The type of the α -hydroxycarboxylic acid salt is not particularly limited. Examples of the α -hydroxycarboxylic acid salt include ammonium salts, alkyl ammonium salts, aryl ammonium salts, lithium salts, sodium salts, potassium salts, cesium salts, calcium salts, and magnesium salts of the α -hydroxycarboxylic acid.

[0032]

Among these salts, the ammonium salt, the alkyl ammonium salt, the sodium salt, and the potassium salt are preferable and the ammonium salt is more preferable in terms of high safety, high ease of handling, and cost efficiency. When the α -hydroxycarboxylic acid, a base, and water are mixed to form an aqueous solution, the aqueous solution of the α -hydroxycarboxylic acid salt can be obtained. The type of an alkyl group of the alkyl ammonium salt is not particularly limited insofar as the water solubility of the α -hydroxycarboxylic acid salt is higher than 2 g/100 mL-H₂O. For example, an alkyl group having 4 or less carbons is usable.

[0033]

The type of the α -hydroxycarboxylic acid is not particularly limited insofar as it can form a chelate complex with the lanthanum compound. Examples of the α -hydroxycarboxylic acid include citric acid (C₆H₈O₇),

tartaric acid ($C_4H_6O_6$), malic acid ($C_4H_6O_5$), glycolic acid ($C_2H_4O_3$), lactic acid ($C_3H_6O_3$), 2-methyl lactic acid ($C_4H_8O_3$), tartronic acid ($C_3H_4O_5$), and quinic acid ($C_7H_{12}O_6$).

5 [0034]

Among these α -hydroxycarboxylic acids, citric acid, tartaric acid, malic acid, and lactic acid are preferable in terms of high ease of handling and a high lanthanum compound removal effect.

10 The α -hydroxycarboxylic acid salts described above may be used alone or in combination of two or more types thereof.

[0035]

The content of the α -hydroxycarboxylic acid salt in the treatment liquid for lanthanum compound removal is 0.1 mass% or more and 60 mass% or less, preferably 3 mass% or more and 60 mass% or less, and more preferably 5 mass% or more and 50 mass% or less. When the content of the α -hydroxycarboxylic acid salt in the treatment liquid for lanthanum compound removal is in the numerical ranges above, the removal rate of the lanthanum compound serving as the removal object is higher, which is more practical. The solubility in water (g/100 mL- H_2O) of the α -hydroxycarboxylic acid salt is preferably high, and preferably 2 or more.

25 [0036]

The treatment liquid for lanthanum compound removal may contain components other than the α -hydroxycarboxylic

acid salt. For example, oxidizers, wetting agents, surfactants, colorants, anti-foaming agents, and the like may be contained.

However, it is preferable that the treatment liquid
5 for lanthanum compound removal does not contain fluoride ions and hydrogen peroxides as much as possible. For example, the fluoride ion concentration in the treatment liquid for lanthanum compound removal is preferably 1 mass% or less, more preferably 0.5 mass% or less, still
10 more preferably 500 mass ppm or less, and particularly preferably 100 mass ppm or less. The hydrogen peroxide concentration in the treatment liquid for lanthanum compound removal is preferably 5 mass% or less, more preferably 1 mass% or less, and still more preferably
15 less than 100 mass ppm. The inclusion of fluoride ions or hydrogen peroxides in the treatment liquid for lanthanum compound removal poses risks that the non-removal object is also removed in addition to the fact that the removal rate of the lanthanum compound
20 decreases.

[0037] [Object to be treated]

The object to be treated has the removal object (lanthanum compound) serving as the target to be removed by the treatment liquid for lanthanum compound removal,
25 and the non-removal object not serving as the target to be removed by the treatment liquid for lanthanum compound removal.

The type of the object to be treated to which the method for removing a lanthanum compound according to this embodiment is applicable is not particularly limited insofar as it has the lanthanum compound serving as the removal object and the non-removal object, and includes electronic devices, for example.

[0038]

Specific examples of the electronic devices include liquid crystal displays, semiconductor devices, such as a metal-oxide-semiconductor field-effect transistor (MOSFET), MEMS (Micro Electro Mechanical Systems) devices, and hard disks.

[0039]

The method for removing a lanthanum compound of this embodiment hardly removes silicon oxide, silicon nitride, polysilicon, aluminum oxide, zirconium oxide, hafnium oxide, titanium nitride, and the like, which are the non-removal objects, and therefore can remove the lanthanum compound without adversely affecting the object to be treated, such as the electronic devices.

[0040] [[Method for removing lanthanum compound]]

In the method for removing a lanthanum compound according to this embodiment, examples of the method for bringing the treatment liquid for lanthanum compound removal into contact with the lanthanum compound include, but not particularly limited to, immersion, spraying, coating, and pouring. From the viewpoint of simplifying a device used for bringing the treatment liquid for

lanthanum compound removal into contact with the
lanthanum compound, the immersion method is preferable.

[0041]

The treatment conditions in the immersion method
5 vary depending on the type of the lanthanum compound or
the composition of the treatment liquid for lanthanum
compound removal. For example, the temperature of the
treatment liquid for lanthanum compound removal when the
treatment liquid for lanthanum compound removal is brough
10 into contact with the lanthanum compound (treatment
temperature) is preferably 0°C or more and 100°C or less,
more preferably 10°C or more and 90°C or less, and still
more preferably 20°C or more and 80°C or less.

[0042]

15 The contact time between the lanthanum compound and
the treatment liquid for lanthanum compound removal
(treatment time) is preferably 1 second or more and 180
minutes or less, more preferably 5 seconds or more and 90
minutes or less, and still more preferably 10 seconds or
20 more and 60 minutes or less.

Such immersion treatment may be performed by simply
immersing the object to be treated (for example, a
substrate) having the lanthanum compound serving as the
removal object in the treatment liquid for lanthanum
25 compound removal, or may also be performed by immersing
the object to be treated in the treatment liquid for
lanthanum compound removal under the application of
ultrasonic waves or stirring.

[0043]

When the object to be treated subjected to the treatment of removing the lanthanum compound is cleaned with a cleaning liquid, such as water, the α -
5 hydroxycarboxylic acid salt remaining on the surface of the object to be treated or contaminants containing the lanthanum compound can be removed from the object to be treated. The type of the cleaning liquid is not particularly limited. The cleaning can be performed with
10 only water, such as pure water, and there is no need to use organic solvents, such as alcohol. Since the organic solvents are not required to be used for the treatment liquid for lanthanum compound removal or the cleaning liquid, the method for removing a lanthanum compound,
15 according to this embodiment hardly adversely affects human bodies or environments.

EXAMPLES

[0044]

20 Hereinafter, the present invention is described in more detail with reference to Examples and Comparative Examples.

(Example 1)

As the treatment liquid for lanthanum compound
25 removal, a triammonium citrate aqueous solution having a concentration of 5 mass% was prepared. The pH at 25°C of this treatment liquid for lanthanum compound removal is 7.6. A 100 mL-capacity polypropylene container

containing 40 mL of the treatment liquid for lanthanum compound removal was heated in a water bath to set the temperature of the treatment liquid for lanthanum compound removal to 25°C. The fluoride ion concentration in the treatment liquid for lanthanum compound removal was less than 100 mass ppm.

[0045]

Next, as the object to be treated, eight types of silicon substrates (manufactured by KST WORLD CORP.) each having a thin film formed thereon were prepared. More specifically, the types of the thin films are the eight types of a lanthanum oxide (La_2O_3) film having a film thickness of 100 nm, an aluminum oxide (Al_2O_3) film having a film thickness of 100 nm, a hafnium oxide (HfO_2) film having a film thickness of 100 nm, a zirconium oxide (ZrO_2) film having a film thickness of 100 nm, a titanium nitride (TiN) film having a film thickness of 100 nm, a silicon dioxide (SiO_2) film having a film thickness of 100 nm, a silicon nitride (Si_3N_4) film having a film thickness of 100 nm, and a polysilicon film having a film thickness of 100 nm. The silicon substrates each having one of the thin films formed thereon were individually prepared. The silicon substrates have a 2-cm square shape.

[0046]

The eight types of silicon substrates were immersed in the 25°C treatment liquid for lanthanum compound removal for 5 minutes and allowed to stand for the

removal of the thin films (etching). Each silicon substrate was taken out from the treatment liquid for lanthanum compound removal, and each silicon substrate was entirely cleaned with pure water. Then, the film thickness of the thin film on each silicon substrate was measured. The measurement of the film thickness of each thin film was performed using a F20 film thickness measurement system manufactured by Filmetrics Co., Ltd. [0047]

10 Then, a film thickness difference of each thin film before and after the etching was calculated, and the film thickness difference was divided by the immersion time (treatment time), thereby calculating the removal rate of each thin film. The measurement conditions of the film thickness by the F20 film thickness measurement system are as follows. The measurement results are shown in Table 1.

[0048]

20 Measurement pressure: Atmospheric pressure (101.3 kPa)

Measurement temperature: 28°C

Measurement atmosphere: In atmosphere

Lanthanum oxide measurement wavelength range: 250 to 950 nm

25 Aluminum oxide measurement wavelength range: 300 to 1200 nm

Hafnium oxide measurement wavelength range: 250 to 950 nm

Zirconium oxide measurement wavelength range: 250 to
930 nm

Titanium nitride measurement wavelength range: 150
to 1300 nm

5 Silicon dioxide measurement wavelength range: 200 to
1000 nm

Silicon nitride measurement wavelength range: 900 to
1700 nm

Polysilicon measurement wavelength range: 600 to
10 1100 nm

[0049]

[Table 1]

	α-hydroxycarboxylic acid or salt thereof		Additive		pH	Treatment temperature (°C)	Treatment time (min)	Object to be removed		Removal rate of non-removal object (nm/min)						
	Type	Concentration (mass%)	Type	Concentration (mass%)				Type	Removal rate (nm/min)	Al ₂ O ₃	H ₂ O ₂	ZrO ₂	TiN	SiO ₂	Si ₃ N ₄	Polysilicon
Ex. 1	Triammonium citrate	5	None	0	7.6	25	5	La ₂ O ₃	13	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1
Ex. 2	Triammonium citrate	5	None	0	7.6	50	2	La ₂ O ₃	25	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1
Ex. 3	Triammonium citrate	50	None	0	7.6	25	2	La ₂ O ₃	20	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1
Ex. 4	Triammonium citrate	5	Hydrogen peroxide	5	7.6	25	5	La ₂ O ₃	3	Less than 0.1	Less than 0.1	Less than 0.1	9	Less than 0.1	Less than 0.1	Less than 0.1
Ex. 5	Diammonium hydrogen citrate	5	None	0	5	25	5	La ₂ O ₃	9	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1
Ex. 6	Diammonium tartrate	5	None	0	7.6	25	5	La ₂ O ₃	15	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1
Ex. 7	Diammonium malate	5	None	0	7.6	25	5	La ₂ O ₃	4	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1
Ex. 8	Ammonium lactate	5	None	0	7.6	25	5	La ₂ O ₃	2	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1
Ex. 9	Triammonium citrate	5	Ammonium fluoride	0.5	8	25	10	La ₂ O ₃	4 ²⁾	0.2	0.3	Less than 0.1	Less than 0.1	0.2	0.4	1
Ex. 10	Triammonium citrate	5	None	0	7.6	25	5	LaN	10	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1
Ex. 11	Triammonium citrate	5	None	0	7.6	25	10	Lanthanum heptate	5	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1
Ex. 12	Triammonium citrate	5	None	0	7.6	25	10	Lanthanum aluminate	3	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1
Ex. 13	Triammonium citrate	5	None	0	7.6	25	5	Lanthanum titanate oxynitride	7	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1
Ex. 14	Trisodium citrate	5	None	0	8	25	5	La ₂ O ₃	15	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1
Ex. 15	Trisodium citrate	5	None	0	8	25	5	La ₂ O ₃	11	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1
Comp. Ex. 1	None	0	Ammonia	5	14	25	10	La ₂ O ₃	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	3
Comp. Ex. 2	Citric acid	5	None	0	2	25	10	La ₂ O ₃	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1
Comp. Ex. 3	Ammonium propionate	5	None	0	8	25	10	La ₂ O ₃	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1
Comp. Ex. 4	Ammonium γ-hydroxybutyrate	5	None	0	8	25	10	La ₂ O ₃	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.1
Comp. Ex. 5	Citric acid	5	Ammonium fluoride	0.5	2	25	5	La ₂ O ₃	Less than 0.1 ²⁾	6	2	1	6	2	3	4

1) The units of the numeric values are mass ppm excluding Example 9.

2) Lanthanum fluoride was generated.

[0050] [Examples 2 to 15 and Comparative Examples 1 to 5]

The etching was performed in the same manner as in Example 1, except that the composition of the treatment liquid for lanthanum compound removal (type and concentration of α -hydroxycarboxylic acid salt, type and concentration of additives, and the like), the fluoride ion concentration, the pH at the treatment temperature, the treatment temperature, and the treatment time were set as shown in Table 1, and the removal rate of each thin film was calculated. The results are shown in Table 1.

[0051]

As is understood from the results of Examples 1 to 3, the lanthanum oxide can be removed at a practical rate by using the triammonium citrate aqueous solution as the treatment liquid for lanthanum compound removal. The higher the temperature of the treatment liquid for lanthanum compound removal, the higher the removal rate. The higher the triammonium citrate concentration in the treatment liquid for lanthanum compound removal, the higher the removal rate.

[0052]

As is understood from the results of Examples 1, 4, when hydrogen peroxide was contained in the treatment liquid for lanthanum compound removal, the removal rate of the lanthanum oxide decreased. With regard to the non-removal object, the removal rate of the titanium nitride was improved, but the removal of the other non-

removal objects hardly proceeded.

As is understood from the results of Examples 5 to 8, the selective removal of the lanthanum oxide proceeded without any problem even when diammonium citrate, diammonium tartrate, diammonium malate, and ammonium lactate were used as the α -hydroxycarboxylic acid salt.

[0053]

As is understood from the results of Example 9, when ammonium fluoride was contained in the treatment liquid for lanthanum compound removal, the removal of the lanthanum oxide proceeded, but the removal of aluminum oxide, hafnium oxide, silicon dioxide, silicon nitride, and polysilicon also simultaneously proceeded. Further, the lanthanum oxide was partially fluorinated to generate lanthanum fluoride, which remained on the silicon substrate.

[0054]

As is understood from the results of Example 10 to 13, the selective removal of the lanthanum compound proceeded without any problem even when the removal objects were lanthanum nitride, lanthanum hafnate, lanthanum aluminate, and lanthanum titanate oxynitride.

As is understood from the results of Examples 14, 15, even when trisodium citrate and tripotassium citrate were used as the α -hydroxycarboxylic acid salt, the selective removal of the lanthanum oxide proceeded without any problem.

[0055]

As is understood from the results of Comparative Examples 1, 2, even when ammonia and citric acid were used in place of the α -hydroxycarboxylic acid salt, the removal of the lanthanum oxide did not proceed. This shows that the removal of the lanthanum compound is promoted by the coexistence of ammonium ions and citric acid ions.

[0056]

As is understood from the results of Comparative Examples 3, 4, even when ammonium propionate and ammonium γ -hydroxybutyrate were used in place of the α -hydroxycarboxylic acid salt, the removal of the lanthanum oxide did not proceed. This shows that, when the α -hydroxycarboxylic acid salt was used, the removal of the lanthanum compound is likely to proceed.

[0057]

As is understood from the results of Comparative Example 5, when the silicon substrate was treated using a mixed aqueous solution of citric acid and ammonium fluoride, the removal of the lanthanum oxide did not proceed and lanthanum fluoride was generated. Further, the etching of aluminum oxide, hafnium oxide, zirconium oxide, titanium nitride, silicon oxide, silicon nitride, and polysilicon proceeded.

25

CLAIMS

1. A method for removing a lanthanum compound comprising:

5 a removal step of removing, from an object to be treated having a lanthanum compound serving as a target to be removed and a non-removal object not serving as the target to be removed, the lanthanum compound by bringing a treatment liquid for lanthanum compound removal into
10 contact with the object to be treated, wherein

the treatment liquid for lanthanum compound removal is an aqueous solution containing an α -hydroxycarboxylic acid salt and having a pH of 5 or more and 10 or less.

15 2. The method for removing a lanthanum compound according to claim 1, wherein the α -hydroxycarboxylic acid salt is an α -hydroxycarboxylic acid ammonium salt.

3. The method for removing a lanthanum compound
20 according to claim 1 or 2, wherein the α -hydroxycarboxylic acid is at least one selected from citric acid, tartaric acid, malic acid, lactic acid, and glycolic acid.

25 4. The method for removing a lanthanum compound according to any one of claims 1 to 3, wherein the non-removal object contains at least one selected from polysilicon, silicon oxide, silicon nitride, aluminum

oxide, hafnium oxide, zirconium oxide, and titanium nitride.

5 5. The method for removing a lanthanum compound
according to any one of claims 1 to 4, wherein a ratio of
a removal rate of the lanthanum compound to a removal
rate of the non-removal object is 10 or more.

10 6. The method for removing a lanthanum compound
according to any one of claims 1 to 5, wherein a fluoride
ion concentration in the treatment liquid for lanthanum
compound removal is 0.5 mass% or less.

15 7. The method for removing a lanthanum compound
according to any one of claims 1 to 6, wherein a hydrogen
peroxide concentration in the treatment liquid for
lanthanum compound removal is 5 mass% or less.

20 8. A treatment liquid for lanthanum compound
removal, wherein

the treatment liquid for lanthanum compound removal
is used for removing, from an object to be treated having
a lanthanum compound serving as a target to be removed
and a non-removal object not serving as the target to be
25 removed, by being brought into contact with the object to
be treated, wherein

the treatment liquid for lanthanum compound removal
is an aqueous solution containing an α -hydroxycarboxylic

acid salt and having a pH of 5 or more and 10 or less,
and has a content of the α -hydroxycarboxylic acid salt of
0.1 mass% or more and 60 mass% or less.

5 9. The treatment liquid for lanthanum compound
removal according to claim 8, wherein the α -
hydroxycarboxylic acid salt is an α -hydroxycarboxylic
acid ammonium salt.

10 10. The treatment liquid for lanthanum compound
removal according to claim 8 or 9, wherein a fluoride ion
concentration is 0.5 mass% or less.

15 11. The treatment liquid for lanthanum compound
removal according to any one of claims 8 to 10, wherein a
hydrogen peroxide concentration is 5 mass% or less.