DESCRIPTION

CLEANING LIQUID AND CLEANING METHOD

TECHNICAL FIELD

[0001]

The invention relates to a cleaning liquid that makes it possible to clean and remove cerium oxide deposited on the object to be cleaned, and to a cleaning method using such a cleaning liquid.

BACKGROUND ART

[0002]

To make high-performance ultra large scale integrated circuits (ULSI), finer circuits have been designed. To form a very fine circuit structure whose size is reduced to the order of nanometers, new manufacturing techniques, which have not been used yet, are necessary in many manufacturing processes.

[0003]

In particular, an exposure and development process using an optical technique is one of the most important processes for forming a fine structure on a semiconductor substrate. Uniform focusing over the surface of a semiconductor substrate so that such a fine structure can be formed is closely related to the flatness of the

substrate surface. Therefore, if the substrate surface has poor flatness, some parts of the substrate surface will be in focus, but other parts will be out of focus, so that the desired fine structure cannot be formed at the parts out of focus, which causes a large reduction in productivity. As the processing becomes finer, the tolerance for the flatness decreases, which further increases the demand for planarization of the substrate surface.

[0004]

In addition to the demand for planarization, there is also a demand for a process time reduction for the purpose of improving production efficiency. Therefore, a technique capable of increasing not only the accuracy of fine processing but also the process speed is necessary. Under the technical background, chemical mechanical polishing (CMP) is generally performed as a technique to ensure flatness. In a CMP process, the surface of a semiconductor substrate is polished (planarized) using a polishing pad, while a polishing agent (slurry) containing polishing abrasive grains is supplied.

[0005]

In the CMP, silica slurry is widely used as a polishing agent. Ceria slurry is also used in the CMP, in which a cleaning process for removing residues remaining on the substrate surface is also necessary as in the case of

silica slurry. For example, the cleaning agents described below are proposed to be used in such a cleaning process.

[0006]

Patent Document 1 proposes a cleaning liquid chemical containing three ingredients: an acid, a reducing agent, and fluoride ions.

[0007]

Patent Document 2 proposes a cleaning liquid containing hydrofluoric acid and sulfuric acid, nitric acid, or phosphoric acid.

[0008]

Unfortunately, the conventional cleaning liquids have a problem in which they contain an acid as a main ingredient and therefore can easily corrode various metals, although they can remove cerium oxide residues. For example, if a metal film on a semiconductor substrate is dissolved by corrosion, the thickness of the metal film will decrease so that the surface resistance of the metal film will increase. This is not preferred, because the wiring resistance of the integrated circuit will increase so that the power consumption will increase.

PRIOR ART DOCUMENT

Patent Document

[0009]

Patent Document 1: Japanese Patent Application Laid-Open (JP-A) No. 2004-59419.

Patent Document 2: Japanese Patent Application Laid-Open (JP-A) No. 2000-140778.

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0010]

An object of the invention is to provide a cleaning liquid which is less corrosive to various metal materials and with which cerium oxide deposited on the surface of the object to be cleaned can be dissolved to form cerium ions and thus cleaned and removed, and to provide a cleaning method using such a cleaning liquid.

MEANS FOR SOLVING THE PROBLEMS

[0011]

To solve the conventional problems, the inventors have made studies on cleaning liquids and cleaning methods therewith. As a result, the invention has been accomplished based on the finding that cerium oxide remaining on the surface of the object to be cleaned can be efficiently cleaned and removed by using a cleaning liquid containing hydrogen fluoride and a specific ammonium salt.

[0012]

Thus, the invention is directed to a cleaning liquid for removing cerium oxide remaining on the surface of the object to be cleaned, which includes (1) hydrogen fluoride and (2) at least one ammonium salt selected from the group consisting of ammonium chloride, ammonium nitrate, ammonium sulfate, tetramethylammonium chloride, tetramethylammonium nitrate, and tetramethylammonium sulfate.

[0013]

In one embodiment, there is provided a cleaning liquid for removing cerium oxide remaining on a surface of an object to be cleaned, comprising:

(1) hydrogen fluoride; and

(2) at least one ammonium salt selected from the group consisting of ammonium chloride, ammonium nitrate, and ammonium sulfate.

In one embodiment, there is provided a cleaning method, comprising bringing a cleaning liquid into contact with a surface of an object on which cerium oxide is deposited, so that the cerium oxide is dissolved to form cerium ions and removed, wherein

the cleaning liquid comprises:

(1) hydrogen fluoride; and

(2) at least one ammonium salt selected from the group consisting of ammonium chloride, ammonium nitrate, and ammonium sulfate.

When a cleaning liquid containing hydrogen fluoride is used, cerium oxide can be dissolved to form cerium ions. However, dissolved cerium ions can be deposited again as impurities on the surface of the object being cleaned, so that the cerium component becomes difficult to be removed. The inventors have found that a cleaning liquid containing hydrogen fluoride and a specific ammonium salt can stabilize and keep cerium ions being dissolved in the cleaning liquid and efficiently remove them from the surface of the object being cleaned. In addition, the cleaning liquid of the invention does not contain an acid such as sulfuric acid, nitric acid, or phosphoric acid as a main ingredient in contrast to conventional cleaning liquids. Therefore, the cleaning liquid of the invention can suppress corrosion of various metal materials. As used herein, the term "cerium ions" means Ce^{3+}, Ce^{4+}, hydrates thereof, or complex ions thereof.

[0014]

The concentration of hydrogen fluoride in the cleaning liquid is preferably from 0.001 to 5% by weight. If the hydrogen fluoride concentration is less than 0.001% by weight, the ability to dissolve cerium oxide will tend to be low. If the hydrogen fluoride concentration is more than 5% by weight, the object being cleaned may be etched or corroded, so that the object planarized by polishing may tend to have an increased surface roughness. In addition, it may increase the cost and time required to make harmless the hydrogen fluoride in the cleaning liquid which becomes wastewater after the cleaning treatment.

[0015]

The concentration of the ammonium salt in the cleaning liquid is preferably from 0.1 to 20% by weight. If the concentration of the ammonium salt is less than 0.1% by weight, it may be difficult to stabilize or keep cerium ions being dissolved in the cleaning liquid, so that the cerium component may tend to be difficult to be cleaned or removed from the surface of the object being cleaned. If the concentration of the ammonium salt is more than 20% by weight, the ability to dissolve cerium oxide may decrease, or the cleaning liquid may produce a precipitate, so that it may be difficult to keep the cleaning liquid in a solution state, which may tend to cause troubles during

cleaning.

[0016]

The cleaning liquid preferably contains a surfactant. When a surfactant is added to the cleaning liquid, the surface tension of the cleaning liquid can be reduced, and the wettability on the object to be cleaned can be increased. This makes uniform the cleaning and removing effect over a wide area of the surface of the object being cleaned, so that productivity can be increased.

[0017]

The invention is also directed to a cleaning method, which includes bringing a cleaning liquid into contact with the surface of an object on which cerium oxide is deposited, so that the cerium oxide is dissolved to form cerium ions and removed, wherein the cleaning liquid used includes (1) hydrogen fluoride and (2) at least one ammonium salt selected from the group consisting of ammonium chloride, ammonium nitrate, ammonium sulfate, tetramethylammonium chloride, tetramethylammonium nitrate, and tetramethylammonium sulfate.

[0018]

In the cleaning method, the concentration of hydrogen fluoride in the cleaning liquid is preferably from 0.001 to 5% by weight, and the concentration of the ammonium salt is preferably from 0.1 to 20% by weight. The reason for this

is as described above.

[0019]

In the cleaning method, the cleaning liquid preferably contains a surfactant. The reason for this is as described above.

[0020]

The cleaning method is advantageously employed when the object to be cleaned is a semiconductor substrate, a glass substrate, a ceramic substrate, a quartz substrate, or a rock crystal substrate.

EFFECTS OF THE INVENTION

[0021]

According to the invention, cerium oxide remaining on the surface of the object to be cleaned, which has been polished by using a polishing agent containing cerium oxide, can be efficiently removed, while corrosion of various metal materials is advantageously inhibited. For example, this makes it possible to efficiently clean and remove cerium oxide residues from polished semiconductor substrates, so that the productivity of semiconductor devices can be improved. In addition, corrosion of metal materials on semiconductor substrates or corrosion of metal materials that form semiconductor devices is successfully inhibited, so that the performance of semiconductor devices

can be improved.

EMBODIMENTS FOR CARRYING OUT THE INVENTION

[0022]

Embodiments of the cleaning liquid of the invention are described below.

[0023]

The cleaning liquid of the invention contains (1) hydrogen fluoride and (2) at least one ammonium salt selected from the group consisting of ammonium chloride, ammonium nitrate, ammonium sulfate, tetramethylammonium chloride, tetramethylammonium nitrate, and tetramethylammonium sulfate, and is suitable for use in cleaning and removing cerium oxide remaining on the surface of the object to be cleaned, which has been polished by using a polishing agent (slurry) containing polishing abrasive grains of cerium oxide. In particular, the cleaning liquid of the invention is suitable for use in cleaning and removing cerium oxide remaining on the surface of the object to be cleaned, which has undergone chemical mechanical polishing (CMP) using a cerium oxide slurry.

[0024]

The concentration of hydrogen fluoride in the cleaning liquid is preferably from 0.001 to 5% by weight, more preferably from 0.001 to 2% by weight. Such a low

hydrogen fluoride concentration enables suppression of etching or corrosion of the surface material of the object being cleaned, as well as efficient cleaning and removal of cerium oxide.

[0025]

The concentration of the ammonium salt in the cleaning liquid is preferably from 0.1 to 20% by weight, more preferably from 0.1 to 10% by weight, even more preferably from 0.1 to 5% by weight. When the ammonium salt concentration is kept low, resource and cost savings can be achieved at the chemical preparation stage. Specifically, a cleaning liquid stock solution containing concentrated ingredients may be prepared, and the stock solution may be diluted with water or the like to form the cleaning liquid with the above concentration immediately before a cleaning treatment. This leads to substantial saving of resources or costs for the production of the cleaning liquid or filling of transportation containers with the cleaning liquid or substantial saving of resources or costs for the transportation of containers filled with the cleaning liquid, and thus leads to an increase in production efficiency.

[0026]

Besides the above ingredients, the cleaning liquid of the invention preferably contains water as a main

ingredient and may also contain any other ingredient than water. Examples of such an ingredient include a surfactant, a chelating agent, a pH adjuster, and an organic solvent. It will be understood that if these materials are used, it will be necessary to take into account the resistance of the cleaning apparatus to the organic ingredient, costs for waste management, hazard level during use, and so on.

[0027]

The cleaning liquid of the invention preferably contains a surfactant. Examples of the surfactant include, but are not limited to, an anionic surfactant such as an aliphatic carboxylic acid or a salt thereof, a nonionic surfactant such as polyethylene glycol alkyl ether, and a cationic surfactant such as an aliphatic amine or a salt thereof.

[0028]

The content of the added surfactant is preferably in the range of 0.001 to 0.1% by weight, more preferably in the range of 0.003 to 0.05% by weight. The surfactant added can suppress roughening of the surface of the object being cleaned. The surfactant can also increase the wettability on the object to be cleaned so that in-plane uniformity of the cleaning effect can be achieved. However, if the content is less than 0.001% by weight, the reduction in the surface tension of the cleaning liquid may be

insufficient so that the effect of increasing the wettability may be insufficient. If the content is more than 0.1% by weight, not only the resulting effect may fail to be proportional to the content, but also defoaming ability may be degraded so that foam may adhere to the surface of the object being cleaned to cause uneven cleaning.

[0029]

The purity and cleanliness of the cleaning liquid may be determined taking into account the manufacturing cost and the issue of the contamination of the object to be undergone in the cleaning treatment. For example, when the cleaning liquid of the invention is for use in an integrated circuit manufacturing process, the content of metal impurities in the cleaning liquid is preferably 0.1 ppb or less.

[0030]

The cleaning liquid of the invention may be prepared by mixing, in any order, hydrogen fluoride, the ammonium salt, and any other ingredients. Alternatively, compounds, with which the respective ingredients can be synthesized, may be mixed as raw materials so that a cleaning liquid containing the above ingredients at the above concentrations can be finally prepared. More specifically, hydrogen fluoride, sulfuric acid, ammonia, and water may be

mixed to form the cleaning liquid of the invention. Namely, ammonium sulfate is produced by neutralizing sulfuric acid with ammonia. Alternatively, for example, ammonium fluoride, sulfuric acid, and ammonia may be mixed to form the cleaning liquid of the invention.

[0031]

The cleaning liquid of the invention may be prepared using any formulation as long as the above composition can be provided at the cleaning stage, namely, the stage when it is used. For example, a concentrated stock solution for the cleaning liquid may be prepared and transferred to the point of use, and the cleaning liquid of the invention may be prepared by diluting the stock solution immediately before use. Alternatively, for example, the ingredients may be each independently provided and then mixed immediately before use to form the cleaning liquid of the invention.

[0032]

The temperature at which the cleaning liquid of the invention is used is not restricted at all. Practically, the cleaning liquid of the invention is advantageously used at room temperature, which is in the useful temperature range. Depending on the cleaning conditions, for example, the cleaning may be performed at a temperature 10°C lower than room temperature so that side reactions other than the

cleaning can be reduced, or for example, the cleaning may be performed at a high temperature 80°C higher than room temperature so that the cleaning performance can be increased.

[0033]

The cleaning liquid of the invention can be used on objects of varying materials and shapes. Examples of the material to be cleaned include silicon, glass, and ceramics. For example, the surface material of the object capable of being cleaned with the cleaning liquid of the invention include may be, but not limited to, single crystal silicon, polycrystalline silicon, amorphous silicon, a thermal silicon oxide film, a non-doped silicate glass film, a phosphorus-doped silicate glass film, a boron-doped silicate glass film, a boron-and-phosphorus-doped silicate glass film, a TEOS film, a plasma CVD oxide film, a silicon nitride film, a silicon carbide film, a silicon oxide carbide film, or a silicon oxide carbide nitride film. The cleaning liquid may also be applied to glass, quartz, rock crystal, ceramics, etc. The object may comprise one of these materials, two or more of these materials distributed in a certain pattern, or a laminate of any of these materials.

[0034]

The cleaning liquid of the invention is also suitable

for use in cleaning an object that has been planarized by a polishing process. The surface of the object to be cleaned may be polished by using any of various known conventional methods. The polishing method may be appropriately selected depending on the shape of the object to be cleaned or the desired polishing accuracy. Specifically, for example, mechanical polishing, chemical mechanical polishing (CMP), or the like may be used, and the cleaning liquid of the invention is advantageous for chemical mechanical polishing (CMP) with a cerium oxide slurry. The cerium oxide slurry is a dispersion of polishing abrasive grains of cerium oxide in a solution.

[0035]

The cleaning liquid of the invention may be used in various wet cleaning methods. For example, immersion treatment methods may be used, in which an object is immersed in the cleaning liquid placed in a cleaning tank. Piece-by-piece treatment methods may also be used, in which the cleaning treatment is performed by discharging or spraying the cleaning liquid on an object such as a silicon wafer being rotated. The immersion treatment method may also be performed while an ultrasonic wave is applied to the cleaning liquid. Brush scrubbing methods may also be used, in which cleaning with a brush is performed while the cleaning liquid is sprayed. It will be understood that the

cleaning may be performed twice or more. In this case, the composition or concentration of the cleaning liquid used may vary from one cleaning procedure to another.

[0036]

The cleaning time is not restricted and may be appropriately determined depending on the degree of staining with cerium oxide deposited on the object to be cleaned. In general, the cleaning time is preferably 10 minutes or less, more preferably 1 minute or less. If the cleaning time is more than 10 minutes, the surface of the object being cleaned may be etched, so that the surface roughness may increase.

[0037]

In the cleaning method of the invention, if necessary, a rinsing process with a rinse agent such as ultrapure water may also be performed after the cleaning treatment. This can prevent the cleaning liquid from remaining on the surface of the object cleaned.

EXAMPLES

[0038]

Hereinafter, preferred examples of the invention are illustratively described in detail. It will be understood that the materials, the amounts, and so on described in the examples are illustrative only and are not intended to

limit the scope of the invention, unless otherwise specified.

[0039]

(Method for Preparing Cleaning Liquid)

The cleaning liquid according to each example or comparative example was prepared by appropriately adding any of the materials shown below. The salts for use in examples were each obtained by selecting the acid and the base for forming the salt from the materials shown below and allowing them to react. Specifically, the cleaning liquid was prepared by mixing in a predetermined ratio at least one of (1) 50% by weight high-purity hydrofluoric acid (manufactured by Stella Chemifa Corporation), (2) EL grade, 36% by weight hydrochloric acid (manufactured by Mitsubishi Chemical Corporation), (3) EL grade, 69% by weight nitric acid (manufactured by Mitsubishi Chemical Corporation), (4) EL grade, 97% by weight sulfuric acid (manufactured by Mitsubishi Chemical Corporation), (5) EL grade, 28% by weight aqueous ammonia (manufactured by HAYASHI PURE CHEMICAL IND., LTD.), and (6) tetramethylammonium hydroxide (TOKUSO SD-25 (trade name) manufactured by Tokuyama Corporation).

[0040]

In each example, when a surfactant was necessary, any one of the materials shown below was added as appropriate.

Specifically, any one of (1) polyoxyethylene alkyl ether (a nonionic surfactant), (2) heptylamine (a cationic surfactant), and (3) heptanoic acid (an anionic surfactant) was added at a predetermined concentration.

[0041]

(Method for measuring the state of residues left on the surface of the object cleaned)

TREX 610-T (manufactured by Technos Co., Ltd.) was used to measure the state of cerium oxide solid residues present on the surface of the object cleaned. The measurement was performed before and after the cleaning treatment with the cleaning liquid to determine the cleaning effect of the cleaning liquid.

[0042]

(Examples 1 to 13)

As shown in Table 1, each cleaning liquid was prepared by mixing 0.001 to 5% by weight of hydrogen fluoride as ingredient (a), 1 to 20% by weight of ammonium sulfate as ingredient (b), and water as ingredient (c).

[0043]

(Examples 14 to 17)

As shown in Table 1, each cleaning liquid was prepared by mixing 0.01 to 0.1% by weight of hydrogen fluoride as ingredient (a), 1 to 10% by weight of tetramethylammonium sulfate as ingredient (b), and water as

ingredient (c).

[0044]

(Example 18)

As shown in Table 1, a cleaning liquid was prepared by mixing 0.1% by weight of hydrogen fluoride as ingredient (a), 5% by weight of ammonium sulfate and 5% by weight of ammonium chloride as ingredient (b), and water as ingredient (c).

[0045]

(Comparative Example 1)

As shown in Table 1, an aqueous solution of 20% by weight of ammonium sulfate was prepared.

[0046]

(Comparative Example 2)

As shown in Table 1, an aqueous solution of 20% by weight of ammonium fluoride was prepared.

[0047]

(Comparative Example 3)

As shown in Table 1, a cleaning liquid was prepared by mixing 0.5% by weight of hydrogen fluoride as ingredient (a), 20% by weight of ammonium fluoride as ingredient (b), and water as ingredient (c).

[0048]

(Comparative Example 4)

As shown in Table 1, an aqueous solution of 5% by

weight of hydrogen fluoride was prepared.

[0049]

Subsequently, a 200 mm diameter silicon substrate having a 5,000 Å TEOS film formed on its surface was subjected to chemical mechanical polishing with cerium oxide abrasive grains, and the resulting substrate was used as the object to be cleaned. The object to be cleaned was measured for the state of remaining cerium residues as described above, and as a result, about $1x10^{12}$ atoms/cm^2 of cerium oxide was identified as a residual component.

[0050]

Subsequently, the cleaning liquid was placed in a cleaning liquid tank with a volume of 90 L, and the temperature of the cleaning liquid was adjusted to 25°C and stabilized. The object was then immersed in the cleaning liquid tank for 30 seconds, while held on a silicon substrate holding member made of PFA resin. After the immersion, the object was lifted together with the silicon substrate holding member out of the cleaning liquid tank and immersed in an ultrapure water rinse tank with a volume of 90 L, which was provided in advance, so that the cleaning liquid deposited on the surface of the object was rinsed off. Subsequently, the object was dried and measured again for the state of remaining cerium residues. The removal performance was evaluated as good when the

amount of the cerium component after the treatment was reduced to 8.5×10^9 atoms/cm^2 or less, which corresponds to the lower limit of detection of the residue state evaluation instrument or less, and the removal performance was evaluated as poor when the amount of the cerium component after the treatment was not reduced to 8.5×10^9 atoms/cm^2. The results of the evaluation of the cleaning performance based on this procedure are shown in Table 1 below.

[0051]

[Table 1]

No.	Ingredient (a)	Ingredient (b)		Ingredient (c)	Cleaning performance
	HF [wt%]	Type	[wt%]	Water [wt%]	
Example 1	0.001	Ammonium sulfate	10	89.999	Good
Example 2	0.01	Ammonium sulfate	1	98.99	Good
Example 3	0.01	Ammonium sulfate	10	89.99	Good
Example 4	0.01	Ammonium sulfate	20	79.99	Good
Example 5	0.1	Ammonium sulfate	1	98.9	Good
Example 6	0.1	Ammonium sulfate	10	89.9	Good
Example 7	0.1	Ammonium sulfate	20	79.9	Good
Example 8	1	Ammonium sulfate	1	98	Good
Example 9	1	Ammonium sulfate	10	89	Good
Example 10	1	Ammonium sulfate	20	79	Good
Example 11	5	Ammonium sulfate	1	94	Good
Example 12	5	Ammonium sulfate	10	85	Good
Example 13	5	Ammonium sulfate	20	75	Good
Example 14	0.01	Tetramethylammonium sulfate	5	94.99	Good
Example 15	0.1	Tetramethylammonium sulfate	1	98.9	Good
Example 16	0.1	Tetramethylammonium sulfate	5	94.9	Good
Example 17	0.1	Tetramethylammonium sulfate	10	89.9	Good
Example 18	0.1	Ammonium sulfate	5	89.9	Good
		Ammonium chloride	5		
Comparative Example 1	0	Ammonium sulfate	20	80	Poor
Comparative Example 2	0	Ammonium fluoride	20	80	Poor
Comparative Example 3	0.5	Ammonium fluoride	20	79.5	Poor
Comparative Example 4	5	Absent	0	95	Poor

[0052]

The results in Table 1 show that when the cleaning liquid according to each of Examples 1 to 18 was used, the amount of the cerium component on the surface of the cleaned object was reduced to 8.5×10^9 atoms/cm^2 or less, and therefore the effect of cleaning and removing cerium oxide was high.

[0053]

In contrast, it is apparent that when the cleaning liquid according to each of Comparative Examples 1 to 4 was

used, the cerium component was not reduced to the lower limit of detection of the evaluation instrument, and the effect of cleaning and removing cerium oxide was low.

[0054]

(Examples 19 to 31)

Each cleaning liquid was prepared as in Example 1, except that the composition and concentration of the cleaning liquid were changed as shown in Table 2. The cleaning treatment and so on were also carried out by using each cleaning liquid as in Example 1. The results are shown in Table 2 below.

[0055]

(Comparative Example 5)

A cleaning liquid was prepared as in Example 1, except that the composition and concentration of the cleaning liquid were changed as shown in Table 2. The cleaning treatment and so on were also carried out by using the cleaning liquid as in Example 1. The results are shown in Table 2 below.

[0056]

[Table 2]

No.	Ingredient (a)	Ingredient (b)		Ingredient (c)	Cleaning performance
	HF [wt%]	Type	[wt%]	Water [wt%]	
Example 19	0.001	Ammonium chloride	10	89.999	Good
Example 20	0.01	Ammonium chloride	1	98.99	Good
Example 21	0.01	Ammonium chloride	10	89.99	Good
Example 22	0.01	Ammonium chloride	20	79.99	Good
Example 23	0.1	Ammonium chloride	1	98.9	Good
Example 24	0.1	Ammonium chloride	10	89.9	Good
Example 25	0.1	Ammonium chloride	20	79.9	Good
Example 26	1	Ammonium chloride	1	98	Good
Example 27	1	Ammonium chloride	10	89	Good
Example 28	1	Ammonium chloride	20	79	Good
Example 29	5	Ammonium chloride	1	94	Good
Example 30	5	Ammonium chloride	10	85	Good
Example 31	5	Ammonium chloride	20	75	Good
Comparative Example 5	0	Ammonium chloride	20	80	Poor

[0057]

The results in Table 2 show that when the cleaning liquid according to each of Examples 19 to 31 was used, the amount of the cerium component on the surface of the cleaned object was reduced to 8.5×10^9 atoms/cm^2 or less, and therefore the effect of cleaning and removing cerium oxide was high.

[0058]

In contrast, it is apparent that when the cleaning liquid according to Comparative Example 5 was used, the cerium component was not reduced to the lower limit of detection of the evaluation instrument, and the effect of cleaning and removing cerium oxide was low.

[0059]

(Examples 32 to 44)

Each cleaning liquid was prepared as in Example 1,

except that the composition and concentration of the cleaning liquid were changed as shown in Table 3. The cleaning treatment and so on were also carried out by using each cleaning liquid as in Example 1. The results are shown in Table 3 below.

[0060]

(Comparative Example 6)

A cleaning liquid was prepared as in Example 1, except that the composition and concentration of the cleaning liquid were changed as shown in Table 3. The cleaning treatment and so on were also carried out by using the cleaning liquid as in Example 1. The results are shown in Table 3 below.

[0061]

[Table 3]

No.	Ingredient (a)	Ingredient (b)		Ingredient (c)	Cleaning performance
	HF [wt%]	Type	[wt%]	Water [wt%]	
Example 32	0.001	Ammonium nitrate	10	89.999	Good
Example 33	0.01	Ammonium nitrate	1	98.99	Good
Example 34	0.01	Ammonium nitrate	10	89.99	Good
Example 35	0.01	Ammonium nitrate	20	79.99	Good
Example 36	0.1	Ammonium nitrate	1	98.9	Good
Example 37	0.1	Ammonium nitrate	10	89.9	Good
Example 38	0.1	Ammonium nitrate	20	79.9	Good
Example 39	1	Ammonium nitrate	1	98	Good
Example 40	1	Ammonium nitrate	10	89	Good
Example 41	1	Ammonium nitrate	20	79	Good
Example 42	5	Ammonium nitrate	1	94	Good
Example 43	5	Ammonium nitrate	10	85	Good
Example 44	5	Ammonium nitrate	20	75	Good
Comparative Example 6	0	Ammonium nitrate	20	80	Poor

[0062]

The results in Table 3 show that when the cleaning

liquid according to each of Examples 32 to 44 was used, the amount of the cerium component on the surface of the cleaned object was reduced to 8.5×10^9 atoms/cm^2 or less, and therefore the effect of cleaning and removing cerium oxide was high.

[0063]

In contrast, it is apparent that when the cleaning liquid according to Comparative Example 6 was used, the cerium component was not reduced to the lower limit of detection of the evaluation instrument, and the effect of cleaning and removing cerium oxide was low.

[0064]

(Examples 45 to 47)

As shown in Table 4, each cleaning liquid was prepared by mixing 0.1% by weight of hydrogen fluoride as ingredient (a), 10% by weight of ammonium sulfate as ingredient (b), water as ingredient (c), and a nonionic, cationic, or anionic surfactant. Subsequently, the cleaning treatment and so on were carried out by using each cleaning liquid as in Example 1. The results are shown in Table 4 below.

[0065]

[Table 4]

No.	Ingredient (a)	Ingredient (b)		Ingredient (c)	Surfactant		Cleaning performance
	HF [wt%]	Type	[wt%]	Water [wt%]	Type	[ppm]	
Example 45	0.1	Ammonium sulfate	10	89.9	Nonionic	100	Good
Example 46	0.1	Ammonium sulfate	10	89.9	Cationic	100	Good
Example 47	0.1	Ammonium sulfate	10	89.9	Anionic	100	Good

[0066]

The results in Table 4 show that when the cleaning liquid according to each of Examples 45 to 47 was used, the amount of the cerium component on the surface of the cleaned object was reduced to 8.5×10^9 atoms/cm^2 or less, and therefore the effect of cleaning and removing cerium oxide was high.

[0067]

(Examples 48 to 59)

As shown in Table 5, each cleaning liquid was prepared by mixing 0.1 to 5% by weight of hydrogen fluoride as ingredient (a), 5% by weight of ammonium sulfate, ammonium chloride, ammonium nitrate, or tetramethylammonium sulfate as ingredient (b), and water as ingredient (c).

[0068]

(Comparative Example 7)

As shown in Table 5, an aqueous solution of 5% by weight of ammonium sulfate was prepared.

[0069]

(Comparative Example 8)

As shown in Table 5, an aqueous solution of 20% by weight of ammonium fluoride was prepared.

[0070]

(Comparative Example 9)

As shown in Table 5, a cleaning liquid was prepared by mixing 0.5% by weight of hydrogen fluoride as ingredient (a), 20% by weight of ammonium fluoride as ingredient (b), and water as ingredient (c).

[0071]

(Comparative Example 10)

As shown in Table 5, an aqueous solution of 5% by weight of hydrogen fluoride was prepared.

[0072]

Subsequently, a 200 mm diameter silicon substrate having a 1,000 Å non-doped polysilicon film formed on its surface was subjected to chemical mechanical polishing with cerium oxide abrasive grains, and the resulting substrate was used as the object to be cleaned. The object to be cleaned was measured for the state of remaining residues as described below, and as a result, about $1x10^{12}$ atoms/cm^2 of cerium oxide was identified as a residual component.

[0073]

Subsequently, the cleaning treatment and so on were carried out by using each cleaning liquid as in Example 1. The results are shown in Table 5 below.

[0074]

[Table 5]

No.	Ingredient (a)	Ingredient (b)		Ingredient (c)	Cleaning performance on polysilicon film
	HF [wt%]	Type	[wt%]	Water [wt%]	
Example 48	0.1	Ammonium sulfate	5	94.9	Good
Example 49	1	Ammonium sulfate	5	94	Good
Example 50	5	Ammonium sulfate	5	90	Good
Example 51	0.1	Ammonium chloride	5	94.9	Good
Example 52	1	Ammonium chloride	5	94	Good
Example 53	5	Ammonium chloride	5	90	Good
Example 54	0.1	Ammonium nitrate	5	94.9	Good
Example 55	1	Ammonium nitrate	5	94	Good
Example 56	5	Ammonium nitrate	5	90	Good
Example 57	0.1	Tetramethylammonium sulfate	5	94.9	Good
Example 58	1	Tetramethylammonium sulfate	5	94	Good
Example 59	5	Tetramethylammonium sulfate	5	90	Good
Comparative Example 7	0	Ammonium sulfate	5	95	Poor
Comparative Example 8	0	Ammonium fluoride	20	80	Poor
Comparative Example 9	0.5	Ammonium fluoride	20	79.5	Poor
Comparative Example 10	5	Absent	0	95	Poor

[0075]

The results in Table 5 show that when the cleaning liquid according to each of Examples 48 to 59 was used, the amount of the cerium component on the surface of the cleaned object was reduced to 8.5×10^9 atoms/cm^2 or less, and therefore the effect of cleaning and removing cerium oxide was high.

[0076]

In contrast, it is apparent that when the cleaning liquid according to each of Comparative Examples 7 to 10 was used, the cerium component was not reduced to the lower

limit of detection of the evaluation instrument, and the effect of cleaning and removing cerium oxide was low.

[0077]

(Examples 60 to 71)

As shown in Table 6, each cleaning liquid was prepared by mixing 0.1 to 5% by weight of hydrogen fluoride as ingredient (a), 5% by weight of ammonium sulfate, ammonium chloride, ammonium nitrate, or tetramethylammonium sulfate as ingredient (b), and water as ingredient (c).

[0078]

(Comparative Example 11)

As shown in Table 6, an aqueous solution of 5% by weight of ammonium sulfate was prepared.

[0079]

(Comparative Example 12)

As shown in Table 6, an aqueous solution of 20% by weight of ammonium fluoride was prepared.

[0080]

(Comparative Example 13)

As shown in Table 6, a cleaning liquid was prepared by mixing 0.5% by weight of hydrogen fluoride as ingredient (a), 20% by weight of ammonium fluoride as ingredient (b), and water as ingredient (c).

[0081]

(Comparative Example 14)

As shown in Table 6, an aqueous solution of 5% by weight of hydrogen fluoride was prepared.

[0082]

Subsequently, a 200 mm diameter silicon substrate having a 1,000 Å silicon nitride film formed on its surface was subjected to chemical mechanical polishing with cerium oxide abrasive grains, and the resulting substrate was used as the object to be cleaned. The object to be cleaned was measured for the state of remaining cerium residues as described above, and as a result, about $1x10^{12}$ atoms/cm^2 of cerium oxide was identified as a residual component.

[0083]

Subsequently, the cleaning treatment and so on were carried out by using each cleaning liquid as in Example 1. The results are shown in Table 6 below.

[0084]

[Table 6]

No.	Ingredient (a)	Ingredient (b)		Ingredient (c)	Cleaning performance on silicon nitride film
	HF [wt%]	Type	[wt%]	Water [wt%]	
Example 60	0.1	Ammonium sulfate	5	94.9	Good
Example 61	1	Ammonium sulfate	5	94	Good
Example 62	5	Ammonium sulfate	5	90	Good
Example 63	0.1	Ammonium chloride	5	94.9	Good
Example 64	1	Ammonium chloride	5	94	Good
Example 65	5	Ammonium chloride	5	90	Good
Example 66	0.1	Ammonium nitrate	5	94.9	Good
Example 67	1	Ammonium nitrate	5	94	Good
Example 68	5	Ammonium nitrate	5	90	Good
Example 69	0.1	Tetramethylammonium sulfate	5	94.9	Good
Example 70	1	Tetramethylammonium sulfate	5	94	Good
Example 71	5	Tetramethylammonium sulfate	5	90	Good
Comparative Example 11	0	Ammonium sulfate	5	95	Poor
Comparative Example 12	0	Ammonium fluoride	20	80	Poor
Comparative Example 13	0.5	Ammonium fluoride	20	79.5	Poor
Comparative Example 14	5	Absent	0	95	Poor

[0085]

The results in Table 6 show that when the cleaning liquid according to each of Examples 60 to 71 was used, the amount of the cerium component on the surface of the cleaned object was reduced to 8.5×10^9 atoms/cm^2 or less, and therefore the effect of cleaning and removing cerium oxide was high.

[0086]

In contrast, it is apparent that when the cleaning liquid according to each of Comparative Examples 11 to 14 was used, the cerium component was not reduced to the lower limit of detection of the evaluation instrument, and the effect of cleaning and removing cerium oxide was low.

[0087]

(Examples 72 to 74)

As shown in Table 7, each cleaning liquid was prepared by mixing 0.01 to 0.5% by weight of hydrogen fluoride as ingredient (a), 10% by weight of ammonium sulfate as ingredient (b), and water as ingredient (c).

[0088]

(Comparative Examples 15 to 17)

As shown in Table 7, each cleaning liquid was prepared by mixing 0.01 to 0.5% by weight of hydrogen fluoride as ingredient (a), 10% by weight of sulfuric acid as ingredient (b), and water as ingredient (c).

[0089]

(Comparative Example 18)

A cleaning liquid was prepared by mixing 0.01% by weight of hydrogen fluoride as ingredient (a), 10% by weight of sulfuric acid and 0.1% by weight of ascorbic acid as ingredient (b), and water as ingredient (c).

[0090]

Subsequently, a 200 mm diameter silicon substrate having a 2,000 Å titanium film formed on its surface and a 200 mm diameter silicon substrate having a 5,000 Å aluminum film formed on its surface were prepared, respectively, and each used as the object to be cleaned.

[0091]

Subsequently, the cleaning liquid was placed in a cleaning liquid tank with a volume of 90 L, and the temperature of the cleaning liquid was adjusted to 25°C and stabilized. The objects, namely, the titanium film-carrying silicon substrate and the aluminum film-carrying silicon substrate, were immersed in the cleaning liquid for the time shown in Table 7, while held on a silicon substrate holding member made of PFA resin. After the immersion, the objects were lifted together with the silicon substrate holding member out of the cleaning liquid tank and immersed in an ultrapure water rinse tank with a volume of 90 L, which was provided in advance, so that the cleaning liquid deposited on the surface of the objects was rinsed off. Subsequently, the objects were dried and measured for surface resistance by using a four-probe surface resistance meter (K705-RS, manufactured by KYOWARIKEN. CO. LTD). The results of the measurement are shown in Table 7 below.

[0092]

[Table 7]

No.	Ingredient (a)	Ingredient (b)		Ingredient (c)	pH	Treatment time	Titanium film surface resistance	Aluminum film surface resistance
	HF	Type	[wt%]	Water				
	[wt%]			[wt%]	[-]	[minute(s)]	[Ω/□]	[mΩ/□]
No treatment						0	6.9	60
Example 72	0.01	Ammonium sulfate	10	90.0	2.8	60.0	7.1	97
Example 73	0.1	Ammonium sulfate	10	89.9	2.5	3.0	7.0	110
Example 74	0.5	Ammonium sulfate	10	89.5	2.0	0.75	7.0	130
Comparative Example 15	0.01	Sulfuric acid	10	90.0	<1	60	25	183
Comparative Example 16	0.1	Sulfuric acid	10	89.9	<1	3	154	236
Comparative Example 17	0.5	Sulfuric acid	10	89.5	<1	0.75	219	255
Comparative Example 18	0.01	Sulfuric acid	10	88.9	<1	60	18	208
		Ascorbic acid	0.1					

[0093]

The results in Table 7 show that when the cleaning liquid according to each of Examples 72 to 74 was used, the increase in the surface resistance of the titanium film and the aluminum film on the surfaces of the objects cleaned was smaller than that in each of Comparative Examples 15 to 17 and that the effect of the cleaning liquid according to each of Examples 72 to 74 on the titanium and aluminum films was small. Thus, it is apparent that the cleaning liquid of the invention can not only clean and remove cerium oxide but also prevent an increase in the resistance of metal films in contrast to the cleaning liquids of comparative examples.

[0094]

It is also apparent that in contrast, the use of the cleaning liquid of Comparative Example 18 produces a significant increase in the surface resistance of titanium and aluminum films and therefore increases the resistance of metal films, although it can clean and remove cerium oxide.

CLAIMS

1. A cleaning liquid for removing cerium oxide remaining on a surface of an object to be cleaned, comprising:

(1) hydrogen fluoride; and

(2) at least one ammonium salt selected from the group consisting of ammonium chloride, ammonium nitrate, and ammonium sulfate.

2. The cleaning liquid according to claim 1, wherein the hydrogen fluoride has a concentration of 0.001 to 5% by weight, and the ammonium salt has a concentration of 0.1 to 20% by weight.

3. The cleaning liquid according to claim 1 or 2, further comprising a surfactant.

4. A cleaning method, comprising bringing a cleaning liquid into contact with a surface of an object on which cerium oxide is deposited, so that the cerium oxide is dissolved to form cerium ions and removed, wherein

the cleaning liquid comprises:

(1) hydrogen fluoride; and

(2) at least one ammonium salt selected from the group consisting of ammonium chloride, ammonium nitrate, and ammonium sulfate.

5. The cleaning method according to claim 4, wherein the hydrogen fluoride has a concentration of 0.001 to 5% by weight, and the ammonium salt has a concentration of 0.1 to 20% by weight.

6. The cleaning method according to claim 4 or 5, wherein the cleaning liquid further comprises a surfactant.

7. The cleaning method according to any one of claims 4 to 6, wherein the object is a semiconductor substrate, a glass substrate, a ceramic substrate, a quartz substrate, or a rock crystal substrate.