

DESCRIPTION

Cleaner for Semiconductor Device Production Process
or for Liquid Crystal Device Production Process

5 TECHNICAL FIELD

The present invention relates to a cleaner for a semiconductor device production process or for a liquid crystal device production process, which is used for cleaning a metal or glass surface in the semiconductor
10 device production process and the liquid crystal device production process.

TECHNICAL BACKGROUND

For washing wafers, etc., in the process of the
15 production of semiconductor devices of silicon and compounds such as GaAs or in the process of the production of liquid crystal devices (LCD), and for removing dry-etching residual substance (residue) in the above processes, there are used strong acids (hydrochloric acid, sulfuric
20 acid, nitric acid and fluoric acid), strong alkalis (sodium hydroxide, ammonia, hydrazine and hydroxylamine), ammonium fluoride, alkanolamines, organic solvents, and the like.

The above substances are all deleterious substances or hazardous substances and involve many
25 problems in respect of working and environmental safety.

More specifically, for the removal of impurity ion, particles, an organic substance and an oxide layer on a metal (including a semimetal such as silicon) surface or a glass surface of a wafer, etc., in the above processes,
30 there is required a complicated process (so-called RCA process) according to an object to be removed, in which a chemical such as a strong acid, a strong alkali or the like

is used depending upon the object and cleaning is repeated. These chemicals involve problems in respect of both operability and safety.

For removing a dry etching residue, further,
5 there is used hydroxylamine, tetramethylammonium hydroxide (TMAH), ammonium fluoride, alkanolamine, a mixture of an organic solvent with any one of these compounds, or an organic solvent itself, while these compounds have a problem in view of working safety or environmental
10 pollution. Further, when the material of an object to be treated is a metal, the above compounds have another problem that they remain in the metal to corrode the metal.

DISCLOSURE OF THE INVENTION

15 It is an object of the present invention to provide a cleaner for a semiconductor device production process or for a liquid crystal device production process, which has high environmental and working safety and which makes it possible to clean a metal (including semimetal) or
20 glass surface of an etching residue, impurities, etc., effectively without causing the problem of metal corrosion in a semiconductor device production process or a liquid crystal device production process.

The above object is achieved by any one of the
25 following cleaners.

(1) A cleaner for a semiconductor device production process or for a liquid crystal device production process, which contains a polyphosphoric-acid-urea condensate or phosphoric-acid-urea polymer which is a
30 reaction product from orthophosphoric acid and urea, and water, and which is for use for cleaning a metal and/or glass surface in at least one process of a semiconductor

device production process and a liquid crystal device production process.

(2) The cleaner for a semiconductor device production process or for a liquid crystal device production process, according to the above (1), which contains, as an active ingredient, the polyphosphoric acid-urea condensate or phosphoric acid-urea polymer obtained by reacting an orthophosphoric acid with urea in an orthophosphoric acid:urea molar ratio of 1:1 to 1:5.

(3) The cleaner for a semiconductor device production process or for a liquid crystal device production process, according to the above (1) or (2), which contains 0.01 to 60 % by weight of the polyphosphoric acid-urea condensate or phosphoric acid-urea polymer which is a reaction product from orthophosphoric acid and urea.

(4) The cleaner for a semiconductor device production process or for a liquid crystal device production process, according to any one of the above (1) to (3), which further contains hydrogen peroxide.

(5) The cleaner for a semiconductor device production process or for a liquid crystal device production process, according to any one of the above (1) to (4), which is for use for the removal of a dry etching residue.

(6) The cleaner for a semiconductor device production process or for a liquid crystal device production process, according to the above (5), wherein the dry etching residue contains an organometal and/or a metal oxide formed from the organometal.

(7) The cleaner for a semiconductor device production process or for a liquid crystal device production process, according to any one of the above (1)

to (4), which is for use for cleaning a wafer.

(8) The cleaner for a semiconductor device production process or for a liquid crystal device production process, according to the above (7), which is
5 for use for cleaning off metal ion and/or halide ion.

JP-A-8-132093 discloses a cleaner composition containing, as active ingredients, hydrogen peroxide, an ammonium phosphate condensate and a urea compound. The above Publication discloses the removal of scales and slime.
10 Differing from the present invention, however, it discloses nothing concerning the use of the above composition for cleaning off an etching residue or impurities on a metal or glass surface in the semiconductor device production process or the liquid crystal device production process,
15 and it is not at all possible to infer the effect of the present invention on the basis of the above Publication. Further, JP-B-59-5670 discloses a water-soluble metal cleaner containing an ammonium phosphate condensate as a main cleaner ingredient and containing urea or its modified
20 component as an auxiliary agent. Differing from the present invention, however, it discloses nothing concerning the use of the above cleaner for cleaning off an etching residue or impurities on a metal or glass surface in the semiconductor device production process or the liquid
25 crystal device production process, and it is not at all possible to infer the effect of the present invention on the basis of the above Publication.

BRIEF DESCRIPTION OF DRAWINGS

30 Fig. 1 is an SEM photograph of a silicon wafer treated with a cleaner of the present invention (having a polyphosphoric-acid-urea condensate concentration of 40 %

by weight).

Fig. 2 is an SEM photograph of an untreated silicon wafer.

Fig. 3 is an SEM photograph of an
5 Si/Ti/TiN/Al/TiN laminated substrate treated with a cleaner of the present invention (having a polyphosphoric-acid-urea condensate concentration of 0.5 % by weight).

Fig. 4 is an SEM photograph of an
10 Si/Ti/TiN/Al/TiN laminated substrate treated with a cleaner of the present invention (having a polyphosphoric-acid-urea condensate concentration of 40 % by weight).

Fig. 5 is an SEM photograph of an untreated Si/Ti/TiN/Al/TiN laminated substrate.

15 BEST MODES FOR PRACTICING THE INVENTION

The present invention will be explained in detail hereinafter.

The cleaner for a semiconductor device production process and for a liquid crystal device production process,
20 provided by the present invention, contains, as a main active ingredient, a polyphosphoric-acid-urea condensate or phosphoric-acid-urea polymer which is a reaction product from orthophosphoric acid and urea and contains water as a solvent. Being a cleaner containing a less toxic compound
25 alone, the cleaner of the present invention is preferred in view of environmental and working safety.

Further, in a semiconductor device production process or in a liquid crystal device (LCD) production process, the cleaner of the present invention can remove
30 all of substances which deteriorate device characteristics, such as impurity ions (e.g., ions of metals such as Na, K, Ca, Al, Fe, Ni and Cu and ions of halogens such as

chlorine), particles, an organic substance and an oxide layer on the surface of a silicon wafer or a glass substrate, not by carrying out a complicated step but by only bringing the above surface into contact with the cleaner. Further, it can remove an etching residue called a polymer, which contains an organometal formed during the dry etching in the above production process and a metal oxide formed from the above organometal due to oxygen plasma ashing treatment for removing a resist.

Further, the cleaner of the present invention is free of a problem that it remains in a metal, etc., to be treated and corrodes the metal.

That is, the cleaner for a semiconductor device production process and for a liquid crystal device production process, provided by the present invention, is promising for use as:

1) a remover liquid for removing a dry etching residue,

2) a substitute for a chemical liquid used for so-called RCA cleaning for removing impurities such as metal and halogen ions on a silicon wafer, etc.,

3) a cleaner liquid for scrubbing a wafer, etc.,

4) a cleaner liquid for cleaning a wafer, etc., after a CMP (chemico-mechanical polishing) process, and

5) a cleaner liquid for cleaning a glass substrate for use in a liquid crystal device.

In particular, the cleaner of the present invention is preferred for use in the above 1) and 2). In the above 2), it is no longer required to repeat the steps of cleaning with liquid chemicals selected for each purpose in conventional RCA cleaning, liquid chemicals containing deleterious substances or hazardous substances such as

sulfuric acid, ammonia, hydrochloric acid or fluoric acid and washing with water. All the impurities, etc., can be removed with the cleaner of the present invention alone.

The cleaner for a semiconductor device production process and for a liquid crystal device production process, provided by the present invention, contains a polyphosphoric-acid-urea condensate or phosphoric acid-urea polymer as an active ingredient. The polyphosphoric-acid-urea condensate or phosphoric-acid-urea polymer, which is a reaction product from orthophosphoric acid and urea and is contained, as an active ingredient, in the cleaner for a semiconductor device production process and for a liquid crystal device production process, provided by the present invention, is a known product formed by the condensation of orthophosphoric acid and urea. The reaction in the above condensation is preferably carried out under conditions where the orthophosphoric acid:urea molar ratio is 1:1 to 1:5. The condensation degree of the polyphosphoric-acid-urea condensate or phosphoric-acid-urea polymer which is a reaction product from orthophosphoric acid and urea is not specially limited, while the above condensation degree is generally approximately 3 to 150, preferably approximately 8 to 50.

Besides these, there may be a salt of the polyphosphoric-acid-urea condensate or phosphoric-acid-urea polymer and a product in which an alkali which neutralizes the polyphosphoric-acid-urea condensate or phosphoric-acid-urea polymer which is a reaction product from orthophosphoric acid and urea and the polyphosphoric-acid-urea condensate or phosphoric-acid-urea polymer which is a reaction product from orthophosphoric acid and urea bond to each other. The above salt or the above product includes

ammonium salt, hydrazine salt, hydroxylamine salt, alkanolamine salt, cyclohexylamine salt, cyclic amine salt, potassium salt and sodium salt of the polyphosphoric-acid-urea condensate or phosphoric-acid-urea polymer which is a reaction product from orthophosphoric acid and urea. The above polyphosphoric-acid-urea condensates or phosphoric-acid-urea polymers which are reaction products from orthophosphoric acid and urea may be used alone or in combination.

10 While the content of the polyphosphoric-acid-urea condensate or phosphoric-acid-urea polymer which is a reaction product from orthophosphoric acid and urea is generally 0.01 to 60 % by weight, it may be changed depending upon fields where it is used and conditions under
15 which it is used.

 When the cleaner of the present invention is used for cleaning a silicon wafer or a glass substrate, i.e., a substrate having no metal layer where almost no influence is caused on a metal, in particular, when there is a
20 contact hole, the above content may be 5 to 60 % by weight, particularly, 10 to 60 % by weight. When the above content exceeds the above upper limit, no further improvement is observed, and it is disadvantageous in view of a cost performance. When the above content is less than the above
25 lower limit, the cleaning power is low.

 However, the above amount in use brings an environmental problem, e.g., an effluent disposal problem. The above content is therefore preferably 10 % by weight or less. Further, for example, in a substrate having metal
30 layers of Si/Ti/TiN/Al/TiN, etc., there is a problem that Al or other metals having a low melting point such as Cu, Ni, etc., is/are liable to be corroded with an increase in

the content of the polyphosphoric-acid-urea condensate or phosphoric acid-urea polymer. In the above case, even when the content of the polyphosphoric-acid-urea condensate or phosphoric-acid-urea polymer is 0.1 % by weight or less, a
5 sufficient cleaning effect can be obtained and the degree of metal corrosion is low. The above content is 0.01 to less than 10 % by weight, preferably 0.01 to less than 5 % by weight, more preferably 0.05 to 4.5 % by weight. When the content of the polyphosphoric-acid-urea condensate or
10 phosphoric-acid-urea polymer is within the above range, and in particular when a line width is in the range of about sub-micron, e.g., 0.1 μm to less than 1 μm , the "eating" of a metal layer is effectively prevented.

The water to be contained in the cleaner of the
15 present invention is not specially limited, and it can be selected from tap water, ground water, deionized water or pure water, and of these, deionized water and pure water are preferred.

The amount of water can constitute a balance
20 other than the amount of the chemical component.

The cleaner of the present invention may contain hydrogen peroxide. The hydrogen peroxide serves to improve cleaning power, so that a treatment temperature and the time period of treatment can be therefore decreased.

25 The hydrogen peroxide can be selected from hydrogen peroxide per se, known compounds which can release hydrogen peroxide in water and a mixture of these.

Although not specially limited, the content of the hydrogen peroxide is preferably 1 to 30 % by weight,
30 more preferably 5 to 25 % by weight.

In addition to the above, the cleaner of the present invention may further contain urea or a urea

derivative (biuret and triuret), various surfactants (nonionic, cationic, anionic and amphoteric), and a chelating agent (ethylenediamine tetraacetic acid: EDTA, etc.).

5 In cleaning in the fields of a semiconductor and a liquid crystal, impurities, particularly, iron, sodium and potassium influence the characteristics of a device. The cleaner of the present invention can be therefore prepared so as to have such a product quality that the
10 impurities are decreased to a predetermined level or lower depending upon fields where it is used. For example, the impurities can be removed from the cleaner of the present invention by electric dialysis, or the like.

 The cleaning with the cleaner of the present
15 invention is carried out by bringing the cleaner liquid and an object to be treated into contact with each other. The above contact may be carried out by a method in which the cleaner is sprayed to that portion of the object which is to be treated. Preferably, the object to be treated is
20 immersed in the cleaner of the present invention filled in a tank. In the treatment in the tank, it is preferred to stir or agitate the cleaner.

 Although the temperature at which the cleaner is brought into contact and the time period for which the
25 cleaner is kept in contact differ depending upon the properties of a substance to be cleaned off and an object to be treated, it is sufficient to keep the object and the cleaner in contact with each other at a temperature of approximately 15 to 100°C for approximately 2 to 60 minutes.

30 In the treatment in a tank, for maintaining the cleaning effect at a constant level, the entire cleaner in the tank may be replaced with a new cleaner at regular

intervals of predetermined treatment in a batch treatment. In a continuous treatment, the cleaner may be discharged at a predetermined rate at regular intervals of predetermined treatment by an overflow with the supplement of a new
5 cleaner (supplement liquid).

The volume of the tank for the treatment is approximately 20 to 300 liters.

An object which has been cleaned with the cleaner of the present invention is preferably further washed with
10 water, or it may be dried and directly used without washing it with water.

EXAMPLES

The present invention will be more specifically
15 explained with reference to Examples hereinafter.

Example 1

A positive photoresist layer of a novolak resin material was formed on a silicon oxide layer of a 630 μm
20 thick silicon wafer (oxide layer wafer) having a diameter of 6 inches, the photoresist was patterned for forming a contact hole, and then, plasma etching was carried out. As an etching gas, a chlorine-containing gas and a fluorine-containing gas were used. After the etching, the
25 photoresist was removed by oxygen plasma ashing.

Then, the wafer was cleaned by immersing it in a cleaner, which was an aqueous solution (deionized water was used as water) having a polyphosphoric-acid-urea condensate concentration shown in Table 1 and was filled in a tank
30 having a volume of 20 liter, at a treat temperature shown in Table 1 for a treatment time shown in Table 1. The tank was provided with a stirrer within it, and the treatment

was carried out with stirring the cleaner at 70 to 75 rpm.

Fig. 1 shows a scanning electron microscope (SEM) photograph of a wafer which was treated with a cleaner of a 40 wt% aqueous solution under conditions of 65°C and 20 minutes, and Fig. 2 shows a scanning electron microscope (SEM) photograph of an untreated wafer.

It is seen from Figs. 1 and 2 that the treatment with the cleaner of the present invention fully removes an etching residue in the hole.

Further, surfaces of wafers treated under conditions shown in Table 1 were evaluated on the basis of scanning electron microscope (SEM) photographs. Table 1 shows the results including the result shown in Fig. 1. The evaluation results of a cleaning effect are expressed by ○ (the removal of etching residue is complete, i.e., at the same level as that in Fig. 1) and × (the removal of etching residue was incomplete).

Table 1

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Concentration of polyphosphoric-acid-urea condensate (aqueous solution wt%)	Treatment temperature (°C)	Treatment time (minute)	Cleaning effect
1	100	20	○
5	100	15	○
10	65	20	○
20	65	20	○
40	65	20	○
60	65	20	○

Table 1 shows that the treatment with the cleaner of the present invention can produce an excellent cleaning effect.

25

Example 2

The same object as that used in Example 1 was cleaned with a cleaner which was an aqueous solution containing a polyphosphoric-acid-urea condensate and hydrogen peroxide as shown in Table 2, at a treatment temperature shown in Table 2 for a treatment time shown in Table 2, and cleaning results were evaluated in the same manner as in Example 1. Table 2 shows the results.

10

Table 2

Concentration of polyphosphoric-acid-urea condensate (aqueous solution wt%)	Amount of H ₂ O ₂ (aqueous solution wt %)	Treatment temperature (°C)	Treatment time (minute)	Cleaning effect
5	20	65	20	○
20	15	50	20	○
40	10	40	20	○
40	20	20	20	○
60	5	35	20	○

Table 2 shows that sufficient cleaning effects can be produced due to the addition of hydrogen peroxide even when the treatment temperature is decreased.

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Example 3

A positive photoresist layer of a novolak resin material was formed on a 630 μm thick Si/Ti/TiN/Al/TiN laminated substrate having a diameter of 6 inches, the photoresist was patterned, and then, plasma etching was carried out. As an etching gas, a chlorine-containing gas and a fluorine-containing gas were used. After the etching, the photoresist was removed by oxygen plasma ashing.

20

Then, the laminated substrate was subjected to cleaning treatment with a cleaner having the composition shown in Example 1 under conditions shown in Table 3, and then washed with water.

5 In this case, the cleaner was filled in a 20-liter tank with a cover for the above treatment. Further, pure water was filled in a tank having the same volume as the above, to carry out the above washing with water at 25°C for 5 minutes.

10 Of the so-treated laminated substrates, Fig. 3 shows an SEM photograph of the laminated substrate treated with a cleaner of a 0.5 wt% aqueous solution under conditions of 65°C and 20 minutes, Fig. 4 shows an SEM photograph of the laminated substrate treated with a
15 cleaner of a 40 wt% aqueous solution under conditions of 65°C and 20 minutes, and Fig. 5 shows an SEM photograph of an untreated laminated substrate.

 Figs. 3 to 5 show that when the content of the polyphosphoric-acid-urea condensate or phosphoric-acid-urea
20 polymer is large, the metal Al is corroded but that when the above content is low, almost no corrosion takes place, and further an etching residue is fully cleaned off.

 Further, the laminated substrates treated under the conditions shown in Table 3 were evaluated for surfaces
25 in which a narrow line and a space/line of 0.35 μm /0.35 μm were formed, on the basis of scanning electron microscope (SEM) photographs thereof. Table 3 shows the results. The evaluation results of the metal corrosion are expressed by $\bigcirc$ (no metal corrosion was observed), $\triangle$ (slight metal
30 corrosion was observed) and $\times$ (metal corrosion was observed).

Table 3

Concentration of polyphosphoric-acid- urea condensate (aqueous solution wt%)	Treatment temperature (°C)	Treatment time (minute)	Metal corrosion
0.1	65	20	○
0.5	65	20	○
1	65	20	○
5	65	20	△
10	65	20	×
20	65	20	×
40	65	20	×
60	65	20	×

Table 3 shows that when a composition of the
 5 cleaner and treatment conditions are selected, almost no
 metal corrosion is caused and an excellent cleaning effect
 can be obtained.

Example 4

10 An untreated silicon bare wafer having a diameter
 of 6 inches and a thickness of 630 μm was used as a sample.
 As shown in Table 4, the sample was tested in a cleaning
 apparatus with a chemical concentration shown in Table 4 at
 a predetermined temperature shown in Table 4. In this case,
 15 an amount of metal impurities (Na, Mg, Ca, Al, Fe, Ni, Cu)
 on the wafer surface was measured with a total reflection
 fluorescent X-ray analyzer.

The amount of the metal impurities before the
 cleaning was 10^{12} to 10^{13} pieces-atoms (each atom of the
 20 above elements) per cm^2 of the wafer.

Table 4 shows the results.

Table 4

Concentration of polyphosphoric- acid-urea condensate (aqueous solution wt%)	Treatment Temperature (°C)	Treatment time (minute)	Amount of metal impurities (pieces-atom/cm ²)
5	80	20	10 ¹⁰⁻¹¹ (each atom of Na, Mg, Ca, Al, Fe, Ni, Cu)
10	80	20	10 ¹⁰⁻¹¹ (each atom of Na, Mg, Ca, Al, Fe, Ni, Cu)
20	80	20	10 ¹⁰⁻¹¹ (each atom of Na, Mg, Ca, Al, Fe, Ni, Cu)
40	80	20	10 ¹⁰⁻¹¹ (each atom of Na, Mg, Ca, Al, Fe, Ni, Cu)

Table 4 shows that metal impurities which have a detrimental influence on a device can be decreased in amount by the cleaning.

5 Example 5

The same untreated oxide layer wafer as that used in Example 1 was used as a sample, and as shown in Table 5, the sample was tested in a cleaning apparatus (overflow type cleaning apparatus) with a chemical concentration shown in Table 5 at a predetermined temperature shown in Table 5. Particles (at least $0.3 \mu\text{m}$) on the wafer were measured for a number with a surface scanning type particle counter.

For the number of particles, particles having a maximum length of at least $0.3 \mu\text{m}$ were counted, and the result is shown by the number of particles per a wafer diameter of 6 inches (pieces-at least $0.3 \mu\text{m}/6$ inches). In this case, particles having a maximum length of 0.3 to $0.5 \mu\text{m}$ were counted. The number of particles before the cleaning was 208 pieces-at least $0.3 \mu\text{m}/6$ inches. The wafer was subjected to the above analysis after it was washed with pure water according to an overflow method (5 minutes).

Table 5

25

Concentration of polyphosphoric-acid-urea condensate (aqueous solution wt%)	Treatment temperature ($^{\circ}\text{C}$)	Treatment time (minute)	Number of particles (pieces-at least $0.3 \mu\text{m}/6$ inches)
5	80	20	55
10	80	20	32
20	80	20	8
40	80	20	7

Table 5 shows that particles which have an detrimental influence on a device can be decreased in number by the cleaning.

5 Example 6

 The same test as that in Example 5 was carried out except that conditions shown in Table 6 were employed and that an untreated glass substrate (400 mm x 500 mm) for LCD was treated.

10 For the number of particles, particles having a maximum length of at least 0.5 μm were counted, and the result is shown by the number of particles per 400 mm x 500 mm (pieces-at least 0.5 μm /400 mm x 500 mm). In this case, particles having a maximum length of 0.5 to 1.0 μm were
15 counted. The number of particles before the cleaning was 320 pieces-at least 0.5 μm /400 mm x 500 mm. Table 6 shows the results.

Table 6

Concentration of polyphosphoric-acid-urea condensate (aqueous solution wt%)	Treatment temperature (°C)	Treatment time (minute)	Number of particles (pieces-at least 0.5 $\mu\text{m}/400\text{ mm x }500\text{ mm}$)
5	65	20	23
10	65	20	18

Table 6 shows that particles which have an detrimental influence on a device can be decreased in number by the cleaning.

5 EFFECT OF THE INVENTION

According to the present invention, an etching residue, impurities, etc., on a metal (including semi-metal) or glass surface in a semiconductor device production process or a liquid crystal device production process can be effectively cleaned off. Further, there is no detrimental influences on an object to be cleaned, such as the corrosion of a metal.

CLAIMS

1. A cleaner for a semiconductor device production process or for a liquid crystal device production process, which contains, as an active ingredient, a polyphosphoric-acid-urea condensate or phosphoric-acid-urea polymer which is a reaction product from orthophosphoric acid and urea.
2. The cleaner for a semiconductor device production process or for a liquid crystal device production process, according to claim 1, which contains, as an active ingredient, the polyphosphoric acid-urea condensate or phosphoric acid-urea polymer obtained by reacting an orthophosphoric acid with urea in an orthophosphoric acid:urea molar ratio of 1:1 to 1:5.

