

DESCRIPTION

Title of the Invention: CLEANING AGENT COMPOSITION FOR REMOVING RESIN MASK

Technical Field

[0001] The present disclosure relates to a cleaning composition for stripping a resin mask and a cleaning method using the cleaning composition.

Background Art

[0002] In recent years, personal computers and various electronic devices have made great advances in low power consumption, high processing speed, and miniaturization. Accordingly, wiring on package substrates or the like to be mounted on them has become increasingly finer year by year. A metal masking method has been mainly used to form such fine wiring and connection terminals, e.g., pillars and bumps. However, the metal masking method is gradually replaced by other new methods because it has low versatility and difficulty in enabling much finer wiring.

One of the new methods is to use a dry film resist as a thick resin mask instead of a metal mask. The resin mask is finally stripped and removed by using an alkaline stripping cleaner.

[0003] A semiconductor device can be produced in the following manner. A resist is applied to a semiconductor substrate and patterned by exposure and development. Using this resist pattern as a mask, the unmasked area of the semiconductor substrate is etched to form a fine circuit. Then, the photoresist is stripped from the semiconductor substrate. Alternatively, after the fine circuit is formed in the same manner, resist residues are stripped from the semiconductor substrate by ashing.

As an example of the resist stripping cleaner, JP 2005-55701 A (Patent Document 1) proposes a resist stripping agent composition that contains an amine, an organic solvent with a Hansen solubility parameter of 18 to 33 MPa^{1/2}, a sugar, and 0 to 5% by weight of water.

Disclosure of the Invention

[0004] An aspect of the present disclosure relates to a cleaning composition for stripping a resin mask. The cleaning composition contains a polyhydric alcohol (component A), amines

(component B), and an organic solvent (component C) with a Hansen solubility parameter, SP value, of 18 to 33 MPa^{1/2}, excluding the component A and the component B. A mass ratio A/B of the component A to the component B is 2 or more and 8 or less. The component C is at least one selected from the group consisting of a sulfur-containing compound and a nitrogen-containing compound.

[0005] An aspect of the present disclosure relates to a cleaning method that includes stripping a resin mask from an object to be cleaned, to which the resin mask is attached, by using the cleaning composition of the present disclosure.

[0006] An aspect of the present disclosure relates to a method for producing a semiconductor device that includes stripping a resin mask from an object to be cleaned, to which the resin mask is attached, by using the cleaning composition of the present disclosure.

[0007] An aspect of the present disclosure relates to a method for producing a semiconductor device that includes stripping a resin mask from an object to be cleaned, to which the resin mask is attached, by using the cleaning method of the present disclosure.

Description of the Invention

[0008] In the manufacturing process of semiconductor devices, residues of resin masks adhering to, e.g., semiconductor substrates, metal wiring, and interlayer insulating thin films can cause connection failures between semiconductor chips and other components or damage to electronic components. This leads to defective products and a poor yield of semiconductor chips. Therefore, a cleaning composition is required to have a high ability to remove (strip) a resin mask. The cleaning composition disclosed in Patent Document 1 still has room for improvement in the ability to remove a resin mask. Usually, it is more difficult to strip a negative resist than a positive resist. When the resin mask is a negative resist, the removal of the negative resist needs to be performed under severe conditions (e.g., maintaining contact with a treatment agent (cleaning agent) at a high temperature for a long time). Thus, the cleaning composition should be able to strip the negative resist under moderate treatment conditions, that is, the cleaning composition should have excellent resin mask removal capability.

[0009] With the foregoing in mind, the present disclosure provides a cleaning composition for stripping a resin mask that has high resin mask removal capability, a cleaning method, and a method for producing a semiconductor device.

[0010] The present disclosure is based on the findings that the use of a cleaning composition that contains a polyhydric alcohol (component A), amines (component B), and a specific organic solvent (component C) in predetermined proportions can efficiently remove a resin mask from an object to be cleaned.

[0011] In one aspect, the present disclosure relates to a cleaning composition for stripping a resin mask (also referred to as a “cleaning composition of the present disclosure” in the following). The cleaning composition of the present disclosure contains a polyhydric alcohol (component A), amines (component B), and an organic solvent (component C) with a Hansen solubility parameter, SP value, of 18 to 33 MPa^{1/2}, excluding the component A and the component B. A mass ratio A/B of the component A to the component B is 2 or more and 8 or less. The component C is at least one selected from the group consisting of a sulfur-containing compound and a nitrogen-containing compound.

[0012] The present disclosure provides a cleaning composition with high resin mask removal (stripping) capability. The cleaning composition of the present disclosure enables the production of high-quality semiconductor device circuits, particularly compound semiconductor device circuits.

[0013] The details of the mechanism of the effects of the present disclosure are not fully clear, but can be assumed as follows.

Resin materials used to form resin masks usually contain acidic functional groups, e.g., a phenol resin.

In the present disclosure, the reaction between the amines (component B) and the acidic functional groups in a resin mask (resist) may increase the solubility of the resin mask (resist) in the specific organic solvent (component C), and thus facilitate the removal of the resin mask (resist). Moreover, the combination of the polyhydric alcohol (component A) and the amines (component B) at a predetermined ratio may promote penetration of the amines (component B) into the resin mask (resist), thereby enhancing the stripping capability.

However, the present disclosure should not be interpreted solely by the above mechanism.

[0014] In the present disclosure, the resin mask serves to protect the surface of a material from treatments such as etching, plating, and heating, and functions as a protective film.

In one or more embodiments, the resin mask may be, e.g., a resist layer that has undergone both exposure and development, a resist layer that has undergone at least one of

exposure or development (also referred to as an "exposed and/or developed" resist layer in the following), or a cured resist layer.

In one or more embodiments, the resin mask is composed of a resist having physical properties (e.g., solubility in a developing solution) that change with light, an electron beam, etc. Resists are broadly classified into a negative type and a positive type depending on how they react with light or an electron beam. A negative resist has properties such that the solubility in a developing solution decreases when it is exposed to light. In a layer containing the negative resist (also referred to as a "negative resist layer" in the following), the exposed portion is used as a resin mask after the exposure and development processes. A positive resist has properties such that the solubility in a developing solution increases when it is exposed to light. In a layer containing the positive resist (also referred to as a "positive resist layer" in the following), the exposed portion is removed after the exposure and development processes, and the unexposed portion is used as a resin mask. The use of the resin mask with these properties can form fine connections of a circuit board, including, e.g., metal wiring, metal pillars, and solder bumps.

In one or more embodiments, the resin materials for the resin mask may include, e.g., a film-like photosensitive resin, a resist film, and a photoresist. Any general-purpose resist film may be used.

Examples of the resin mask include a polyhydroxystyrene resin film, an acrylic acid polymer film, and a polyimide polymer film. The polyimide polymer film may be a solvent-soluble polyimide film, e.g., an alkali-soluble polyimide film.

The thickness of the resin mask is chosen based on a step height due to the unevenness of the outermost surface of the front side of a semiconductor substrate, and is sufficient if the resin mask can fully protect the surface of the front side of the semiconductor substrate. The thickness of the resin mask is, e.g., 1 μm or more and 100 μm or less, and is preferably 3 μm or more and 50 μm or less from the viewpoint of fully protecting the surface of the front side of the semiconductor substrate and from the viewpoint of the curing time and removal time of a resist used as the resin mask.

[0015] [Component A: polyhydric alcohol]

The polyhydric alcohol (also referred to as a "component A" in the following) contained in the cleaning composition of the present disclosure may be a polyhydric alcohol having 2 to 5 hydroxyl groups in the molecule from the viewpoint of improving the resin mask removal capability. In this case, the component A does not include a sugar alcohol.

The component A is preferably any of dihydric to pentahydric alcohols, more preferably any of dihydric to tetrahydric alcohols, even more preferably a dihydric or trihydric alcohol, and still more preferably a dihydric alcohol from the viewpoint of improving the resin mask removal capability. Examples of the dihydric alcohol include ethylene glycol and diethylene glycol.

The component A is preferably at least one selected from the group consisting of ethylene glycol and diethylene glycol from the viewpoint of improving the resin mask removal capability. The component A may be one type or a combination of two or more types.

[0016] In the present disclosure, the content of the component A in the cleaning composition at the time of use is preferably 4% by mass or more, more preferably 6% by mass or more, and even more preferably 8% by mass or more from the viewpoint of improving the resin mask removal capability. From the same viewpoint, the content of the component A in the cleaning composition at the time of use is preferably 16% by mass or less, more preferably 14% by mass or less, and even more preferably 12% by mass or less. From the same viewpoint, the content of the component A in the cleaning composition at the time of use is preferably 4% by mass or more and 16% by mass or less, more preferably 6% by mass or more and 14% by mass or less, and even more preferably 8% by mass or more and 12% by mass or less. When the component A is a combination of two or more types, the content of the component A is the total content of the two or more types.

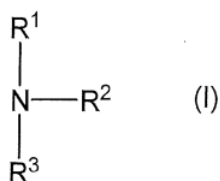
[0017] In the present disclosure, the "content of each component in the cleaning composition at the time of use" means the amount of each component at the time of cleaning, i.e., at the time the cleaning composition starts to be used for cleaning.

In one or more embodiments, the content of each component in the cleaning composition of the present disclosure may be considered as the blending amount of each component in the cleaning composition of the present disclosure.

[0018] [Component B: amines]

In one or more embodiments, the amines (also referred to as a "component B" in the following) contained in the cleaning composition of the present disclosure may include an alkanolamine (amino alcohol). Examples of the alkanolamine include a compound represented by the following formula (I). The component B may be one type or a combination of two or more types.

[Chemical Formula 1]



[0019] In the formula (I), R¹ represents a hydrogen atom, a methyl group, an ethyl group, or an aminoethyl group, R² represents a hydrogen atom, a hydroxyethyl group, a hydroxypropyl group, a methyl group, or an ethyl group, and R³ represents a hydroxyethyl group or a hydroxypropyl group.

[0020] The component B may be, e.g., at least one selected from the group consisting of: monoethanolamine (MEA); monoisopropanolamine; N-methylmonoethanolamine; N-methylisopropanolamine; N-ethylmonoethanolamine; N-ethylisopropanolamine; diethanolamine; diisopropanolamine; N-dimethylmonoethanolamine; N-dimethylmonoisopropanolamine; N-methyldiethanolamine; N-methyldiisopropanolamine; N-diethylmonoethanolamine; N-diethylmonoisopropanolamine; N-ethyldiethanolamine; N-ethyldiisopropanolamine; N-(β-aminoethyl)ethanolamine; N-(β-aminoethyl)isopropanolamine; N-(β-aminoethyl)diethanolamine; and N-(β-aminoethyl)diisopropanolamine. Among these, the component B is preferably at least one selected from the group consisting of monoethanolamine (MEA) and N-methylmonoethanolamine from the viewpoint of improving the resin mask removal capability.

[0021] In the present disclosure, the content of the component B in the cleaning composition at the time of use is preferably 0.5% by mass or more, more preferably 1% by mass or more, and even more preferably 1.6% by mass or more from the viewpoint of improving the resin mask removal capability and reducing corrosiveness of the substrate members. From the same viewpoint, the content of the component B in the cleaning composition at the time of use is preferably 8% by mass or less, more preferably 5% by mass or less, and even more preferably 3% by mass or less. From the same viewpoint, the content of the component B in the cleaning composition at the time of use is preferably 0.5% by mass or more and 8% by mass or less, more preferably 1% by mass or more and 5% by mass or less, and even more preferably 1.6% by mass or more and 3% by mass or less. When the component B is a combination of two or more types, the content of the component B is the total content of the two or more types.

[0022] The mass ratio A/B of the component A to the component B (the content of the component A/the content of the component B) in the cleaning composition of the present

disclosure is 8 or less, preferably 6 or less, and more preferably 5 or less from the viewpoint of improving the resin mask removal capability. From the same viewpoint, the mass ratio A/B is 2 or more, may be 3 or more, or may be 4 or more. From the same viewpoint, the mass ratio A/B is preferably 1 or more and 8 or less, more preferably 1.5 or more and 6 or less, and even more preferably 2 or more and 5 or less.

[0023] In the present disclosure, the total content of the component A and the component B in the cleaning composition at the time of use is preferably 5% by mass or more, more preferably 8% by mass or more, and even more preferably 10% by mass or more from the viewpoint of improving the resin mask removal capability. From the same viewpoint, the total content of the component A and the component B in the cleaning composition at the time of use is preferably 24% by mass or less, more preferably 20% by mass or less, and even more preferably 17% by mass or less. More specifically, the total content of the component A and the component B in the cleaning composition at the time of use is preferably 5% by mass or more and 24% by mass or less, more preferably 8% by mass or more and 20% by mass or less, and even more preferably 10% by mass or more and 17% by mass or less.

[0024] [Component C: organic solvent]

The cleaning composition of the present disclosure contains the organic solvent (also referred to as a “component C” in the following) with a Hansen solubility parameter, SP value, of 18 to 33 MPa^{1/2}, excluding the component A and the component B. The component C may be one type or a combination of two or more types (i.e., a mixed organic solvent).

[0025] The SP value of the component C is 18 to 33 MPa^{1/2}, preferably 20 to 31.5 MPa^{1/2}, and more preferably 22 to 30 MPa^{1/2} from the viewpoint of improving the resin mask removal capability. In the present disclosure, the Hansen solubility parameter, SP value, is a value described in *Polymer Handbook*, 4th ed., Wiley Interscience, “Solubility Parameter Values,” VII/675-714.

When the component C is a mixed organic solvent of two or more types, the SP value of the component C can be determined by the weighted average of their blending amounts. The above range of the SP value also applies to the mixed organic solvent.

[0026] The component C may be at least one selected from the group consisting of a sulfur-containing compound and a nitrogen-containing compound.

The sulfur-containing compound may be, e.g., a compound containing a sulfur atom and having a molecular weight of 200 or less. Examples of the sulfur-containing compound include dimethyl sulfoxide and sulfolane.

The nitrogen-containing compound may be, e.g., a compound containing a nitrogen atom and having a molecular weight of 200 or less. Examples of the nitrogen-containing compound include: amides, e.g., formamide, N-methylformamide, N-ethylformamide, N,N-dimethylformamide, N,N-diethylformamide, acetamide, N-methylacetamide, N-ethylacetamide, N,N-dimethylacetamide, and N,N-diethylacetamide; pyrrolidones, e.g., N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, N-propyl-2-pyrrolidone, and N-butyl-2-pyrrolidone; and dimethylimidazolidinone.

[0027] From the viewpoint of improving the resin mask removal capability, the component C is at least one selected from the group consisting of a sulfur-containing compound and a nitrogen-containing compound, preferably a mixed organic solvent containing a sulfur-containing compound and a nitrogen-containing compound, more preferably a mixed organic solvent consisting of a sulfur-containing compound and a nitrogen-containing compound, and even more preferably has a configuration in which the sulfur-containing compound is dimethyl sulfoxide and the nitrogen-containing compound is N-methyl-2-pyrrolidone. When the component C is the mixed organic solvent containing dimethyl sulfoxide and N-methyl-2-pyrrolidone or the mixed organic solvent consisting of dimethyl sulfoxide and N-methyl-2-pyrrolidone, the content of dimethyl sulfoxide in the cleaning composition of the present disclosure is preferably 75% by mass or less, more preferably 70% by mass or less, and even more preferably 67% by mass or less from the viewpoint of improving the resin mask removal capability.

[0028] In the present disclosure, the content of the component C in the cleaning composition at the time of use is preferably 60% by mass or more, more preferably 70% by mass or more, and even more preferably 80% by mass or more from the viewpoint of improving the resin mask removal capability. From the same viewpoint, the content of the component C in the cleaning composition at the time of use is preferably 99.5% by mass or less, more preferably 95% by mass or less, and even more preferably 90% by mass or less. From the same viewpoint, the content of the component C in the cleaning composition at the time of use is preferably 60% by mass or more and 99.5% by mass or less, more preferably 70% by mass or more and 95% by mass or less, and even more preferably 80% by mass or more and 90% by mass or less. When the

component C is a combination of two or more types, the content of the component C is the total content of the two or more types.

[0029] The mass ratio A/C of the component A to the component C (the content of the component A/the content of the component C) in the cleaning composition of the present disclosure is preferably 0.01 or more, more preferably 0.05 or more, and even more preferably 0.1 or more from the viewpoint of improving the resin mask removal capability. From the same viewpoint, the mass ratio A/C is preferably 1 or less, more preferably 0.5 or less, even more preferably 0.25 or less, and still more preferably 0.2 or less. More specifically, the mass ratio A/C is preferably 0.01 or more and 1 or less, more preferably 0.05 or more and 0.5 or less, even more preferably 0.1 or more and 0.25 or less, and still more preferably 0.1 or more and 0.2 or less.

[0030] The mass ratio C/B of the component C to the component B (the content of the component C/the content of the component B) in the cleaning composition of the present disclosure is preferably 15 or more, more preferably 20 or more, even more preferably 30 or more, and still more preferably 40 or more from the viewpoint of improving the resin mask removal capability. From the same viewpoint, the mass ratio C/B is preferably 100 or less, more preferably 80 or less, even more preferably 60 or less, and still more preferably 50 or less. More specifically, from the same viewpoint, the mass ratio C/B is preferably 15 or more and 100 or less, more preferably 20 or more and 80 or less, even more preferably 30 or more and 60 or less, and still more preferably 40 or more and 50 or less.

[0031] In the present disclosure, the total content of the component A and the component C in the cleaning composition at the time of use is preferably 90% by mass or more, more preferably 93% by mass or more, and even more preferably 96% by mass or more from the viewpoint of improving the resin mask removal capability. From the same viewpoint, the total content of the component A and the component C in the cleaning composition at the time of use is preferably 99.5% by mass or less, more preferably 99% by mass or less, and even more preferably 98% by mass or less. From the same viewpoint, the total content of the component A and the component C in the cleaning composition at the time of use is preferably 90% by mass or more and 99.5% by mass or less, more preferably 93% by mass or more and 99% by mass or less, and even more preferably 96% by mass or more and 98% by mass or less. The cleaning composition of the present disclosure contains the component A and the component C so that the total content of them falls within the predetermined range, and thus is deemed to be able to increase the solubility of the resin mask (resist) and reduce corrosiveness of the substrate members.

[0032] In the present disclosure, the total content of the component A, the component B, and the component C in the cleaning composition at the time of use is preferably 93% by mass or more, more preferably 95% by mass or more, even more preferably 98% by mass or more, still more preferably 99% by mass or more, yet more preferably 99.5% by mass or more, and much more preferably 100% by mass from the viewpoint of improving the resin mask removal capability.

[0033] [Saccharides (component D)]

In one or more embodiments, the cleaning composition of the present disclosure may further contain saccharides (also referred to as a “component D” in the following) from the viewpoint of preventing corrosion of metal wiring and semiconductors. The component D may be one type or a combination of two or more types.

Examples of the component D include: monosaccharides, e.g., D-xylose, D-glucose, L-idose, and D-fructose; disaccharides, e.g., sucrose; trisaccharides, e.g., raffinose; tetrasaccharides, e.g., stachyose; linear sugar alcohols, e.g., erythritol, xylitol, dulcitol, ribitol, D-sorbitol, D-mannitol, and L-iditol; and cyclic sugar alcohols, e.g., cyclitol, myo-inositol, and quercitol.

[0034] The molecular weight of the component D is preferably 35 or more, more preferably 70 or more, and even more preferably 150 or more from the viewpoint of reducing corrosiveness of the substrate members. From the same viewpoint, the molecular weight of the component D is preferably 700 or less, more preferably 350 or less, and even more preferably 185 or less. From the same viewpoint, the molecular weight of the component D is preferably 35 or more and 700 or less, more preferably 70 or more and 350 or less, and even more preferably 150 or more and 185 or less.

[0035] When the cleaning composition of the present disclosure contains the component D, the content of the component D in the cleaning composition at the time of use is preferably 0.01% by mass or more, more preferably 0.1% by mass or more, and even more preferably 0.5% by mass or more from the viewpoint of improving the resin mask removal capability and preventing corrosion. From the same viewpoint, the content of the component D in the cleaning composition at the time of use is preferably 3% by mass or less, more preferably 2.8% by mass or less, and even more preferably 2.5% by mass or less. More specifically, the content of the component D in the cleaning composition at the time of use is preferably 0.01% by mass or more and 3% by mass or less, more preferably 0.1% by mass or more and 2.8% by mass or less, and even more preferably 0.5% by mass or more and 2.5% by mass or less. When the component D

is a combination of two or more types, the content of the component D is the total content of the two or more types.

[0036] [Component E: water]

In one or more embodiments, the cleaning composition of the present disclosure may further contain water (also referred to as a "component E" in the following). Alternatively, in one or more embodiments, the cleaning composition of the present disclosure may not contain water. Since semiconductors, particularly compound semiconductors such as GaAs, are susceptible to corrosion in the stripping process, it is preferable that the cleaning composition of the present disclosure does not contain water (component). In one or more embodiments, examples of the component E include ion-exchanged water, RO water, distilled water, pure water, and ultrapure water.

[0037] When the cleaning composition of the present disclosure contains the component E, the content of the component E in the cleaning composition may be the remainder obtained by subtracting the component A, the component B, the component C, and optional components (the component D and other components as will be described later) from the amount of the cleaning composition.

In the present disclosure, the content of the component E in the cleaning composition at the time of use is preferably 5% by mass or less, more preferably 3% by mass or less, even more preferably 1% by mass or less, and still more preferably 0% by mass (i.e., the component E is not contained) from the viewpoint of improving the resin mask removal capability and preventing corrosion.

[0038] [Other components]

In one or more embodiments, the cleaning composition of the present disclosure may further contain other components, as appropriate, to the extent that they do not interfere with the effects of the present disclosure. The other components include, e.g., any components that would be used for usual cleaning agents. Specifically, examples of the other components include alcohols other than the component A, alkali agents other than the component B, amines other than the component B, organic solvents other than the component C, surfactants, chelating agents, thickening agents, dispersing agents, rust inhibitors, polymer compounds, solubilizers, antioxidants, preservatives, antifoaming agents, and antibacterial agents.

[0039] [Production method of cleaning composition]

In one or more embodiments, the cleaning composition of the present disclosure can be produced by blending the component A, the component B, and the component C, and the optional components (the component D, the component E, and the other components) as needed, with a known method. For example, the cleaning composition of the present disclosure can be produced by blending at least the component A, the component B, and the component C. Thus, the present disclosure relates to a method for producing a cleaning composition that includes blending at least the component A, the component B, and the component C. In the present disclosure, the term “blend” may include mixing the component A, the component B, and the component C, and the optional components (the component D, the component E, and the other components) as needed, simultaneously or in any order. The preferred blending amount of each component for the production method of the cleaning composition of the present disclosure may be the same as the preferred content of each component in the cleaning composition, as described above.

[0040] The cleaning composition of the present disclosure may be in a form that can be directly used for cleaning, or may be prepared as a concentrate unless the storage stability is not impaired by, e.g., separation or precipitation. The concentrate of the cleaning composition may be diluted so that the content of each component in the cleaning composition falls within the above range at the time of use (i.e., at the time of cleaning).

[0041] The pH of the cleaning composition of the present disclosure is preferably 8 or more and 14 or less, more preferably 9 or more and 14 or less, and even more preferably 10 or more and 14 or less from the viewpoint of improving the resin mask removal capability.

[0042] [Object to be cleaned]

In one or more embodiments, the cleaning composition of the present disclosure may be used to clean an object to be cleaned (i.e., a workpiece), to which the resin mask is attached.

In one or more embodiments, the object to be cleaned, to which the resin mask is attached, may be, e.g., a semiconductor substrate having metal wiring and a resin mask, a semiconductor substrate having an insulating film and a resin mask, or a semiconductor substrate having metal wiring, an insulating film, and a resin mask.

The semiconductor substrate may be made of, e.g., elemental semiconductors such as Si and Ge, compound semiconductors such as GaAs, InP, and CdS, or mixed crystal semiconductors such as InGaAs and HgCdTe.

In one or more embodiments, the metal wiring may be formed by, e.g., plating, CVD, or PVD. The metal wiring may be, e.g., gold, aluminum, copper, tungsten, titanium, tantalum, or chromium wiring. Among these, gold wiring and aluminum wiring are preferred. The metal wiring may be either an alloy of different metals or a pure metal, and may have any shape.

The insulating film may be, e.g., a silicon nitride (Si_3N_4) film. In one or more embodiments, the insulating film is an interlayer insulating film.

[0043] Examples of the object to be cleaned include electronic components and intermediates for manufacturing the electronic components. The electronic components may include, e.g., at least one component selected from the group consisting of a printed circuit board, a wafer, and metal plates such as a copper plate and an aluminum plate. The intermediates may be intermediate products during the manufacturing process of the electronic components and may include intermediate products after the resin mask treatment.

[0044] Specifically, the object to be cleaned, to which the resin mask is attached, may be, e.g., an electronic component obtained by forming wiring, connection terminals, etc. on the substrate surface through at least one process of soldering or plating (e.g., copper plating, aluminum plating, nickel plating, or tin plating) using a resin mask. In the present disclosure, soldering means that solder is applied to a portion of the substrate without the resin mask, and then heated to form a solder bump. In the present disclosure, plating means that at least one plating selected from the group consisting of copper plating, aluminum plating, nickel plating, and tin plating is applied to a portion of the substrate without the resin mask. In this case, the portion of the substrate without the resin mask indicates a portion of a resist pattern (patterned resin mask) where the resin mask has been removed during the formation of the resist pattern by developing the resin mask laminated on the substrate. Thus, in one aspect, the present disclosure relates to use of the cleaning composition of the present disclosure as a cleaning agent in the manufacture of electronic components.

[0045] In one or more embodiments, the substrate having the resist pattern (patterned resin mask), which is formed by developing the resin mask laminated on the substrate, is subjected to at least one process of soldering or plating, and the resulting substrate can be the object to be cleaned. For example, the object to be cleaned may be a substrate having a portion with the resin mask that forms the cured resist layer, and a portion without the resin mask in which the solder bump or plated layer is formed.

[0046] In one or more embodiments, from the viewpoint of a cleaning effect, the cleaning composition of the present disclosure can be suitably used to clean the object to be cleaned, to which a resin mask or a plated and/or heated resin mask is attached. The resin mask may be either a negative resin mask or a positive resin mask. In the present disclosure, the negative resin mask is formed by using a negative resist and may be, e.g., an exposed and/or developed negative resist layer. In the present disclosure, the positive resin mask is formed by using a positive resist and may be, e.g., an exposed and/or developed positive resist layer.

[0047] [Cleaning method]

In one aspect, the present disclosure relates to a cleaning method (also referred to as a “cleaning method of the present disclosure” in the following) that includes stripping a resin mask from an object to be cleaned, to which the resin mask is attached, by using the cleaning composition of the present disclosure (also simply referred to as a “stripping process” in the following). Examples of the object to be cleaned may be those as described above. In one or more embodiments, the stripping process includes bringing the object to be cleaned into contact with the cleaning composition of the present disclosure. The cleaning method of the present disclosure can improve the resin mask removal (stripping) capability.

[0048] Stripping the resin mask from the object to be cleaned by using the cleaning composition of the present disclosure or bringing the object to be cleaned into contact with the cleaning composition of the present disclosure may be performed in the following manner. For example, the object to be cleaned may be immersed in the cleaning composition placed in a cleaning bath, or the cleaning composition may be sprayed onto the object to be cleaned (i.e., a shower method). Alternatively, the object to be cleaned may be irradiated with ultrasonic waves while it is being immersed in the cleaning composition (i.e., an ultrasonic cleaning method). The cleaning composition of the present disclosure can be used for cleaning directly without dilution. Examples of the object to be cleaned may be those as described above.

In one or more embodiments, the cleaning method of the present disclosure may be used in, e.g., a batch type, shower type, or single-wafer type stripping apparatus (cleaning apparatus).

[0049] In one or more embodiments, the cleaning method of the present disclosure may include rinsing the object to be cleaned with water after the object has been in contact with the cleaning composition, and drying the rinsed object. In one or more embodiments, the cleaning

method of the present disclosure may include rinsing the object to be cleaned with water after the object has been in contact with the cleaning composition.

[0050] The cleaning method of the present disclosure preferably includes irradiating the object to be cleaned with ultrasonic waves when the object comes into contact with the cleaning composition of the present disclosure, and more preferably uses the ultrasonic waves of relatively high frequencies, since this can help to enhance the cleaning power of the cleaning composition. The ultrasonic irradiation is, e.g., preferably 26 to 72 kHz and 80 to 1500 W, and more preferably 36 to 72 kHz and 80 to 1500 W for the same reason as described above.

[0051] In the cleaning method of the present disclosure, the temperature of the cleaning composition is preferably 40°C or more, and more preferably 50°C or more, since this can help to enhance the cleaning power of the cleaning composition. Furthermore, the temperature of the cleaning composition is preferably 70°C or less, more preferably less than 70°C, even more preferably 65°C or less, and still more preferably 60°C or less from the viewpoint of reducing the effect on the substrate.

[0052] [Production method of semiconductor device]

In one or more embodiments, the present disclosure relates to a method for producing a semiconductor device (also referred to as a “production method of a semiconductor device of the present invention in the following) that includes stripping a resin mask from an object to be cleaned, to which the resin mask is attached, by using the cleaning composition or cleaning method of the present disclosure (i.e., a stripping process). Examples of the object to be cleaned may be those as described above. The production method of a semiconductor device of the present disclosure can produce high-quality semiconductor device circuits, particularly compound semiconductor device circuits.

In one or more embodiments, the production method of a semiconductor device of the present disclosure includes the following processes (1) to (4). Any known apparatuses, techniques, etc. may be used in each of the processes (1) to (4).

(1) Lithography process including applying a resist to the surface (front side) of a semiconductor substrate on which metal wiring and an interlayer insulating film are formed, patterning, exposure, and development

(2) Etching process including shaping the semiconductor substrate, the metal wiring, and a thin film of the interlayer insulating film

(3) Ion implantation process

(4) Resist stripping process

In one or more embodiments, the cleaning composition and cleaning method of the present disclosure are preferably used in the lithography process (1) and/or the resist stripping process (4). Consequently, the resist applied to a semiconductor substrate, particularly a compound semiconductor substrate, the resist remaining after dry etching, or resist residues remaining after dry etching and ashing can be easily stripped at a low temperature in a short time.

In one or more embodiments, the cleaning composition and cleaning method of the present disclosure may be used for a lift-off process in the manufacturing process of compound semiconductor devices.

[0053] [Production method of electronic component]

In one aspect, the present disclosure relates to a method for producing an electronic component (also referred to as a “production method of an electronic component of the present invention” in the following) that includes stripping a resin mask from an object to be cleaned, to which the resin mask is attached, by using the cleaning composition or cleaning method of the present disclosure (i.e., a stripping process). Examples of the object to be cleaned may be those as described above.

In one or more embodiments, the production method of an electronic component of the present disclosure may include, before the cleaning process, subjecting at least one electronic component selected from the group consisting of a printed circuit board, a wafer, and a metal plate to at least one process of soldering or plating using a resin mask.

The production method of an electronic component of the present disclosure uses the cleaning method of the present disclosure for cleaning, and thus can improve the resin mask removal (stripping) capability and produce highly reliable electronic components. Moreover, the use of the cleaning method of the present disclosure facilitates the removal of the resin mask adhering to electronic components, thereby reducing the cleaning time and improving the production efficiency of electronic components.

[0054] [Kit]

In one or more embodiments, a kit of the present disclosure is used to produce the cleaning composition of the present disclosure. The kit of the present disclosure provides a cleaning composition that can improve the resin mask removal capability.

In one embodiment, the kit of the present disclosure may be, e.g., a kit (two-part cleaning composition) that includes a solution (first solution) containing the component A and a solution (second solution) containing the component B and the component C so that the two solutions are not mixed with each other. The first solution and the second solution are mixed at the time of use. Each of the first solution and the second solution may contain the above optional components as needed.

[0055] In one or more embodiments, the present disclosure further relates to the following cleaning composition for stripping a resin mask, cleaning method, and production method of a semiconductor device.

<1> A cleaning composition for stripping a resin mask, containing:

a polyhydric alcohol (component A);

amines (component B); and

an organic solvent (component C) with a Hansen solubility parameter, SP value, of 18 to 33 MPa^{1/2}, excluding the component A and the component B,

wherein a mass ratio A/B of the component A to the component B is 2 or more and 8 or less, and

the component C is at least one selected from the group consisting of a sulfur-containing compound and a nitrogen-containing compound.

<2> The cleaning composition according to <1>, wherein the mass ratio of the component A to the component B is 1.5 or more and 6 or less.

<3> The cleaning composition according to <1> or <2>, wherein the component A is at least one selected from the group consisting of ethylene glycol and diethylene glycol.

<4> The cleaning composition according to any one of <1> to <3>, wherein the component B is an alkanolamine.

<5> The cleaning composition according to any one of <1> to <4>, wherein the component B is at least one selected from the group consisting of monoethanolamine and N-methylmonoethanolamine.

<6> The cleaning composition according to any one of <1> to <5>, wherein the component C is at least one selected from the group consisting of dimethyl sulfoxide and N-methyl-2-pyrrolidone.

<7> The cleaning composition according to any one of <1> to <6>, wherein the component C is substantially a mixed organic solvent consisting of a sulfur-containing compound and a nitrogen-containing compound.

<8> The cleaning composition according to any one of <1> to <7>, wherein the component C substantially consists of dimethyl sulfoxide and N-methyl-2-pyrrolidone.

<9> The cleaning composition according to any one of <1> to <8>, wherein a content of the component A is 4% by mass or more and 16% by mass or less.

<10> The cleaning composition according to any one of <1> to <9>, wherein a content of the component B is 0.5% by mass or more and 8% by mass or less.

<11> The cleaning composition according to any one of <1> to <10>, wherein a total content of the component A and the component C is 90% by mass or more and 99.5% by mass or less.

<12> The cleaning composition according to any one of <1> to <11>, further containing saccharides (component D),

wherein a content of the component D is 0.01% by mass or more and 3% by mass or less.

<13> The cleaning composition according to <12>, wherein a molecular weight of the component D is 35 or more and 700 or less.

<14> The cleaning composition according to any one of <1> to <13>, wherein a content of water (component E) is 3% by mass or less.

<15> A cleaning method including:

stripping a resin mask from an object to be cleaned, to which the resin mask is attached, by using the cleaning composition according to any one of <1> to <14>.

<16> A method for producing a semiconductor device, including:

stripping a resin mask from an object to be cleaned, to which the resin mask is attached, by using the cleaning composition according to any one of <1> to <14>.

<17> A method for producing a semiconductor device, including:

stripping a resin mask from an object to be cleaned, to which the resin mask is attached, by using the cleaning method according to <15>.

Examples

[0056] Hereinafter, the present disclosure will be described in detail by way of examples.

However, the present disclosure is not limited to the following examples.

[0057] 1. Preparation of cleaning compositions in Examples 1 to 9 and Comparative Examples 1 to 2

Cleaning compositions in Examples 1 to 9 and Comparative Examples 1 to 2 were each prepared by blending the components in their respective amounts (% by mass, active part) as shown in Tables 1 to 2, and stirring and mixing them together.

[0058] The following components were used in the preparation of the cleaning compositions in Examples 1 to 9 and Comparative Examples 1 to 2.

(Component A)

Diethylene glycol (manufactured by FUJIFILM Wako Pure Chemical Corporation)

Ethylene glycol (manufactured by FUJIFILM Wako Pure Chemical Corporation)

(Component B)

Monoethanolamine (manufactured by NIPPON SHOKUBAI CO., LTD.)

N-methylethanolamine (amino alcohol MMA, manufactured by NIPPON NYUKAZAI CO., LTD.)

(Component C)

Dimethyl sulfoxide (manufactured by FUJIFILM Wako Pure Chemical Corporation)

N-methyl-2-pyrrolidone (manufactured by FUJIFILM Wako Pure Chemical Corporation)

(Component D)

Sorbitol (D-sorbitol, manufactured by FUJIFILM Wako Pure Chemical Corporation)

(Component E)

Water (pure water of 1 μ S/cm or less, produced with a water purification system G-10DSTSET manufactured by ORGANO CORPORATION)

[0059] 2. Evaluation of cleaning compositions

The cleaning compositions in Examples 1 to 9 and Comparative Examples 1 to 2 were evaluated as follows.

[0060] [Test piece for evaluating stripping capability]

An insulating film (Si_3N_4) with a height of 90 nm and a width of 10 μm was formed in stripes spaced 350 μm apart on a GaAs substrate (compound semiconductor substrate).

Thereafter, a negative resist (polyhydroxystyrene resin) was applied to the entire surface of the

substrate to have a dry film thickness of 3 μm , exposed to an i-line spectrum with a wavelength of 365 nm, and then post-baked at 130°C for 5 minutes. Subsequently, the substrate was treated with CF_4 gas, i.e., a reactive ion etching gas to prepare a test piece.

[0061] [Evaluation of stripping capability]

The test piece was immersed in each of the cleaning compositions prepared in Examples 1 to 9 and Comparative Examples 1 to 2 at 60°C for 30 minutes. Next, the test piece was immersed in water at room temperature for 1 minute while it was being rocked. This rinsing process was repeated twice, followed by blow drying with nitrogen gas. Then, the appearance of the test piece was observed with a field emission scanning electron microscope at a magnification of 5000X and 50000X. Based on the presence or absence of resist residues on the insulating film (Si_3N_4) and the GaAs substrate, and the state of the resist thus stripped, the stripping capability was evaluated in accordance with the following evaluation criteria. Tables 1 and 2 show the results.

<Evaluation criteria>

3: No resist residue was found on the substrate, and the stripped resist was dissolved in the cleaning composition.

2: No resist residue was found on the substrate, but the stripped resist was suspended in the cleaning composition.

1: A resist residue was found on the substrate.

The evaluation results confirmed that the resist residues on the substrate and the stripped resist were as follows.

Example 1: No resist residue was present on the substrate, but the stripped resist was suspended in the cleaning composition.

Example 2: No resist residue was present on the substrate, and the stripped resist was dissolved in the cleaning composition.

Example 3: No resist residue was present on the substrate, and part of the resist was stripped and suspended in the cleaning composition, which was then finally dissolved.

Examples 4 to 9: No resist residue was present on the substrate, and the stripped resist was dissolved in the cleaning composition.

Comparative Examples 1 and 2: A resist residue was present on the substrate.

[0062] [Evaluation of GaAs etchability]

An insulating film (Si_3N_4) with a height of 90 nm and a width of 10 μm was formed in stripes spaced 350 μm apart on a GaAs substrate, and the etching amount of GaAs was determined through the following procedure (1) to (4). The GaAs etchability was evaluated in accordance with the following evaluation criteria. Table 2 shows the results.

(1) The initial step height 1 (the thickness of the insulating film) was measured with an atomic force microscope.

(2) The substrate was immersed in the cleaning composition (Examples 5 to 7) at 70°C for 13 hours.

(3) The step height 2 after immersion (the total thickness of the insulating film and the etched portion) was measured with an atomic force microscope.

(4) The etching amount was calculated using the following formula.

Etching amount = (step height 2) – (step height 1)

<Evaluation criteria>

A: The etching amount was less than 10 nm.

B: The etching amount was 10 nm or more and less than 50 nm.

C: The etching amount was 50 nm or more.

[0063] [TABLE 1]

Table 1		Example							Comparative Example	
		1	2	3	4	5	8	9	1	2
Component A	diethylene glycol	10	10	10			9	4	10	2.5
	ethylene glycol				10	10				
Component B	monoethanolamine	1.5	2	5	2		2	1	1	2.5
	N-methylethanolamine					2				
Component C	dimethyl sulfoxide	68.5	68	65	68	68	69	75	69	75
	N-methyl-2-pyrrolidone	20	20	20	20	20	20	20	20	20
Total (% by mass)		100	100	100	100	100	100	100	100	100
Total amount of component A and component C (% by mass)		98.5	98.0	95.0	98.0	98.0	98.0	97.5	99.0	97.5
Mass ratio A/B (alcohol/amine)		6.7	5.0	2.0	5.0	5.0	4.5	5.0	10.0	1.0
Stripping capability (60°C, 30 min)		2	3	3	3	3	3	3	1	1

[0064] [TABLE 2]

Table 2		Example		
		5	6	7
Component A	ethylene glycol	10	10	10
Component B	N-methylethanolamine	2	2	2
Component C	dimethyl sulfoxide	68	67	63
	N-methyl-2-pyrrolidone	20	20	20
Component D	sorbitol	0	1	0
Component E	water	0	0	5
Total (% by mass)		100	100	100
Total amount of component A and component C (% by mass)		98.0	97.0	93.0
Mass ratio A/B (alcohol/amine)		5.0	5.0	5.0
Stripping capability (60°C, 30 min)		3	3	3
GaAs low etchability		B	A	C
GaAs low etchability (etching amount, nm)		43	4	92

[0065]

The results shown in Table 1 revealed that the cleaning compositions in Examples 1 to 5 and 8 to 9, having a mass ratio A/B of 2 or more and 8 or less, were superior in the ability to remove (strip) the resin mask of the negative resist at an immersion temperature of 60°C to the cleaning composition in Comparative Example 1, having a mass ratio A/B of more than 8, and the cleaning composition in Comparative Example 2, having a mass ratio A/B of 1.0.

The results shown in Table 2 revealed that the cleaning composition in Example 6, containing sorbitol (component D, saccharides), was superior in the effect of preventing corrosion of GaAs to the cleaning compositions in Examples 5 and 7, containing no saccharides (component D). Moreover, the cleaning composition in Example 7, containing water (component E), was inferior in the effect of preventing corrosion of GaAs to the cleaning compositions in Examples 5 and 6, containing no water (component E).

Industrial Applicability

[0066] The present disclosure provides a cleaning composition that can improve the resin mask removal capability. The cleaning composition of the present disclosure enables high performance and high reliability of semiconductor devices produced, resulting in high productivity of semiconductor apparatuses.

CLAIMS

- [Claim 1] A cleaning composition for stripping a resin mask, comprising:
a polyhydric alcohol (component A);
amines (component B); and
an organic solvent (component C) with a Hansen solubility parameter, SP value, of 18 to 33 MPa^{1/2}, excluding the component A and the component B,
wherein a mass ratio A/B of the component A to the component B is 2 or more and 8 or less, and
the component C is at least one selected from the group consisting of a sulfur-containing compound and a nitrogen-containing compound.
- [Claim 2] The cleaning composition according to claim 1, wherein the component A is at least one selected from the group consisting of ethylene glycol and diethylene glycol.
- [Claim 3] The cleaning composition according to claim 1 or 2, wherein the component B is an alkanolamine.
- [Claim 4] The cleaning composition according to any one of claims 1 to 3, wherein the component B is at least one selected from the group consisting of monoethanolamine and N-methylmonoethanolamine.
- [Claim 5] The cleaning composition according to any one of claims 1 to 4, wherein the component C is a mixed organic solvent consisting of a sulfur-containing compound and a nitrogen-containing compound.
- [Claim 6] The cleaning composition according to any one of claims 1 to 5, wherein a content of the component A is 4% by mass or more and 16% by mass or less.
- [Claim 7] The cleaning composition according to any one of claims 1 to 6, wherein a content of the component B is 0.5% by mass or more and 8% by mass or less.

[Claim 8] The cleaning composition according to any one of claims 1 to 7, wherein a total content of the component A and the component C is 90% by mass or more and 99.5% by mass or less.

[Claim 9] The cleaning composition according to any one of claims 1 to 8, further comprising saccharides (component D),

wherein a content of the component D is 0.01% by mass or more and 3% by mass or less.

[Claim 10] The cleaning composition according to claim 9, wherein a molecular weight of the component D is 35 or more and 700 or less.

[Claim 11] The cleaning composition according to any one of claims 1 to 10, wherein a content of water (component E) is 3% by mass or less.

[Claim 12] A cleaning method comprising:

stripping a resin mask from an object to be cleaned, to which the resin mask is attached, by using the cleaning composition according to any one of claims 1 to 11.

[Claim 13] A method for producing a semiconductor device, comprising:

stripping a resin mask from an object to be cleaned, to which the resin mask is attached, by using the cleaning composition according to any one of claims 1 to 11.

[Claim 14] A method for producing a semiconductor device, comprising:

stripping a resin mask from an object to be cleaned, to which the resin mask is attached, by using the cleaning method according to claim 12.