

DESCRIPTION

TITLE OF THE INVENTION

CHEMICAL SOLUTION, METHOD OF REGENERATING FILM-FORMED
5 SUBSTRATE, METHOD OF MANUFACTURING FILM-FORMED
SUBSTRATE, AND METHOD OF MANUFACTURING REFLECTIVE MASK
BLANK

FIELD OF THE INVENTION

10 [0001] The present invention relates to a chemical
solution, a method of regenerating a film-formed
substrate, a method of manufacturing a film-formed
substrate, and a method of manufacturing a reflective
mask blank.

15

BACKGROUND OF THE INVENTION

[0002] In recent years, with miniaturization of
semiconductor devices, EUV lithography (EUVL), which is
an exposure technique using Extreme Ultra-Violet (EUV)
20 rays, has been developed. EUV rays includes soft X-
rays and vacuum ultraviolet rays, and particularly
refers to rays having wavelengths of approximately 0.2
nm to 100 nm. At the present time, EUV rays having
wavelengths of approximately 13.5 nm is mainly studied.

25 [0003] In EUVL, an opening pattern of a reflective
mask is transferred to a semiconductor substrate. The
reflective mask is obtained by forming an opening
pattern in the absorption film of the reflective mask
blank. The reflective mask blank includes a substrate
30 such as a glass substrate, a multilayer reflective film
formed on the substrate, and an absorption film formed
on the multilayer reflective film.

[0004] In the reflective mask, if there are

irregularities in the vicinity of the opening pattern,
the positional accuracy and contrast of the pattern to
be transferred deteriorate, which becomes a problem.
The irregularities are caused by defects such as
5 scratches and foreign matter.

[0005] Therefore, inspections such as a surface
defect inspection and an in-film defect inspection are
performed on the film-formed substrate for each step so
that irregularities do not exist in the vicinity of the
10 opening pattern. When unacceptable size defects are
found as a result of inspection, the defects are
removed by cleaning or the like. On the other hand,
when there is a defect that cannot be removed even by
cleaning or the like, at least the multilayer
15 reflective film is removed to regenerate the substrate,
or the substrate is discarded as a defective product.

[0006] Patent Document 1 discloses a method of
regenerating a multilayer film-formed substrate in
which a multilayer film having a multilayer reflective
20 film is formed on a substrate. In this regenerating
method, the substrate with the multilayer film is
brought into contact with a chemical solution composed
of an aqueous solution containing hydrogen peroxide and
at least one selected from sodium hydroxide, potassium
25 hydroxide, and ammonia to remove the multilayer film
from the substrate, thereby regenerating the substrate.

RELATED-ART DOCUMENTS

Patent Documents

30 [0007]
[Patent Document 1] Japanese Patent Application Laid-
Open No. 2017-181733

SUMMARY OF THE INVENTION

Problems to be Solved by the Invention

[0008] However, in the method described in Patent Document 1, there is a problem in that the processing
5 time when the film is removed from the substrate of the film-formed substrate is long and the damage of the removed surface of the substrate is still large.

[0009] An object of one embodiment of the present invention is to shorten a processing time when a film
10 is removed from a film-formed substrate. Furthermore, another object of one embodiment of the present invention is to suppress damage to the surface of the substrate from which the film was removed.

15 Means for Solving the Problem

[0010] The present invention is the following [1] to [12].

[0011] [1] A chemical solution used for removing
20 at least a multilayer reflective film containing silicon and molybdenum from a glass substrate of a film-formed substrate in which a film having the multilayer reflective film is formed on one surface of the glass substrate, wherein the chemical solution includes: a pH adjusting agent; and at least one
25 oxidizing agent selected from the group consisting of metaperiodic acid, sodium metaperiodate, orthoperiodic acid, sodium orthoperiodate, permanganic acid, permanganate, and N-methylmorpholine N-oxide.

[0012] [2] The chemical solution according to [1],
30 wherein a pH of the chemical solution is 10 or higher and 16 or lower.

[0013] [3] The chemical solution according to [1], wherein the pH adjusting agent is sodium hydroxide or

potassium hydroxide.

[0014] [4] The chemical solution according to [1], wherein the oxidizing agent is metaperiodic acid, sodium metaperiodate, orthoperiodic acid, or sodium
5 orthoperiodate.

[0015] [5] The chemical solution according to [1], wherein the oxidizing agent is permanganic acid or permanganate.

[0016] [6] The chemical solution according to [1],
10 further includes at least one selected from the group consisting of a metal having an oxidation-reduction potential higher than an oxidation-reduction potential of chromium (VI) and an ion thereof in an amount of 0.0001 molar equivalent to 10 molar equivalent with
15 respect to the oxidizing agent.

[0017] [7] The chemical solution according to [1], further includes an aminocarboxylic acid-based chelating agent, a hydroxy acid-based chelating agent, or a phosphonic acid-based chelating agent as a
20 chelating agent.

[0018] [8] A method of regenerating a film-formed substrate includes: bringing a film-formed substrate having a multilayer reflective film containing silicon and molybdenum formed on one surface of a glass
25 substrate into contact with a chemical solution containing a pH adjusting agent and at least one oxidizing agent selected from the group consisting of metaperiodic acid, sodium metaperiodate, orthoperiodic acid, sodium orthoperiodate, permanganic acid,
30 permanganate, and N-methylmorpholine N-oxide; and removing at least the multilayer reflective film from the glass substrate to regenerate a surface of the glass substrate on which the multilayer reflective film

was formed.

[0019] [9] The method of regenerating a film-formed substrate according to [8], wherein the film-formed substrate has a protective film containing
5 ruthenium on the multilayer reflective film.

[0020] [10] The method of regenerating a film-formed substrate according to [8], wherein the film-formed substrate has an absorption film containing at least one selected from the group consisting of
10 ruthenium, tantalum, niobium, and boron on the multilayer reflective film.

[0021] [11] The method of regenerating a film-formed substrate according to [8], wherein the film-formed substrate has a conductive film containing
15 chromium or tantalum on a surface opposite to a surface on which the multilayer reflective film is formed.

[0022] [12] A method of manufacturing a film-formed substrate includes forming a multilayer reflective film containing at least silicon and
20 molybdenum on one surface of the glass substrate regenerated by the method of regenerating the film-formed substrate according to any one of [8] to [11].

[0023] [13] A method of manufacturing a multilayer reflective film includes: forming the multilayer
25 reflective film containing silicon and molybdenum on one surface of the glass substrate regenerated by the method of regenerating the film-formed substrate of any one of [8] to [11]; forming a protective film containing ruthenium or rhodium on the multilayer
30 reflective film; forming an absorption film containing at least one selected from the group consisting of ruthenium, tantalum, chromium, iridium, boron, niobium, rhenium, and palladium on the protective film; and

forming a conductive film containing at least one selected from the group consisting of chromium, tantalum, and boron on a surface of the glass substrate opposite to the surface on which the multilayer
5 reflective film is formed.

BRIEF DESCRIPTION OF THE DRAWINGS

[0024] FIG. 1 is a flowchart illustrating a method of producing a reflective mask blank according to an
10 embodiment;

FIG. 2 is a cross-sectional view illustrating an example of a substrate;

FIG. 3 is a plan view of the substrate of FIG. 2;

15 FIG. 4 is a cross-sectional view illustrating an example of the reflective mask blank;

FIG. 5 is a cross-sectional view illustrating an example of a reflective mask; and

FIG. 6 is a graph illustrating the results
20 of a reference experiment.

DETAILED DESCRIPTION OF THE INVENTION

[0025] Hereinafter, an embodiment for carrying out the present invention (hereinafter simply referred to
25 as the present embodiment) will be described. In the drawings, positional relationships such as up, down, left, and right are based on the positional relationships illustrated in the drawings unless otherwise specified. The dimensional ratios in the
30 drawings are not limited to the ratios illustrated in the drawings. In addition, in the specification, "to" indicating a numerical range means that numerical values described before and after the "to" are included

as a lower limit value and an upper limit value. The lower limit value and the upper limit value include rounding ranges. Furthermore, "%", "ppm", and "ppb" are intended to represent mass fractions and
5 "equivalent" is intended to represent molar equivalents.

[0026] (Method of Producing Reflective Mask Blank)

As illustrated in FIG. 1, the method of producing a reflective mask blank includes steps S1 to
10 S7. For example, a substrate 2 illustrated in FIGS. 2 and 3 is used for producing the reflective mask blank. The substrate 2 includes a first main surface 21 and a second main surface 22 opposite to the first main surface 21. The first main surface 21 has a
15 rectangular shape. In this specification, a rectangular shape includes a shape in which corners are chamfered. The rectangle includes a square. The second main surface 22 is placed opposite to the first main surface 21. The second main surface 22 is also
20 rectangular shape, as is the first main surface 21.

[0027] The substrate 2 includes four end surfaces 23, four first chamfered surfaces 24, and four second chamfered surfaces 25. The end surface 23 is perpendicular to the first main surface 21 and the
25 second main surface 22. The first chamfered surface 24 is formed at a boundary between the first main surface 21 and the end surface 23. The second chamfered surface 25 is formed at a boundary between the second main surface 22 and the end surface 23. The first
30 chamfered surface 24 and the second chamfered surface 25 are what is known as C-chamfered surfaces in the present embodiment, but may be R-chamfered surfaces.

[0028] The substrate 2 is, for example, a glass

substrate. The glass of the substrate 2 is preferably silica glass containing titanium dioxide (TiO_2). Silica glass has a smaller linear expansion coefficient and a smaller dimensional change due to a temperature change than general soda lime glass. The silica glass may contain 80% to 95% of silica oxide (SiO_2) and 4% to 17% of TiO_2 . When the TiO_2 content is 4% to 17%, the linear expansion coefficient at around room temperature is substantially zero, and a dimensional change at around room temperature hardly occurs. The silica glass may contain a third ingredient or an impurity other than SiO_2 and TiO_2 . As such silica glass, for example, ULE (registered trademark) 7973 series, manufactured by Corning may be used.

[0029] The size of the substrate 2 in plan view is, for example, 152 mm in length and 152 mm in width. The length and width dimensions may be equal to or greater than the 152 mm.

[0030] The substrate 2 has a central region 27 and a peripheral region 28 on the first main surface 21. The central region 27 is a square region having 142 mm in length and 142 mm in width excluding the peripheral region 28 surrounding the central region 27, is a region processed to have a desired flatness by steps S1 to S4, and is a quality-guaranteed region. The quality-guaranteed region may have length and width; dimensions equal to or greater than the 142 mm. The four sides of the central region 27 are parallel to the four end surfaces 23. The center of central region 27 coincides with the center of first main surface 21.

[0031] Although the second main surface 22 of the substrate 2 is not illustrated, the second main surface 22 of the substrate 2 also has a central region and a

peripheral region, similarly to the first main surface 21. In the same manner as the central region of the first main surface 21, the central region of the second main surface 22 is a square region having 142 mm in length and 142 mm in width, is a region processed to have a desired flatness obtained by steps S1 to S4 in FIG. 1, and is a quality-guaranteed region. The quality-guaranteed region may have length and width dimensions equal to or greater than the 142 mm.

10 [0032] First, in the step S1, the first main surface 21 and the second main surface 22 of the substrate 2 are polished. The first main surface 21 and the second main surface 22 are simultaneously polished by a double-side polishing machine (not illustrated) in the present embodiment, but may be sequentially polished by a single-side polishing machine (not illustrated). In the step S1, the substrate 2 is polished while supplying the polishing slurry between a polishing pad and the substrate 2.

20 [0033] As the polishing pad, for example, a urethane-based polishing pad, a nonwoven fabric-based polishing pad, a suede-based polishing pad, or the like is used. The polishing slurry contains a polishing agent and a dispersion medium. The polishing agent is, for example, cerium oxide particles. The dispersion medium is, for example, water or an organic solvent. The first main surface 21 and the second main surface 22 may be polished multiple times with polishing agents of different materials or particle sizes.

30 [0034] The polishing agent used in the step S1 is not limited to ceric oxide particles. For example, the polishing agent used in the step S1 may be silicon oxide particles, aluminum oxide particles, zirconium

oxide particles, titanium dioxide particles, diamond particles, silicon carbide particles, or the like.

[0035] Next, in the step S2, the shapes of the first main surface 21 and the second main surface 22 of the substrate 2 are measured. In the measurement of the surface shape, for example, a non-contact measuring device such as a laser interference type measuring device is used so that the surface is not damaged. The measuring device measures the surface shapes of the central region 27 of the first main surface 21 and the central region of the second main surface 22.

[0036] Next, in the step S3, with reference to the measurement result in the step S2, the first main surface 21 and the second main surface 22 of the substrate 2 are locally processed in order to improve the flatness. The first main surface 21 and the second main surface 22 are locally processed in order. The order is not particularly limited and may be any order. The localized processing method is, for example, a gas cluster ion beam (GCIB) method or a plasma chemical vaporization machining (PCVM) method. The localized processing method may be a polishing method using a magnetic fluid, a polishing method using a rotary polishing tool, a catalyst-based etching method, or the like. If the flatness after the step S1 is sufficient, the localized processing of the step S3 need not be performed.

[0037] Next, in the step S4, the first main surface 21 and the second main surface 22 of the substrate 2 are subjected to final polishing. The first main surface 21 and the second main surface 22 are simultaneously polished by a double-side polishing machine (not illustrated) in the present embodiment,

but may be sequentially polished by a single-side polishing machine (not illustrated). In the step S4, the substrate 2 is polished while supplying a polishing slurry between the polishing pad and the substrate 2.

5 The polishing slurry includes a polishing agent. The polishing agent is, for example, colloidal silica particles.

[0038] Next, in step S5, a conductive film 5 illustrated in FIG. 4 is formed in the central region

10 27 of the first main surface 21 of the substrate 2. The conductive film 5 is used to adsorb a reflective mask to an electrostatic chuck of an exposure device. The conductive film 5 is preferably formed of a metal nitride or a metal boride containing one or more

15 elements selected from the group consisting of chromium (Cr), tantalum (Ta), titanium (Ti), zirconium (Zr), and niobium (Nb). Specific examples of the conductive film 5 include a CrN film, a TaN film, a TaB film, a CrTaN film, a TiN film, and a ZrN film. The conductive film

20 5 may contain at least one selected from the group consisting of chromium, tantalum, and boron.

[0039] Next, in step S6, a multilayer reflective film 3 illustrated in FIG. 4 is formed in the central region of the second main surface 22 of the substrate

25 2. The multilayer reflective film 3 reflects EUV rays. The multilayer reflective film 3 is formed by alternately laminating, for example, high-refractive index layers and low-refractive index layers. The high refractive index layer is formed of, for example,

30 silicon (Si), and the low-refractive index layer is formed of, for example, molybdenum (Mo). As a method of forming the multilayer reflective film 3, for example, a sputtering method such as an ion beam

sputtering method, a magnetron sputtering method, or the like is used.

[0040] Finally, in step S7, an absorption film 4 illustrated in FIG. 4 is formed on the multilayer reflective film 3 formed in the step S6. The absorption film 4 absorbs EUV rays. The absorption film 4 is formed of, for example, a single metal, an alloy, a nitride, an oxide, an oxynitride, or the like containing at least one element selected from Ta, Cr, and palladium (Pd). As a method of forming the absorption film 4, for example, an ion beam sputtering method or a sputtering method is used. The absorption film 4 may contain at least one selected from the group consisting of ruthenium, tantalum, chromium, iridium, boron, niobium, rhenium, and palladium. The absorption film 4 may contain at least one selected from the group consisting of ruthenium, tantalum, niobium, and boron.

[0041] It should be noted that the steps S6 to S7 are performed after the step S5 in the present embodiment, but may be performed before the step S5.

[0042] By the above steps S1 to S7, a reflective mask blank 1 illustrated in FIG. 4 is obtained. The reflective mask blank 1 has a first main surface 11 and a second main surface 12 opposite to the first main surface 11, and has the conductive film 5, the substrate 2, the multilayer reflective film 3, and the absorption film 4 in this order from the first main surface 11 side to the second main surface 12 side.

[0043] Although the reflective mask blank 1 is not illustrated, in the same manner as the substrate 2, the reflective mask blank 1 has a central region and a peripheral region on the first main surface 11. The central region is a square region having 142 mm in

length and 142 mm in width excluding a rectangular frame-shaped peripheral region surrounding the central region, and is a quality-guaranteed region. In the same manner as the substrate 2, the reflective mask blank 1 also has a central region and a peripheral region on the second main surface 12. The central region is a square region having 142 mm in length and 142 mm in width excluding a rectangular frame-shaped peripheral region surrounding the central region, and is a quality-guaranteed region. The quality-guaranteed region may have length and width dimensions equal to or greater than the 142 mm.

[0044] The reflective mask blank 1 may include another film in addition to the conductive film 5, the substrate 2, the multilayer reflective film 3, and the absorption film 4.

[0045] For example, the reflective mask blank 1 may further include a protective film. The protective film is formed between the multilayer reflective film 3 and the absorption film 4. The protective film protects the multilayer reflective film 3 so that the multilayer reflective film 3 is not etched when the absorption film 4 is etched to form an opening pattern 41 in the absorption film 4. The protective film is formed of, for example, ruthenium (Ru), Si, or TiO₂. The protective film may contain ruthenium or rhodium. As a method of forming the protective film, for example, a sputtering method is used.

[0046] The reflective mask blank 1 may further include a low-reflective film. The low-reflective film is formed on the absorption film 4. Thereafter, the opening pattern 41 is formed in both the low-reflective film and the absorption film 4. The low-reflective

film is used for inspection of the opening pattern 41 and has a lower reflection characteristic than the absorption film 4 with respect to inspection light.

The low-reflective film is formed of, for example, tantalum oxynitride (TaON) or tantalum oxide (TaO). As a method of forming the low-reflective film, for example, a sputtering method is used.

[0047] As illustrated in FIG. 5, the reflective mask is obtained by forming the opening pattern 41 in the absorption film 4. The opening pattern 41 is formed by a photolithography method and an etching method. Therefore, a resist film used for forming the opening pattern 41 may be included in the reflective mask blank 1.

[0048] (Method of Regenerating Film-Formed Substrate)

In the reflective mask, if there are irregularities in the vicinity of the opening pattern 41, the positional accuracy and contrast of the pattern to be transferred deteriorate, which becomes a problem. The irregularities are caused by defects such as scratches and foreign matter.

[0049] Therefore, a surface defect inspection is performed on the film-formed substrate for each step so that irregularities do not exist in the vicinity of the opening pattern 41. As a result of the surface defect inspection, when defects of unacceptable size are found, the defects are removed by cleaning. On the other hand, when there is a defect that cannot be removed even by cleaning, at least the multilayer reflective film 3 is removed to regenerate the second main surface 22 of the substrate 2 or the substrate 2 is discarded as a defective product.

[0050] Here, the film-formed substrate means the substrate 2 on which at least the multilayer reflective film 3 is formed, which is obtained after the step S6 in FIG. 1. When the steps S6 to S7 are performed
5 before the step S5, the conductive film 5 need not be formed on the substrate 2. That is, the film-formed substrate is the substrate 2 on which the multilayer reflective film 3 is formed, the substrate 2 on which the multilayer reflective film 3 and the absorption
10 film 4 are formed, the substrate 2 on which the conductive film 5 and the multilayer reflective film 3 are formed, the substrate 2 on which the conductive film 5, the multilayer reflective film 3, and the absorption film 4 are formed (reflective mask blank 1),
15 or the like. The film-formed substrate may include another film in addition to the conductive film 5, the multilayer reflective film 3, and the absorption film 4. For example, the film-formed substrate may include the above-described protective film or low-reflective
20 film. Further, the film-formed substrate may be a reflective mask in which the opening pattern 41 is formed.

[0051] In the present embodiment, in order to remove at least the multilayer reflective film 3 from
25 the substrate 2 of the film-formed substrate and regenerate the second main surface 22 of the substrate 2, the film-formed substrate is brought into contact with a chemical solution. At this time, when the film-formed substrate includes another film on the
30 multilayer reflective film 3, it is necessary to remove the films at the same time. When the film-formed substrate includes the conductive film 5, the conductive film 5 is preferably removed simultaneously

with the multilayer reflective film 3. However, when the conductive film 5 cannot be removed simultaneously, the conductive film 5 may be removed by another method such as using a chemical solution different from the chemical solution according to the present invention.

5 [0052] The method of bringing the film-formed substrate into contact with the chemical solution is not particularly limited, but may be, for example, a method of immersing the film-formed substrate in the chemical solution stored in a treatment tank
10 (hereinafter referred to as an immersion method). Alternatively, a chemical solution may be sprayed onto the surface of the film-formed substrate. Among these methods, the immersion method is more preferable from the viewpoint of productivity and cost. In the case of
15 the immersion method, it is easy to repeatedly use the chemical solution. It is preferable that the chemical solution whose performance has deteriorated is replaced.

20 [0053] The processing time for bringing the film-formed substrate into contact with the chemical solution is preferably as short as possible from the viewpoint of productivity. The processing time is set longer than the time required to remove the multilayer reflective film 3 from the substrate 2 of the film-formed substrate (hereinafter referred to as T_3). If
25 the chemical solution can remove the conductive film 5 together with the multilayer reflective film 3, the processing time is set longer than either T_3 or the time required to remove the conductive film 5
30 (hereinafter referred to as T_5), whichever is longer. The processing time of both T_3 and T_5 are preferably short because the shorter the T_3 and T_5 , the shorter

the processing time.

[0054] The temperature at which the film-formed substrate and the chemical solution are brought into contact with each other is 20°C to 150°C, and
5 preferably 40°C to 100°C. When the temperature is 20°C or higher, the processing time can be sufficiently shortened. When the temperature is 150°C or lower, there is little possibility that the substrate 2 will be excessively damaged by the chemical solution.

10 [0055] The regenerated substrate 2 is subjected to at least the steps S6 to S7 in FIG. 1 again to manufacture the reflective mask blank 1. At this time, depending on the state of the substrate 2, the steps S1 to S5 may be performed as necessary. For example, in
15 the case where the flatness is not sufficient in the substrate 2 from which all the films are removed, the film may be formed after performing local polishing or final polishing in order to obtain a desired flatness.

[0056] When the substrate 2 is regenerated to
20 manufacture the reflective mask blank 1 as described above, if a defect that cannot be removed even by cleaning occurs again, the above operation may be repeated until such a defect does not occur.

[0057] (Chemical Solution)
25 Next, the chemical solution according to the present embodiment will be described in detail.

[0058] The chemical solution contains a solvent and an additive. The additive includes at least a pH adjusting agent and an oxidizing agent, and may further
30 include an optional additive. The optional additive is, for example, a specific metal or a chelating agent.

[0059] The solvent is water or an organic solvent, and water is preferably used. The water is preferably

distilled water, ion-exchanged water, or ultrapure water.

[0060] The pH adjusting agent is an organic base or an inorganic base, preferably an inorganic base.

5 When the pH adjusting agent is an inorganic base, the conductive film 5 can be removed when the film-formed substrate has the conductive film 5 containing Ta. Further examples of the inorganic base include hydroxides of alkali metals or alkaline earth metals.
10 Among them, sodium hydroxide (NaOH), potassium hydroxide (KOH), or rubidium hydroxide (RbOH) is preferable from the viewpoint of basicity and water solubility, NaOH or KOH is more preferable from the viewpoint of cost, and KOH is even more preferable from
15 the viewpoint of shortening the T₅.

[0061] The concentration of the pH adjusting agent is adjusted in such a range that the pH of the chemical solution becomes a desired value. The pH of the chemical solution is 10 to 16, preferably 12 to 15, and
20 more preferably 13 to 15. When the pH is 10 or higher, the T₃ can be sufficiently shortened in the case where the multilayer reflective film 3 contains Si and Mo. Further, when the pH is 16 or lower, in the case where the reflective mask blank 1 has a protective film
25 containing Ru, the protective film can be removed in a sufficiently short time.

[0062] The oxidizing agent is contained at least for the purpose of removing the multilayer reflective film 3. Therefore, the oxidizing agent has a higher
30 oxidation-reduction potential than at least the oxidation-reduction potential of the components constituting the multilayer reflective film 3. For example, when the multilayer reflective film 3 contains

Si and Mo, the standard electrode potential of the oxidizing agent is preferably 0.8 V to 2.0 V, and specific examples thereof include at least one selected from the group consisting of metaperiodic acid (HIO_4),
5 sodium metaperiodate, orthoperiodic acid (H_5IO_6), sodium orthoperiodate, permanganic acid (HMnO_4), permanganate, and N-methylmorpholine N-oxide (abbreviation: NMO).

[0063] Among the above-mentioned oxidizing agents, metaperiodic acid, sodium metaperiodate, orthoperiodic
10 acid, sodium orthoperiodate, permanganic acid, or permanganate is preferable from the viewpoint that the T_3 can be shortened, and metaperiodic acid, sodium metaperiodate, orthoperiodic acid, or sodium
15 orthoperiodate is more preferable from the viewpoint that high activity is exhibited even at a pH 10 to pH 16 and the by-product is water-soluble. In addition, in the case where the film-formed substrate has the conductive film 5 containing Cr, permanganic acid or a
20 permanganate is also preferable from the viewpoint that the conductive film 5 can be removed.

[0064] Further, when the chemical solution contains an oxidizing agent, the T_5 can be shortened in the case where the film-formed substrate has the
25 conductive film 5 containing Ta.

[0065] The concentration of the oxidizing agent is 0.1 ppm to 40%, preferably 0.1% to 10%, and more preferably 0.1% to 2% with respect to the chemical solution. When the concentration of the oxidizing
30 agent is 0.1 ppm or more, the multilayer reflective film 3 can be removed. When the concentration of the oxidizing agent is 40% or less, hardly soluble by-products are less likely to be precipitated.

[0066] The optional additives are, for example, specific metals or chelating agents.

[0067] The specific metal is at least one selected from the group consisting of metals having a higher oxidation-reduction potential than the oxidation-reduction potential of Cr (VI) and ions thereof. Specific examples of such metals include Ru or cerium (Ce). When the chemical solution contains the specific metals, the conductive film 5 can be removed when the film-formed substrate has the conductive film 5 containing Cr. The Ru ion or the Ce ion may be added when the chemical solution is prepared, or may be eluted from the removed film (for example, the protective film containing Ru).

[0068] Hereinafter, a mechanism in which the conductive film 5 containing Cr is removed by the specific metal will be described by taking Ru as an example. The Ru or Ru ion added to the chemical solution is oxidized to Ru (VII) or Ru (VIII) by the oxidizing agent in the chemical solution to be in a RuO_4^- or RuO_4 state. These Ru oxide ions oxidize Cr contained in the conductive film 5 to form water soluble CrO_4^{2-} , whereby the conductive film 5 containing Cr is removed.

[0069] The concentration of the specific metal is 0.0001 equivalent to 10 equivalents, preferably 0.001 equivalent to 1 equivalent, and more preferably 0.01 equivalent to 0.1 equivalent with respect to the oxidizing agent. When the concentration of the specific metal is 0.0001 equivalent or more, the removing of the conductive film 5 containing Cr proceeds sufficiently. When the concentration of the specific metal is 10 equivalents or less, the substrate

damage can be sufficiently suppressed.

[0070] The chelating agent is an aminocarboxylic acid-based chelating agent, a hydroxy acid-based chelating agent, or a phosphonic acid-based chelating agent. Examples of the aminocarboxylic acid-based chelating agent include ethylenediaminetetraacetic acid (abbreviation: EDTA), triethylenetetramine hexaacetic acid (abbreviation: TTHA), nitrilotrismethylenephosphonic acid (abbreviation: NTPO), and N,N-bis(2-hydroxyethyl)glycine (abbreviation: Bicine). Example of hydroxy acid chelating agent includes tartaric acid. Examples of the phosphonic acid-based chelating agent include hydroxyethylidene diphosphonic acid (abbreviation: HEDP) and phosphonoacetic acid. When the chemical solution contains the chelating agent, the processing time can be shortened.

[0071] Among the chelating agents described above, EDTA or phosphonoacetic acid is more preferable from the viewpoint of further shortening the processing time, and TTHA is more preferable from the viewpoint of less damage to the substrate 2.

[0072] The concentration of the chelating agent is 0.01% to 10%, preferably 0.1% to 5%, and more preferably 0.5% to 2% with respect to the chemical solution. When the concentration of the chelating agent is 0.01% or more, the processing time can be significantly reduced. In addition, when the concentration of the chelating agent is 10% or less, there is little possibility that a hardly soluble by-product will be precipitated.

[0073] The above additives are mixed with a solvent to prepare a chemical solution. In this case,

the additive agent is selected such that the additive agent is soluble in the solvent and hardly soluble by-products do not precipitate out. One or more of each type of pH adjusting agent and oxidizing agent are
5 included. The specific metals need not be contained, or one or more specific metals thereof may be contained. The chelating agent need not be contained, or one or more chelating agents may be contained.

10 EXAMPLES

[0074] Next, experimental data will be described with reference to Table 1. In Table 1, experimental examples 1 to 23 are Examples, and experimental examples 24 and 25 are Comparative Examples.

15 [0075]
[Table 1]

Experimental Examples	pH	Additives			Conductive film	Temperature [°C]	Results		
		pH adjusting agent	Oxidizing agent	Additive			T ₃	T ₅	Substrate damage
1	13.5	NaOH (4.0%)	NaIO ₄ (1%)		CrN	55	E	X	◎
2	13.5	KOH (5.6%)	NaIO ₄ (1%)		CrN	55	D	X	◎
3	14.5	KOH (22.4%)	NaIO ₄ (1%)		CrN	45	B	X	◎
4	14.5	KOH (22.4%)	NaIO ₄ (1%)		CrN	79	A	X	○
5	15.5	KOH (44.8%)	NaIO ₄ (1%)		CrN	55	A	X	○
6	14.5	KOH (22.4%)	NaIO ₄ (1%)	RuCl ₃ (0.01 molar equivalent)	CrN	45	B	E	◎
7	14.5	KOH (22.4%)	NaIO ₄ (1%)	RuCl ₃ (0.1 molar equivalent)	CrN	45	C	D	◎
8	14.5	KOH (22.4%)	NaIO ₄ (1%)	Ru powder (10 molar equivalent)	CrN	45	C	D	◎
9	13.5	KOH (5.6%)	NaIO ₄ (1%)	EDTA (0.1%)	CrN	55	B	X	○
10	13.5	KOH (5.6%)	NaIO ₄ (1%)	TTHA (0.1%)	CrN	55	C	X	◎
11	13.5	KOH (5.6%)	NaIO ₄ (1%)	NTPO (0.1%)	CrN	55	C	X	○
12	13.5	KOH (5.6%)	NaIO ₄ (1%)	Bicine (0.1%)	CrN	55	C	X	○
13	13.0	KOH (5.6%)	NaIO ₄ (1%)	tartaric acid (0.1%)	CrN	55	C	X	○
14	13.0	KOH (5.6%)	NaIO ₄ (1%)	phosphonoacetic acid (0.1%)	CrN	55	B	X	○
15	13.5	KOH (11.2%)	H ₅ IO ₆ (1%)		CrN	55	C	X	◎
16	14.0	KOH (22.4%)	H ₅ IO ₆ (1%)		CrN	55	A	X	◎
17	15.0	KOH (44.8%)	H ₅ IO ₆ (1%)		CrN	55	A	X	○
18	13.5	KOH (5.6%)	NaIO ₄ (1%)		Ta based	55	D	B	◎
19	14.5	KOH (22.4%)	NaIO ₄ (1%)		Ta based	55	A	A	◎
20	14.5	KOH (22.4%)	H ₅ IO ₆ (1%)		Ta based	55	A	A	◎
21	14.5	KOH (22.4%)	KMnO ₄ (3%)		CrN	55	B	A	◎
22	14.5	KOH (22.4%)	KMnO ₄ (3%)		CrN	79	A	A	○
23	14.5	KOH (22.4%)	NMO (5%)		CrN	55	E	X	◎
24	13.0	KOH (22.4%)	H ₂ O ₂ (15%)		CrN	55	X	X	—
25	13.0	KOH (22.4%)	H ₂ O ₂ (15%)	EDTA (0.1%)	CrN	55	E	X	○

(Experimental Method)

A conductive film 5 was formed on a first main surface 21 of a substrate 2 made of silica glass containing TiO_2 by a sputtering method. The conductive film 5 is a CrN film or a film containing Ta as a main component (referred to as Ta-based in Table 1). Subsequently, a multilayer reflective film 3 was formed on a second main surface 22 of the substrate 2 by an ion beam sputtering method. The multilayer reflective film 3 was obtained by alternately laminating approximately 4 nm Si films and approximately 3 nm Mo films for 40 cycles, and finally laminating approximately 4 nm Si film. Subsequently, approximately 2.5 nm of a protective film made of Ru was formed on the multilayer reflective film 3 by sputtering. In this way, a film-formed substrate was obtained. From the film-formed substrate, small pieces with a length of approximately 10 mm per side were cut out and used as test pieces.

[0076] Next, a chemical solution was prepared and placed into a container, and then the container was placed on a hot plate with a stirrer function and heated for about 30 minutes so as to be kept at a predetermined temperature. Subsequently, the test piece was put into the container and immersed in the chemical solution for 600 minutes at maximum while stirring, and then the test piece was taken out from the container. However, when removing of all of the multilayer reflective film 3 and the conductive film 5 was confirmed, the test piece was taken out at that time. Removing of the multilayer reflective film 3 or the conductive film 5 was visually confirmed before the test piece was taken out, and even after the test piece was taken out, it was again confirmed that no film

component remained using fluorescent X-ray analysis (ZSX PrimusII, manufactured by Rigaku Corporation). When the multilayer reflective film 3 was removed, the protective film was also removed at the same time.

5 [0077] (Chemical Solution)

Ultrapure water was used as a solvent.

[0078] As the pH adjusting agent, NaOH was used in experimental example 1, and KOH was used in experimental examples 2 to 25 at a predetermined
10 concentration.

[0079] As the oxidizing agent, sodium metaperiodic acid (NaIO_4) was used in experimental examples 1 to 14, 18, and 19, H_5IO_6 was used in experimental examples 15 to 17 and 20, potassium permanganate (KMnO_4) was used
15 in experimental examples 21 and 22, NMO was used in experimental example 23, and hydrogen peroxide (H_2O_2) was used in experimental examples 24 and 25, at predetermined concentrations.

[0080] As the specific metals, RuCl_3 was added in
20 experimental examples 6 and 7, and Ru powder was added in experimental example 8 in predetermined equivalents with respect to the oxidizing agent.

[0081] As chelating agents, EDTA was added in an amount of 0.1% in experimental example 9, TTHA was
25 added in an amount of 0.1% in experimental example 10, NTPO was added in an amount of 0.1% in experimental example 11, Bicine was added in an amount of 0.1% in experimental example 12, tartaric acid was added in an amount of 0.1% in experimental example 13, and
30 phosphonoacetic acid was added in an amount of 0.1% in experimental example 14.

[0082] The pH of the chemical solutions of experimental examples 1 to 25 were measured using a

portable pH·ORP·ion meter (D-73, manufactured by Horiba, Ltd.).

[0083] (Experimental Results)

In Table 1, "A" indicates that the time
5 (T₃) from when the test piece is placed into the container to when the removing of the multilayer reflective film 3 is visually confirmed is within 30 minutes, "B" indicates that the time is longer than 30 minutes and 45 minutes or shorter, "C" indicates that
10 the time is longer than 45 minutes and 60 minutes or shorter, "D" indicates that the time is longer than 60 minutes and 120 minutes or shorter, "E" indicates that the time is longer than 120 minutes and shorter than 600 minutes, and "X" indicates that removing has not
15 yet occurred at 600 minutes. When the multilayer reflective film 3 was removed, the protective film was also removed at the same time, and thus the time required for removing the protective film was not evaluated.

20 [0084] In Table 1, the time (T₅) from when the test piece was placed into the container to when the removing of the conductive film 5 was visually confirmed was evaluated in the same manner as the T₃.

[0085] In Table 1, substrate damage was evaluated
25 as "◎, meaning the highest evaluation in terms of damage suppression" when the root-mean-square (RMS) roughness of second main surface 22 of the substrate 2 measured by an atomic force microscope (Dimension Icon manufactured by Bruker Corporation) was 0.15 nm or less
30 after the experiment, and as "○, meaning the second highest evaluation in terms of damage suppression" when the RMS roughness of second main surface 22 of the substrate 2 measured by an atomic force microscope

(Dimension Icon manufactured by Bruker Corporation) was more than 0.15 nm and 0.5 nm or less. When the root-mean-square value is 0.5 nm or less, it is possible to sufficiently reduce the process load at the time of repolishing the substrate 2 after the substrate 2 is regenerated.

[0086] As indicated by the results of experimental examples 1 to 23, at least the multilayer reflective film 3 could be removed by the chemical solution of the present invention.

[0087] From experimental examples 1 and 2, it was found that KOH as a pH adjusting agent shortens T_3 more than that of NaOH.

[0088] From the comparison between experimental example 3 and experimental examples 6 to 8, it was found that when Ru or Ru ions were added as the specific metal, the conductive film 5 made of CrN could also be removed in addition to the multilayer reflective film 3 while suppressing the substrate damage.

[0089] From the comparison between the experimental example 2 and experimental examples 9 to 14, it was found that T_3 can be shortened by adding a chelating agent.

[0090] On the other hand, when the oxidizing agent was H_2O_2 as in experimental example 24, the multilayer reflective film 3 could not be removed even after 600 minutes has passed. In addition, as in experimental example 25, when the chelating agent was added to the chemical solution of experimental example 24, the multilayer reflective film 3 could be removed, but the time required for the removing was longer than that in experimental examples 1 to 22. In addition, in

experimental example 23, the T₃ was equivalent to that of experimental example 25, but the substrate damage in experimental example 23 was less than that of experimental example 25.

5 [0091] In addition, when removing of a film was tried by the above-described experimental method for a test piece of a Si wafer on which a ruthenium-based, tantalum-based, niobium-based, or boron-based absorption film was formed, it was found that these
10 absorption films could also be removed. Since the uppermost layer of the multilayer reflective film on the glass substrate was a film containing silicon, it was found from this result that the ruthenium-based, tantalum-based, niobium-based or boron-based absorption
15 film on the multilayer reflective film formed on the glass substrate could also be removed.

[0092] (Reference Experiment)

The multilayer reflective film 3 was formed by sputtering on the second main surface 22 of the
20 substrate 2 made of silica glass containing TiO₂. The multilayer reflective film 3 was obtained by alternately laminating approximately 4 nm Si films and approximately 3 nm Mo films for 40 cycles, and finally laminating approximately 4 nm Si film. Subsequently,
25 approximately 2.5 nm of a protective film made of Ru was formed on the multilayer reflective film 3 by sputtering. In this way, a film-formed substrate was obtained.

[0093] Next, a container filled with 1 L (liter)
30 of a chemical solution containing 22.4% of KOH as a pH adjusting agent and 1% of NaIO₄ as an oxidizing agent was kept at 60°C to 65°C, and then the film-formed substrate was placed into the container while stirring

the container. When the removing of the multilayer reflective film 3 was visually confirmed, the film-formed substrate was taken out, and another film-formed substrate prepared in the same manner was newly placed
5 into the container. This procedure was performed eight times in succession.

[0094] The result of the above reference experiment is illustrated in FIG. 6. FIG. 1 indicates that T_3 tended to increase slightly as the number of
10 times the film-formed substrate was placed into the container increased, but the remarkable change was not observed that the chemical solution had to be replaced. This suggests that the chemical solution according to the present invention can be sufficiently repeatedly
15 used.

[0095] Although the chemical solution, the method of regenerating a film-formed substrate, the method of manufacturing a film-formed substrate, and the method of manufacturing a reflective mask blank according to
20 the present invention have been described above, the present invention is not limited to the above-described embodiments and the like. Various changes, modifications, substitutions, additions, deletions, and combinations are possible within the scope described in
25 the claims. These also naturally fall within the technical scope of the present disclosure.

[0096] The present application is based on and claims priority of Patent Application No. 2021-094724, filed June 4, 2021 with the Japan Patent Office, the
30 entire contents of Japanese Patent Application No. 2021-094724 are hereby incorporated by reference.

DESCRIPTION OF THE REFERENCE NUMERALS

[0097]

- 1 Reflective mask blank
- 2 Substrate
- 3 Multilayer reflective film
- 5 4 Absorption film
- 5 Conductive film
- 41 Opening pattern

CLAIMS

[Claim 1] A chemical solution used for removing at least a multilayer reflective film containing silicon
5 and molybdenum from a glass substrate of a film-formed substrate in which a film having the multilayer reflective film is formed on one surface of the glass substrate, the chemical solution comprising:

a pH adjusting agent; and
10 at least one oxidizing agent selected from the group consisting of metaperiodic acid, sodium metaperiodate, orthoperiodic acid, sodium orthoperiodate, permanganic acid, permanganate, and N-methylmorpholine N-oxide.

15 [Claim 2] The chemical solution according to claim 1, wherein a pH of the chemical solution is 10 or higher and 16 or lower.

20 [Claim 3] The chemical solution according to claim 1, wherein the pH adjusting agent is sodium hydroxide or potassium hydroxide.

[Claim 4] The chemical solution according to claim 1,
25 wherein the oxidizing agent is metaperiodic acid, sodium metaperiodate, orthoperiodic acid, or sodium orthoperiodate.

[Claim 5] The chemical solution according to claim 1,
30 wherein the oxidizing agent is permanganic acid or permanganate.

[Claim 6] The chemical solution according to claim 1,

further comprising at least one selected from the group consisting of a metal having an oxidation-reduction potential higher than an oxidation-reduction potential of chromium (VI) and an ion thereof in an amount of
5 0.0001 molar equivalent to 10 molar equivalent with respect to the oxidizing agent.

[Claim 7] The chemical solution according to claim 1, further comprising an aminocarboxylic acid-based
10 chelating agent, a hydroxy acid-based chelating agent, or a phosphonic acid-based chelating agent as a chelating agent.

[Claim 8] A method of regenerating a film-formed
15 substrate comprising:

bringing a film-formed substrate having a multilayer reflective film containing silicon and molybdenum formed on one surface of a glass substrate into contact with a chemical solution containing a pH
20 adjusting agent and at least one oxidizing agent selected from the group consisting of metaperiodic acid, sodium metaperiodate, orthoperiodic acid, sodium orthoperiodate, permanganic acid, permanganate, and N-methylmorpholine N-oxide; and

25 removing at least the multilayer reflective film from the glass substrate to regenerate a surface of the glass substrate on which the multilayer reflective film was formed.

30 [Claim 9] The method of regenerating a film-formed substrate according to claim 8, wherein the film-formed substrate has a protective film containing ruthenium on the multilayer reflective film.

[Claim 10] The method of regenerating a film-formed substrate according to claim 8, wherein the film-formed substrate has an absorption film containing at least
5 one selected from the group consisting of ruthenium, tantalum, niobium, and boron on the multilayer reflective film.

[Claim 11] The method of regenerating a film-formed
10 substrate according to claim 8, wherein the film-formed substrate has a conductive film containing chromium or tantalum on a surface opposite to a surface on which the multilayer reflective film is formed.

[Claim 12] A method of manufacturing a film-formed substrate comprising, forming a multilayer reflective film containing at least silicon and molybdenum on one surface of the glass substrate regenerated by the method of regenerating the film-formed substrate of any
20 one of claims 8 to 11.

[Claim 13] A method of manufacturing a multilayer reflective film comprising:

forming the multilayer reflective film
25 containing silicon and molybdenum on one surface of the glass substrate regenerated by the method of regenerating the film-formed substrate of any one of claims 8 to 11;

forming a protective film containing
30 ruthenium or rhodium on the multilayer reflective film;

forming an absorption film containing at least one selected from the group consisting of ruthenium, tantalum, chromium, iridium, boron, niobium,

rhodium, and palladium on the protective film; and
forming a conductive film containing at
least one selected from the group consisting of
chromium, tantalum, and boron on a surface of the glass
5 substrate opposite to the surface on which the
multilayer reflective film is formed.