

TITLE OF THE INVENTION

CLEANING METHOD OF SUBSTRATE FOR MASK
BLANK, AND MANUFACTURING METHOD OF MASK BLANK FOR
EUVL

5

TECHNICAL FIELD

[0001]

The disclosures herein generally relate to
a cleaning method of a substrate for a mask blank
10 and a manufacturing method of a mask blank for EUVL.

BACKGROUND ART

[0002]

Conventionally, the photolithography
15 technique has been used for manufacturing
semiconductor devices. In the photolithography
technique, by using an exposure device, light is
irradiated to a circuit pattern of a photomask, and
thereby the circuit pattern is transferred to a
20 resist film in a reduced size.

[0003]

Recently, in order to make possible to
transfer a fine pattern, irradiation with short
wavelength exposure light, such as ArF excimer laser
25 light, furthermore, EUV (Extreme Ultra-Violet)
light, has been studied. The EUV light includes
soft X-ray and vacuum ultraviolet light.
Specifically, the EUV light has a wavelength of 0.2
- 100 nm. At present, EUV light with a wavelength
30 ranging from 13 nm to 14 nm is mainly studied as the
exposure light.

[0004]

A photomask for EUVL (Extreme Ultra-Violet

Lithography) is obtained by forming a circuit pattern on a mask blank for EUVL.

[0005]

5 The Mask blank for EUVL includes a glass substrate for EUVL, a conductive film formed on a first main surface thereof, an EUV light reflection film formed on a second main surface opposite to the first main surface, and an EUV light absorption film. The EUV light reflection film and the EUV
10 light absorption film are formed in this order.

[0006]

The Mask blank for EUVLs preferably have less surface defects to improve a transfer accuracy of the circuit pattern. Here, the surface defects
15 refer to concave defects and convex defects that are generated in the manufacturing process of the Mask blank for EUVL.

[0007]

The main cause of the convex defect is
20 particles deposited in the manufacturing process. Thus, in the manufacturing process of the mask blank for EUVL, the surfaces are cleaned repeatedly to remove the particles.

[0008]

25 In the manufacturing process of the mask blank for EUVL, cleaning of the substrate in the middle of the manufacturing process (hereinafter simply referred to as the substrate for a mask blank) is performed by cleaning using a chemical
30 reaction with an acid or an alkali, by using a physical action, or a combination thereof, to remove particles adhered to the surface of the substrate. The cleaning using the physical action includes

scrubbing, ultrasonic cleaning, and two-fluid cleaning by mixing and spraying N₂ gas and cleaning liquid, and the like. However, especially in the cleaning process in which a high cleanliness is required, the ultrasonic cleaning is preferably used because of high power of removing particles and little possibility of re-contamination by the cleaning liquid.

[0009]

Patent Document 1 discloses an ultrasonic cleaning method of a glass substrate for EUVL. A cleaning liquid applied with ultrasonic waves is injected from a nozzle to a surface to be cleaned of the EUVL glass substrate rotating around an axis, and the surface to be cleaned is ultrasonically cleaned.

[0010]

Patent Document 2 discloses an ultrasonic cleaning method of a substrate such as a wafer. A cleaning liquid is supplied from a nozzle having an edge in a plane opposite to the substrate facing the surface to be cleaned, between a surface to be cleaned of the substrate rotating around the axis and the plane opposite to the substrate, and ultrasonic waves are applied to the cleaning liquid from an ultrasonic cleaning member having a vibration surface in the plane opposite to the substrate, thereby the surface to be cleaned is ultrasonically cleaned.

[Prior art documents]

[Patent Documents]

[0011]

[Patent Document 1] Japanese Unexamined
Patent Application Publication No. 2013-158664

[Patent Document 2] Japanese Unexamined
Patent Application Publication No. 2001-87725

5

[Summary of Invention]

[Problem to be solved by the invention]

[0012]

10 The ultrasonic cleaning method disclosed
in Patent Document 1, as described above, has the
feature that the particle removal force is high and
the possibility of re-contamination by the cleaning
liquid is low, but has a problem that concave
defects are easily generated on the surface to be
15 cleaned. For this reason, Patent Document 1
describes that an occurrence of concave defects of
about 50 nm or more in terms of SiO₂ particles can
be suppressed by controlling parameters at the time
of cleaning so that an average center radius of the
20 cavitation bubbles generated during the ultrasonic
cleaning is 0.1 μm or more and 10 μm or less.

[0013]

25 However, as the requirement for the
surface characteristics of the Mask blank for EUVL
against defects becomes severer with the further
micronizing of the circuit pattern, the occurrence
of the concave defect may not be sufficiently
suppressed by the method disclosed in Patent
Document 1.

30 [0014]

Accordingly, inventors of the present
application have attempted to use the ultrasonic
cleaning method of Patent Document 2 for cleaning

the substrate for a mask blank. The ultrasonic cleaning method of Patent Document 2 was expected to reduce an energy density of vibration energy due to the ultrasonic waves applied to the surface to be
5 cleaned compared to the ultrasonic cleaning method of Patent Document 1, thereby further reducing the generation of concave defects while maintaining the high particle removal force.

[0015]

10 However, it was found that when the ultrasonic cleaning method of Patent Document 2 was used for cleaning the substrate for a mask blank, the particle removal force was not sufficient even though the concave defect was sufficiently
15 suppressed.

[0016]

As a result, in the cleaning of a substrate for a mask blank, it has been difficult to obtain a high particle removal force while
20 suppressing occurrence of concave defects.

[0017]

The present invention provides a technique for obtaining a high particle removal force while suppressing occurrence of concave defects in the
25 cleaning of a substrate for a mask blank.

[Means for Solving Problems]

[0018]

A method of cleaning a substrate for a
30 mask blank according to an embodiment of the present invention includes

a step 1 of supporting the substrate for a mask blank so that a surface to be cleaned directs

upward and is horizontal, one of two main surfaces of the substrate for a mask blank being assigned to the surface to be cleaned;

5 a step 2 of rotating the substrate for a mask blank around a rotation axis that is perpendicular to the surface to be cleaned after the step 1;

a step 3 of supplying a cleaning liquid to the surface to be cleaned after the step 1;

10 a step 4 of bringing an ultrasonic cleaning member into proximity of the surface to be cleaned to satisfy formula (1), after the step 1; and

15 a step 5 of ultrasonically cleaning the surface to be cleaned by applying ultrasonic waves to the cleaning liquid supplied in a space between the surface to be cleaned and a vibration surface provided at an edge of the ultrasonic cleaning member, after the steps 1 to 4.

20 [0019]

[Math 1]

$$\frac{n\lambda}{2} - \frac{\lambda}{5} < D < \frac{n\lambda}{2} + \frac{\lambda}{5} \quad \dots(1)$$

25 In the above-described formula (1), D is a distance between the surface to be cleaned and the vibration surface, n is an integer greater than or equal to one, and λ is a wavelength of an ultrasonic wave propagating in the cleaning liquid applied from
30 the vibration surface.

[Effects of the Invention]

[0020]

According to the present invention, in the cleaning of a substrate for a mask blank, high particle removal force can be obtained while
5 suppressing an occurrence of concave defects.

[Brief Description of Drawings]

[0021]

FIG. 1 is a flowchart illustrating a
10 method for manufacturing a mask blank for EUVL according to an embodiment;

FIG. 2 is a cross-sectional view illustrating a glass substrate for EUVL according to the embodiment;

15 FIG. 3 is a plan view illustrating the glass substrate for EUVL according to the embodiment;

FIG. 4 is a cross-sectional view illustrating a mask blank for EUVL according to the
20 embodiment;

FIG. 5 is a cross-sectional view illustrating an example of a photomask for EUVL;

FIG. 6 is a cross-sectional view illustrating an ultrasonic cleaning member according
25 to the embodiment;

FIG. 7 is a cross-sectional view illustrating an ultrasonic measurement tool according to the embodiment;

FIG. 8 is a diagram schematically
30 illustrating a relationship between an ultrasonic intensity and a position on the vibration surface;

FIG. 9 is a plan view illustrating a relationship among an ultrasonic cleaning member, an

oscillation arm, and the substrate according to the embodiment;

FIG. 10 is a diagram illustrating a relationship between the ultrasonic intensity and the position on the vibration surface measured using the ultrasonic measurement tool shown in FIG. 7; and

FIG. 11 is a cross-sectional view illustrating an ultrasonic cleaning member according to a variation of the embodiment.

10

[Mode for Carrying Out the Invention]
[0022]

In the following, embodiments of the present disclosure will be described with reference to the accompanying drawings. In each drawing, to the same or corresponding configurations, the same reference numeral will be assigned, and an explanation may be omitted. In the specification, a symbol "-" representing a numerical range indicates that values before and after the symbol are included as a lower limit value and an upper limit value, respectively.

20 [0023]

As shown in FIG. 1, a manufacturing method for a mask blank for EUVL includes steps S1 - S7. The mask blank for EUVL 1 shown in FIG. 4 is manufactured using a glass substrate for EUVL 2 shown in FIGS. 2 and 3. In the following, the mask blank for EUVL 1 is simply referred to as a mask blank 1. The glass substrate for EUVL 2 is referred to as a glass substrate 2.

30 [0024]

The glass substrate 2, as shown in FIGS. 2

and 3, has 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 rectangular shape. In the specification of the present
5 application, the rectangular shape includes a corner chamfered shape. The rectangular shape also includes a square. The second main surface 22 is opposite to the first main surface 21. The second main surface 22 also has a rectangular shape,
10 similar to the first main surface 21.
[0025]

The glass substrate 2 also includes four end faces 23, four first chamfered surfaces 24, and four second chamfered surfaces 25. The end faces 23
15 are perpendicular to the first main surface 21 and the second main surface 22. The first chamfered surface 24 is formed at the boundary between the first main surface 21 and the end face 23. The second chamfered surface 25 is formed at the
20 boundary between the second main surface 22 and the end face 23.
[0026]

A glass of the glass substrate 2 is preferably quartz glass containing TiO_2 . The quartz
25 glass has a smaller coefficient of linear expansion and smaller dimensional changes due to temperature changes than those of the typical soda lime glass. Quartz glass may contain from 80% to 95% by mass of SiO_2 and from 4% to 17% by mass of TiO_2 . When the
30 TiO_2 content is between 4% and 17% by mass, the linear expansion coefficient around room temperature is almost zero, and there is little dimensional change around room temperature. Quartz glass may

contain a third component or impurity other than SiO_2 and TiO_2 .

[0027]

5 The size of the glass substrate 2 is, for example, 152 mm in height and 152 mm in width in a plan view. The longitudinal dimension and the lateral dimension may be 152 mm or greater.

[0028]

10 The glass 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 with a length of 142 mm and a width of 142 mm, excluding a rectangular frame-like peripheral region 28 surrounding the central region 27, which
15 is processed to a desired flatness by steps S1-S4. The four sides of the central region 27 are parallel to the four end faces 23. The center of the central region 27 coincides with the center of the first main surface 21.

20 [0029]

Although not shown, the second main surface 22 of the glass substrate 2 also has a central region and a peripheral region, similar to those of the first main surface 21. The central
25 region of the second main surface 22 is a square region with a length of 142 mm and a width of 142 mm, which is processed to the desired flatness by steps S1-S4 of FIG. 1, similar to the central region of the first main surface 21.

30 [0030]

First, in step S1, the first main surface 21 and the second main surface 22 of the glass substrate 2 are polished. The first main surface 21

and the second main surface 22 are polished simultaneously by using a double-sided polisher. Alternatively, the surfaces may be polished sequentially by a single-sided polisher. Either of
5 the surfaces may be polished first, i.e. the order is not particularly limited. In step S1, the glass substrate 2 is polished while the polishing slurry is supplied between a polishing pad and the glass substrate 2.

10 [0031]

The polishing pads include, for example, urethane polishing pads, non-woven polishing pads, suede polishing pads, or the like. The polishing slurry includes an abrasive and a dispersion medium.

15 The abrasive includes, for example, cerium oxide particles. The dispersion medium includes, for example, water or an organic solvent. The first main surface 21 and the second main surface 22 may be polished multiple times with abrasives of
20 different materials or different grain sizes.

[0032]

The abrasive used in step S1 is not limited to cerium oxide particles. The abrasive used in step S1 includes, for example, silicon oxide
25 particles, aluminum oxide particles, zirconium oxide particles, titanium oxide particles, diamond particles, silicon carbide particles, or the like.

[0033]

Next, in step S2, a surface geometry of
30 the first main surface 21 and the second main surface 22 of the glass substrate 2 is measured. For example, a non-contact measuring device, such as a laser interference type, is used to measure the

surface geometry so that the surface is not damaged.
The measuring device measures the surface geometry
of the central region 27 of the first main surface
21 and the central region of the second main surface
5 22.
[0034]

Next, in step S3, the first main surface
21 and the second main surface 22 of the glass
substrate 2 are locally machined in order to improve
10 the flatness, according to results of the
measurement in step S2. The first main surface 21
and the second main surface 22 are locally machined
in sequence. Either of the surfaces may be machined
first, i.e. the order is not particularly limited.
15 The local machining method includes, for example,
the GCIB (Gas Cluster Ion Beam) method or the PCVM
(Plasma Chemical Vaporization Machining) method.
The method of local machining may be a polishing
method using a magnetic fluid, a polishing method
20 using a rotary polishing tool, a catalyst-referred
etching method, or the like.
[0035]

Then, in step S4, the finish polishing of
the first main surface 21 and the second main
25 surface 22 of the glass substrate 2 is performed.
The first main surface 21 and the second main
surface 22 are polished simultaneously with a
double-sided polisher. Alternatively, the surfaces
may be polished sequentially by a single-sided
30 polisher. Either of the surfaces may be polished
first, i.e. the order is not particularly limited.
In step S4, the glass substrate 2 is polished while
the polishing slurry is supplied between the

polishing pad and the glass substrate 2. The polishing slurry includes an abrasive. The abrasive is, for example, colloidal silica particles.

[0036]

5 Next, in step S5, a conductive film 5 shown in FIG. 4 is formed in the central area 27 of the first main surface 21 of the glass substrate 2. The conductive film 5 is used to adsorb the EUVL photomask to an electrostatic chuck of an exposure
10 device. The conductive film 5 is formed of, for example, chromium nitride (CrN). For example, a sputtering method is used for forming the conductive film 5.

[0037]

15 Next, in step S6, the EUV light reflection film 3 shown in FIG. 4 is formed in the central area of the second main surface 22 of the glass substrate 2. The EUV light reflection film 3 reflects EUV light. The EUV light reflection film 3 may be, for
20 example, a multi-layered reflection film in which a high refractive index layer and a low refractive index layer are alternately laminated. The high refractive index layer is formed, for example, of silicon (Si), and the low refractive index layer is
25 formed, for example, of molybdenum (Mo). For example, a sputtering method such as an ion beam sputtering method or a magnetron sputtering method is used for the film formation of the EUV light reflection film 3.

30 [0038]

 Finally, in step S7, the EUV light absorption film 4 shown in FIG. 4 is formed on the EUV light reflection film 3 formed in step S6. The

EUV light absorption film 4 absorbs EUV light. The EUV light absorption film 4 is formed of, for example, a single metal containing at least one element selected from tantalum (Ta), chromium (Cr),
5 ruthenium (Ru), and palladium (Pd), an alloy thereof, a nitride thereof, an oxide thereof, an oxynitride thereof, or the like. For the film formation of the EUV light absorption film 4, for example, a sputtering method is used.

10 [0039]

Steps S6 to S7 are performed after step S5 in the present embodiment, but may be performed before step S5.

[0040]

15 According to steps S1 to S7, described as above, the mask blank 1 shown in FIG. 4 is provided. The 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 glass
20 substrate 2, the EUV light-reflection film 3, and the EUV light-absorption film 4 from the first main surface 11 side to the second main surface 12 side in this order.

[0041]

25 The mask blank 1, although not shown, has a central region and a peripheral region on the first main surface 11, similar to the glass substrate 2. The central area is a square area with a length of 142 mm and a width of 142 mm,
30 excluding a rectangular frame-like peripheral area surrounding the central area. Similarly to the glass substrate 2, the mask blank 1 has a central region and a peripheral region also on the second

main surface 12. The central area is a square area with a length of 142 mm and a width of 142 mm, excluding a rectangular frame-like peripheral area surrounding the central area.

5 [0042]

The mask blank 1 may include another film in addition to the conductive film 5, the glass substrate 2, the EUV light reflection film 3, and the EUV light absorption film 4.

10 [0043]

For example, the mask blank 1 may further include a low reflection film. The low reflection film is formed on the EUV light absorption film 4. Thereafter, a circuit pattern 41 is formed on both
15 the low reflection film and the EUV light absorption film 4. The low reflection film is used to inspect the circuit pattern 41 and has a lower reflection characteristic to test light than that of the EUV light absorption film 4. The low reflection film
20 may be formed of, for example, TaON, TaO, or the like. For example, a sputtering method is used for forming the low-reflection film.

[0044]

The mask blank 1 may further include a
25 hard mask film. The hard mask film is formed over the EUV light absorption film 4 and the low reflection film. The hard mask film functions as a mask when the circuit pattern 41 is formed. After the circuit pattern 41 is formed, the hard mask film
30 is removed. The hard mask film may be formed of, for example, a Cr-based material. For forming the hard mask film, for example, a sputtering method is used.

[0045]

The mask blank 1 may further include a protection film. The protection film is formed between the EUV light reflection film 3 and the EUV light absorption film 4. The protection film protects the EUV light reflection film 3 so that the EUV light reflection film 3 is not etched when the EUV light absorption film 4 is etched to form the circuit pattern 41 on the EUV light absorption film 4. The protection film may be formed of, for example, Ru, Si, or TiO₂. For forming the protection film, for example, a sputtering method is used.

[0046]

As shown in FIG. 5, the EUVL photomask is obtained by forming the circuit pattern 41 on the EUV light absorption film 4. The circuit pattern 41 is an opening pattern in which a photolithography method and an etching method are used. Thus, a resist film used to form the circuit pattern 41 may be included in the mask blank 1.

[0047]

The mask blank for EUVL preferably has less surface defects in order to improve the transfer accuracy of the circuit pattern. Here, the surface defects refer to concave defects and convex defects that are generated in the manufacturing process of the mask blank for EUVL.

[0048]

The main cause of the convex defect is particles deposited in the manufacturing process. Thus, in the manufacturing process of the mask blank for EUVL, the surfaces are cleaned repeatedly to remove the particles.

[0049]

In the manufacturing process of the mask blank for EUVL, cleaning of the substrate in the middle of the manufacturing process (substrate for a mask blank), i.e. cleaning between steps S1-S7 in FIG. 1, is performed by cleaning using a chemical reaction with an acid or an alkali, by using a physical action, or a combination thereof, to remove particles adhered to the surface of the substrate.

The cleaning using the physical action includes scrubbing, ultrasonic cleaning, and two-fluid cleaning by mixing and spraying N₂ gas and cleaning liquid, and the like. However, especially in the cleaning process in which a high cleanliness is required, the ultrasonic cleaning is preferably used because of high power of removing particles and little possibility of re-contamination by the cleaning liquid.

[0050]

The ultrasonic cleaning is preferably performed in at least one of intervals between steps S4 and S5, between steps S5 and S6, between steps S6 and S7, and after step S7 in FIG. 1. It is more preferable as the number of times of performing the ultrasonic cleaning is larger. In addition, although not shown, the ultrasonic cleaning may be performed before and after each of the above-described formation processes of the low-reflection film, the hard mask film, and the protection film.

As described above, steps S6 and S7 are performed after step S5 in the present embodiment, but may be performed before step S5. The timing of performing the ultrasonic cleaning is not particularly limited.

[0051]

In the following, the cleaning method according to the embodiment of the present invention will be described in detail with reference to FIGS.

5 6 to 9.

[0052]

FIG. 6 is a cross-sectional view schematically illustrating a configuration of the ultrasonic cleaning member 6. The ultrasonic
10 cleaning member 6 includes a main body 61, a nozzle 62S, a vibration surface 63, a vibration plate 64, a vibrator 65, and an oscillation arm 66.

[0053]

The main body 61 is preferably made of a
15 material having excellent chemical resistance such as quartz, polytetrafluoroethylene, or polyether ether ketone.

[0054]

The nozzle 62S is arranged on a lateral
20 side of the main body 61, to supply cleaning liquid to a substrate for a mask blank W (hereinafter, simply referred to as the substrate W). The nozzle 62S supplies cleaning liquid to the substrate W from outside the main body 61. However, the nozzle 62S
25 may supply cleaning liquid to the subtracted W from inside the main body 61.

[0055]

In the embodiment, the substrate W has any of the following configurations.

30 [0056]

(First configuration)

A configuration provided with a glass substrate 2 having a first main surface 21 having a

rectangular shape, a second main surface 22 having a rectangular shape opposite to the first main surface 21, and four end faces 23 perpendicular to the first main surface 21 and the second main surface 22.

5 [0057]

(Second configuration)

A configuration provided with the glass substrate 2 and a conductive film 5 formed on the first main surface 21.

10 [0058]

(Third configuration)

A configuration provided with the glass substrate 2, the conductive film 5 formed on the first main surface 21, and an EUV light reflection film 3 formed on the second main surface 22.

15

[0059]

(Fourth configuration)

A configuration provided with the glass substrate 2, the conductive film 5 formed on the first main surface 21, the EUV light reflection film 3 formed on the second main surface 22, and an EUV light absorption film 4 formed on the EUV light reflection film 3.

20

[0060]

25 (Fifth configuration)

A configuration provided with the glass substrate 2, the conductive film 5 formed on the first main surface 21, the EUV light reflection film 3 formed on the second main surface 22, the EUV light absorption film 4 formed on the EUV light reflection film 3, and a hard mask film formed on the EUV light absorption film 4.

30

[0061]

(Sixth configuration)

A configuration provided with the glass substrate 2, and the EUV light reflection film 3 formed on the second main surface 22.

5 [0062]

(Seventh configuration)

A configuration provided with the glass substrate 2, the EUV light reflection film 3 formed on the second main surface 22, and the EUV light
10 absorption film 4 formed on the EUV light reflection film 3.

[0063]

(Eighth configuration)

A configuration provided with the glass
15 substrate 2, the EUV light reflection film 3 formed on the second main surface 22, the EUV light absorption film 4 formed on the EUV light reflection film 3, and the hard mask film formed on the EUV light absorption film 4.

20 [0064]

The nozzle 62S is connected to a cleaning liquid supply source 62S2 through a pipe 62S1, to supply cleaning liquid to the substrate W. A valve 62S3 is provided in the middle of the pipe 62S1 for
25 starting or stopping the supply of cleaning liquid from the nozzle 62S. The nozzle 62S is preferably made of a material having excellent chemical resistance such as polytetrafluoroethylene, or perfluoroalkoxyalkane. The plurality of nozzles 62S
30 may or may not be provided depending on the type of cleaning liquid that is used.

[0065]

The vibration surface 63 corresponds to a

bottom surface of the vibration plate 64. A shape of the vibration surface 63 is not particularly limited, but is preferably circular. The larger the area of the vibration surface 63, the lower the energy density of the vibration energy due to ultrasonic waves applied to W1, which is an upper surface of the substrate W, and generation of concave defects is suppressed. As will be described later, the distance between the vibration surface 63 and the upper surface W1 of the substrate (hereinafter referred to as "distance D") significantly affects the cleaning capability of the ultrasonic cleaning. The distance D is, more specifically, a distance between the center of vibration of the vibration surface 63 and the upper surface W1 of the substrate. The vibration surface 63 and the upper surface W1 of the substrate are parallel to each other.

[0066]

The vibrator 65 is attached to the upper surface of the vibration plate 64 and is connected to an ultrasonic oscillator 651 via wiring. The vibrator 65 receives pulses emitted from the ultrasonic oscillator 651 and transmits ultrasonic waves through the vibration plate 64 to the vibration surface 63. The vibration plate 64 and vibrator 65 are preferably made of a material having an acoustic impedance close to the acoustic impedance of the cleaning liquid, so that ultrasonic vibrations are better transmitted through the cleaning liquid to the upper surface W1 of the substrate. Although a single vibrator 65 is provided, a plurality of vibrators 65 may be

provided.

[0067]

The oscillation arm 66 is connected to the main body 61. The oscillation arm 66 is further
5 connected to the oscillation arm moving mechanism 661 to be vertically moved or to be rotated about a rotation axis 662 shown in FIG. 9, so as to move the cleaning position of the substrate W by the ultrasonic cleaning member 6.

10 [0068]

Next, conditions for carrying out the cleaning method according to the embodiment of the present invention will be described.

[0069]

15 The cleaning liquid supplied from the nozzle 62S is, for example, pure water, a mixture of pure water and X (at least one ingredient selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, formic
20 acid, and acetic acid), a mixture of pure water and Y (at least one ingredient selected from the group consisting of ammonia, tetramethylammonium hydroxide, triethanolamine, choline, sodium hydroxide, potassium hydroxide, and cesium
25 hydroxide), a mixture of pure water and Z (at least one ingredient selected from the group consisting of hydrogen peroxide, perchlorate ion, and periodate ion), a mixture of pure water, X and Z, or a mixture of pure water, Y and Z.

30 [0070]

The cleaning liquid may further dissolve at least one gas selected from the group consisting of hydrogen (H_2), carbon dioxide (CO_2), nitrogen

(N₂), oxygen (O₂), ozone (O₃), and argon (Ar). When the cleaning liquid dissolves these gases, an amount of cavitation generated is controlled, and thereby the particle removal force can be controlled. Among
5 these gases, H₂, CO₂ or N₂ is preferable, and CO₂ is more preferable.

[0071]

The pH of the cleaning liquid is 12.5 or less. If the pH is too high, the glass that
10 constitutes the substrate W may melt.

[0072]

The flow rate of cleaning liquid supplied from the nozzle 62S is, for example, 0.1 L/min to 5.0 L/min, and preferably 0.8 L/min to 1.6 L/min.
15 If the flow rate is too small, a space between the vibration surface 63 and the upper surface W1 of the substrate (hereinafter, also referred to as "gap K") is not filled with the cleaning liquid and the vibration surface 63 may contact with air, and a
20 failure of the ultrasonic cleaning member 6 may occur. On the other hand, if the flow rate is too high, the used amount of cleaning liquid becomes too large, and it is not economically preferable.

[0073]

25 The distance D falls within a range from 0.1 mm to 5 mm, and preferably from 1 mm to 4 mm. If the distance D is too small, not only the vibration surface 63 may contact with the substrate W and a failure may occur, but also an irreparable
30 crack may occur in the upper surface W1 of the substrate. On the other hand, if the distance D is too large, the gap K may not be filled with the cleaning liquid, and the vibration surface 63 may

contact with air, and a failure of the ultrasonic cleaning member 6 may occur.

[0074]

The distance D satisfies the following
5 relation (1A).

[0075]

[Math 2]

$$\frac{n\lambda}{2} - \frac{\lambda}{m} < D < \frac{n\lambda}{2} + \frac{\lambda}{m}, \quad \dots (1A)$$

10

where in the formula (1A), n is an integer greater than or equal to one, λ is a wavelength of the ultrasonic wave propagating in the cleaning liquid applied from the vibration surface 63, and m is an
15 integer greater than or equal to 5. In the formula (1A), n is preferably greater than or equal to 1 and less than or equal to 13. Furthermore, m is preferably greater than or equal to 5 and less than or equal to 8, more preferably greater than or equal
20 to 6 and less than or equal to 8, even more preferably greater than or equal to 7 and less than or equal to 8, and especially preferably 8.

[0076]

In the following, the reason why the
25 distance D should satisfy the above-described formula (1A) will be described.

[0077]

When ultrasonic waves are continuously applied from the vibration surface 63 to the
30 cleaning liquid filling the gap K, the ultrasonic wave applied from the vibration surface 63 and an ultrasonic wave reflected at the upper surface W1 of

the substrate are superimposed on each other so that a standing wave is formed. Since the ultrasonic wave is subjected to free end reflection, the upper surface W1 of the substrate corresponds to a
5 position of an anti-node of the standing wave when the distance D is an integer multiple of $\lambda/2$. At the anti-node position, a change in pressure is large and cavitation is easily generated. Thus, particles adhering to the upper surface W1 of the
10 substrate are easily removed. Accordingly, if the distance D satisfies the above-described formula (1A), the upper surface W1 of the substrate is close to the anti-node of the standing wave, and a sufficient particle removal force can be obtained.
15 On the other hand, when the distance D does not satisfy the above-described formula (1A), the upper surface of the substrate W1 is positioned near a node of the standing wave, and a change in pressure is small, so that the particle removal force is low
20 and the yield may be reduced.

[0078]

FIG. 11 shows a case where the vibration plate 64 has the vibration surface 63 that is parallel to the upper surface W1 of the substrate
25 and an inclined surface relative to the vibration surface 63, and the vibrator 65 that applies vibrations to the vibration plate 64 is attached to the inclined surface. An angle formed by a line perpendicular to the inclined surface and a line
30 perpendicular to the vibration surface is denoted by θ . When the angle θ is greater than zero, the distance D satisfies the following formula (2A). When the angle θ is zero, i.e. the surface to which

the vibrator 65 is attached is not inclined relative to the vibration surface 63 and is parallel to the vibration surface 63, the following formula (2A) coincides with the above-described formula (1A).

5 [0079]

[Math 3]

$$\frac{n\lambda}{2\cos\theta} - \frac{\lambda}{m\cos\theta} < D < \frac{n\lambda}{2\cos\theta} + \frac{\lambda}{m\cos\theta}, \quad \dots (2A)$$

10 where in the formula (2A), n is an integer greater than or equal to one, λ is a wavelength of the ultrasonic wave propagating in the cleaning liquid applied from the vibration surface 63, m is an integer greater than or equal to 5, θ is a value
 15 satisfying the following formula (2B) in which v is a velocity of the ultrasonic wave propagating in the cleaning liquid, and v1 is a velocity of the ultrasonic wave propagating in the vibration plate 64 that forms the vibration surface 63. In the
 20 formula (1A), n is preferably greater than or equal to 1 and less than or equal to 13. Furthermore, m is preferably greater than or equal to 5 and less than or equal to 8, more preferably greater than or equal to 6 and less than or equal to 8, even more
 25 preferably greater than or equal to 7 and less than or equal to 8, and especially preferably 8.

[0080]

[Math 4]

30
$$\frac{\sin\theta}{\sin\theta} = \frac{v1}{v} \quad \dots (2B)$$

When the distance D satisfies the above-described formula (2A), the upper surface W1 of the substrate is located at the position that corresponds to an anti-node of a standing wave.

5 [0081]

Next, an example of a method for causing the distance D to satisfy the above-described formula (1A) or the above-described formula (2A) will be described.

10 [0082]

In the ultrasonic cleaning, the velocity v of the ultrasonic wave propagating in the cleaning liquid, and the frequency f and the wavelength λ of the ultrasonic wave propagating in the cleaning liquid applied from the vibration surface 63 satisfy the following formula (3).

[0083]

[Math 5]

20
$$v = f \cdot \lambda \dots (3)$$

One possible method for causing the distance D to satisfy the above-described formula (1A) or the above-described formula (2A) is to theoretically determine the wavelength λ from the above-described formula (3) and to adjust the position of the vibration surface 63 by the oscillation arm moving mechanism 661 so as to satisfy the above-described formula (1A) or the above-described formula (2A).

30 [0084]

When the Z-coordinate axis is set in the vertically downward direction, as shown in FIG. 6 or

FIG. 11, and the Z-coordinate of the vibration surface 63 is denoted by Z_{63} , a value of Z_{63} is displayed as the position of the vibration surface 63 for the cleaning device including the ultrasonic cleaning member 6. Thus, the distance D can be determined by a difference between a value of the Z-coordinate of the upper surface W1 of the substrate Z_{W1} and the value of Z_{63} , if the value of Z_{W1} is given in advance. However, since the vibration surface 63 cannot be contacted with the upper surface W1 of the substrate every time the value of Z_{W1} is measured, the value of Z_{W1} can only be given at the time of starting up the device, and it is not always possible to say that the value is correct. Furthermore, the value of Z_{63} may also include error due to the oscillation arm moving mechanism 661. Therefore, the actual distance D does not necessarily coincide with $Z_{W1}-Z_{63}$. Furthermore, in the above-described formula (3), since the speed v varies slightly depending on the type, temperature or the like of the cleaning liquid, and the value of the frequency f includes error due to the ultrasonic oscillator 651, it is difficult to accurately determine the wavelength λ . Therefore, it is not practical to confirm whether the above-described formula (1A) or the above-described formula (2A) is satisfied according to the above-described procedure.

[0085]

Therefore, a method shown in FIG. 7 and FIG. 8 may be used for confirming whether the above-described formula (1A) or the above-described formula (2A) is satisfied.

[0086]

FIG. 7 is a cross-sectional view schematically illustrating the configuration of the ultrasonic measurement tool 7. The ultrasonic measurement tool 7 includes a main body 71, a main body upper surface 711, a main body lower surface 712, and an ultrasonic probe 72.

[0087]

The main body 71 has a shape substantially identical to that of the substrate W, and is mounted in the same manner as the substrate W when the substrate W is cleaned. The main body 71 is made of a material having an acoustic impedance close to the acoustic impedance of the cleaning liquid, for example, quartz glass, preferably quartz glass containing TiO_2 , so that ultrasonic waves applied to the cleaning liquid are better transmitted to the ultrasonic probe 72.

[0088]

The ultrasonic probe 72 is attached to the main body lower surface 712 by an epoxy resin or the like, and is connected to a measurement device 721 via wiring. The ultrasonic probe 72 is made of a material having a piezoelectric property, such as lead zirconate titanate. Although not shown, the number of ultrasonic probes 72 to be attached is not particularly limited, and any number of probes may be attached to the position to be measured.

[0089]

As shown in FIG. 7, when ultrasonic waves are applied to cleaning liquid from the vibration surface 63 in the state where the main body 71 is supported so that the main body upper surface 711 is

horizontal and a space between the vibration surface 63 and the main body upper surface 711 is filled with the cleaning liquid, ultrasonic waves propagated to the main body upper surface 711
5 propagate to the main body lower surface 712. At this time, the ultrasonic waves propagated to the main body lower surface 712 are converted into an electrical signal by the ultrasonic probe 72 and processed by the measurement device 721, thereby an
10 ultrasonic intensity at the main body upper surface 711 can be obtained as a relative value. When the above-described process is performed while the vibration surface 63 is moved up and down in the Z-axis direction, a relationship between the
15 ultrasonic intensity and the position of the vibration surface 63 can be obtained.
[0090]

FIG. 8 is a diagram schematically illustrating a relationship between an ultrasonic
20 intensity and a position of the vibration surface 63. The horizontal axis represents a difference ($Z_{711}-Z_{63}$) between the Z-coordinate value of the main body upper surface 711 and the Z-coordinate value of the vibration surface 63, and the vertical axis
25 represents the ultrasonic intensity. As shown in FIG. 8, the ultrasonic intensity applied to the main body upper surface 711 tends to decrease as the difference $Z_{711}-Z_{63}$ increases, while having a maximum value and a minimum value in a cycle of $\lambda/4$ due to
30 formation of a standing wave. In FIG. 8, a position A_n corresponds to an n-th anti-node (n is an integer greater than or equal to 1) of the standing wave, and a position B_n corresponds to an n-th node of the

standing wave.

[0091]

As described above, by obtaining the relationship between the ultrasonic intensity and the position of the vibration surface 63 in advance before performing the ultrasonic cleaning of the substrate W, positions of anti-nodes of the standing wave can be determined without accurate Z-coordinate values of the velocity v and the frequency f . When the main body 71 is replaced with the substrate W after the measurement using the ultrasonic measurement tool 7 and the ultrasonic cleaning is performed for the main body 71, if the position of the vibration surface 63 is set to Z_{63} , which was the anti-node of the standing wave in the measurement, the substrate W is cleaned at the same position of anti-node, i.e. $D=n \cdot \lambda/2$, because the main body 71 has substantially the same shape as that of the substrate W. Even if there is a difference in thickness between the main body 71 and the substrate W or a position shift of the substrate W during mounting, its influence is small, and the distance D does not change to the extent that the above-described formula (1A) or the above-described formula (2A) is not satisfied.

[0092]

As described above, an example of a method for causing the distance D to satisfy the above-described formula (1A) or the above-described formula (2A) is shown. However, the method is not limited to the above-described example, in the case where the distance D satisfies the above-described formula (1A) or the above-described formula (2A).

For example, a method of providing an ultrasonic intensity measuring mechanism on substantially the same plane as the upper surface of the substrate W1, and measuring a position dependence of the
5 ultrasonic intensity in advance, to determine the value of Z_{63} , may be used.

[0093]

The frequency f of the ultrasonic wave applied from the vibration surface 63 falls within a
10 range from 0.4 MHz to 5.2 MHz, and preferably a range from 0.8 MHz to 2.2 MHz. If the frequency f is too small, diameters of cavitation bubbles generated during the ultrasonic cleaning may be increased, and concave defects may be easily
15 generated. On the other hand, if the frequency f is too large, the diameters of the cavitation bubbles are small, so that the particle removal force may be significantly reduced.

[0094]

20 An output power of pulses output from the ultrasonic oscillator 651 falls within a range from 0.1 W to 100 W, and preferably a range from 5 W to 30 W. If the output power is too small, the ultrasonic intensity is small, the pressure change
25 on the upper surface W1 of the substrate becomes smaller, and the particle removal force is significantly reduced. On the other hand, if the output power is too large, energy of the cavitation bubbles is significantly increased, and concave
30 defects may be easily generated.

[0095]

The cleaning liquid, a flow rate, the distance D , the frequency f , and the output power

may be appropriately adjusted so as not to adversely affect the glass substrate 2 or a kind of the deposited film depending on the configuration of the substrate W. For example, when the substrate W has
5 the first configuration, the cleaning liquid is preferably pure water, a mixture of pure water, sulfuric acid and hydrogen peroxide, or a mixture of pure water, ammonia and hydrogen peroxide, and the output power preferably falls within a range from 10
10 W to 25 W. On the other hand, for example, when the substrate W has the third configuration, since the EUV light reflection film 3 more easily generates concave defects than the glass substrate 2, the cleaning liquid is preferably pure water, or a
15 mixture of pure water and tetramethyl ammonium hydroxide, the frequency is preferably greater than that of the first configuration, and the output power is preferably smaller than that of the first configuration.

20 [0096]

In the following, a procedure for performing the cleaning method according to the embodiment of the present invention will be described.

25 [0097]

FIG. 9 is a plan view illustrating a positional relationship among the ultrasonic cleaning member 6, the oscillation arm 66, and the substrate W viewed from above.

30 [0098]

First, the substrate W is supported by the support pin 91 so that the upper surface W1 of the substrate is horizontal, and the substrate W is

rotated around a line perpendicular to the upper surface W1 and passing through a center of the upper surface W1, as a rotation axis. In this case, a rotation speed falls within a range from 10 rpm to 5 300 rpm, and preferably a range from 30 rpm to 150 rpm. If the rotation speed is too small, the entirety of the upper surface W1 of the substrate may not be cleaned uniformly. On the other hand, if the rotation speed is too large, a thickness of a 10 liquid film formed on the upper surface W1 of the substrate becomes thin, so that the gap K is not filled with cleaning liquid, and the vibration surface 63 may contact with air. Therefore, there is a risk of a failure of the ultrasonic cleaning 15 member 6.

[0099]

Then, the valve 62S3 is opened, cleaning liquid is supplied from the nozzle 62S, and a liquid film consisting of the cleaning liquid is formed on 20 the upper surface W1 of the substrate.

[0100]

Then, the oscillation arm moving mechanism 661 lowers the oscillation arm 66 to bring the ultrasonic cleaning member 6 close to the substrate 25 W. At this time, the gap K is filled with the cleaning liquid.

[0101]

The order of the step of rotating the substrate W, the step of supplying the cleaning 30 liquid, and the step of bringing the ultrasonic cleaning member 6 close to the substrate W is not particularly limited. The above-described steps may be performed simultaneously.

[0102]

Next, the ultrasonic oscillator 651 emits pulses, ultrasonic waves transmitted to the vibration surface 63 are applied to the cleaning liquid, and thereby the upper surface W1 of the substrate is ultrasonically cleaned through the cleaning liquid. At this time, the oscillation arm moving mechanism 661 causes the oscillation arm 66 to concentrically oscillate from the center of the substrate W toward an outer edge about the rotation axis 662, thereby the entirety of the upper surface W1 of the substrate can be ultrasonically cleaned. An oscillation speed of the oscillation arm in the concentric oscillation may be reduced as the oscillation arm moves toward the outer edge of the substrate W. Thus, the number of times that the vibration surface 63 passes each point on the upper surface W1 of the substrate is the same, and a uniform cleaning can be performed.

[0103]

After the above-described ultrasonic cleaning, a spin drying is performed in which the substrate W is rotated to remove the cleaning liquid from the upper surface W1 of the substrate, and thereby the substrate W is dried. Before the spin drying, pure water, ozone water, or the like may be supplied for rinsing.

[Examples]

[0104]

Next, experimental data will be described with reference to FIG. 10.

[0105]

FIG. 10 is a diagram depicting a relationship between the ultrasonic intensity measured using the ultrasonic measurement tool 7 and the position of the vibration surface 63. The main body 71 of the ultrasonic measurement tool 7 has a shape substantially identical to that of the glass substrate 2. FIG. 10 shows the results of the measurement by a solid line curve obtained by fitting using the least squares method with a seventh order polynomial. The cleaning liquid was pure water, the frequency f was 0.95 MHz, the output power was 15 W, and the value of Z_{711} , given in advance, was 67.8 mm.

[0106]

As can be seen from FIG. 10, when the difference $Z_{711}-Z_{63}$ was 2.35 mm (i.e. Z_{63} was 65.45 mm) and 3.15 mm (i.e. Z_{63} was 64.65 mm), the main body upper surface 711 corresponded to the position of anti-node of the standing wave, and when the difference $Z_{711}-Z_{63}$ was 2.75 mm (i.e. Z_{63} was 65.05 mm), the main body upper surface 711 corresponded to the position of node of the standing wave. Because an interval between adjacent anti-nodes is $\lambda/2$, the wavelength λ was determined to be 1.6 mm. In the present example, the position A_3 of the third anti-node was $3\lambda/2$, i.e. 2.4 mm, which was very close to the difference $Z_{711}-Z_{63}$, i.e. 2.35 mm. Therefore, when the value of Z_{63} was 65.45 mm, the actual distance between the vibration surface 63 and the main body upper surface 711 was 2.4 mm.

[0107]

Incidentally, when the frequency f is assumed to be 0.95 MHz and the sound velocity in

water v is assumed to be 1500 m/sec in the above-described formula (3), the wavelength λ is theoretically determined to be 1.58 mm. Thus, the above-described result of measurement is considered to be reasonable.

[0108]

(Example 1)

The second main surface of the substrate for a mask blank having the third configuration (including the glass substrate 2, the conductive film 5 formed on the first main surface 21, and the EUV light reflection film 3 formed on the second main surface 22) was cleaned by ultrasonic cleaning. Here, since the substrate for a mask blank having the third configuration had a substantially identical shape to that of the main body 71, the value of Z_{711} and the value of Z_{w1} were considered to be substantially the same. Thus, when the value of Z_{63} was 65.45 mm based on the result of measurement shown in FIG. 10, the distance D was $3\lambda/2$, i.e. 2.4 mm. That is, the above-described formula (1A) was satisfied, and ultrasonic cleaning could be performed for the surface to be cleaned of the glass substrate 2 at the position corresponding to the anti-node of the standing wave. For the ultrasonic cleaning, the cleaning liquid was pure water, the frequency f was 0.95 MHz, and the output power was 15 W.

[0109]

After the ultrasonic cleaning, the substrate was dried by spin drying, and from a result of an inspection of defects for the EUV light reflection film 3 before and after the cleaning, the

numbers of defects with sizes of 50 nm or more on a SiO₂ particle conversion basis were compared. A defect removal rate obtained by dividing the number of removed defects (difference between the number of
5 defects before the cleaning and the number of defects after the cleaning) by the number of defects before the cleaning was 89%. In other words, by ultrasonic cleaning in which the distance D satisfies the above-described formula (1A), most of
10 the particles could be removed while suppressing the generation of concave defects. For the inspection of defects, Mask Blanks Inspection and Review System of MAGICS series manufactured by Lasertec Corporation was used.

15 [0110]
(Example 2)

Ultrasonic cleaning was performed under the same cleaning condition as that of Example 1, except that the value Z63 was set to 65.05 mm and a
20 substrate for a mask blank which has the third configuration but is different from that used in Example 1 was used. At this time, the distance D was $3\lambda/2 + \lambda/4$, i.e. 2.8 mm, the distance D did not satisfy the above-described formula (1A), and the
25 ultrasonic cleaning was performed in a state where the surface to be cleaned was at the position near the node of the standing wave.

[0111]

After the ultrasonic cleaning, the numbers
30 of defects before and after the cleaning were compared as in Example 1, and the defect removal rate was 67%. That is, in the ultrasonic cleaning in which the distance D does not satisfy the above-

described formula (1A), the generation of concave defects could be suppressed, but particles could not be sufficiently removed.

[0112]

5 As described above, the method for cleaning a substrate for a mask blank and the method for manufacturing a mask blank in accordance with the present invention have been described. However, the present invention is not limited to the above-
10 described embodiments. Various modifications, modifications, substitutions, additions, deletions, and combinations are possible within the scope of claims. They are also of course within the scope of the present invention.

15 This application is based on Japanese Patent Applications No. 2021-003567, filed January 13, 2021, No. 2021-188888, filed November 19, 2021, and No. 2021-211179, filed December 24, 2021, the content of which is incorporated herein by
20 reference.

[Reference signs list]

[0113]

1 Mask blank
25 2 Glass substrate
3 EUV light reflection film
4 EUV light absorption film
5 Conductive film
6 Ultrasonic cleaning member
30 61 Main body
62S Nozzle
63 Vibration surface
64 Vibration plate

	65	Vibrator
	66	Oscillation arm
	7	Ultrasonic measurement tool
	71	Main unit
5	72	Ultrasonic probe

WHAT IS CLAIMED IS

1. A cleaning method of a substrate for a
5 mask blank, the method comprising:

a step 1 of supporting the substrate for a
mask blank so that a surface to be cleaned directs
upward and is horizontal, one of two main surfaces
of the substrate for a mask blank being assigned to
10 the surface to be cleaned;

a step 2 of rotating the substrate for a
mask blank around a rotation axis that is
perpendicular to the surface to be cleaned after the
step 1;

15 a step 3 of supplying a cleaning liquid to
the surface to be cleaned after the step 1;

a step 4 of bringing an ultrasonic
cleaning member into proximity of the surface to be
cleaned to satisfy formula (1),

20 [Math 1]

$$\frac{n\lambda}{2} - \frac{\lambda}{5} < D < \frac{n\lambda}{2} + \frac{\lambda}{5}, \quad \dots (1)$$

where D is a distance between the surface to be
25 cleaned and a vibration surface provided at an edge
of the ultrasonic cleaning member, n is an integer
greater than or equal to one, and λ is a wavelength
of an ultrasonic wave propagating in the cleaning
liquid applied from the vibration surface, after the
30 step 1; and

a step 5 of ultrasonically cleaning the
surface to be cleaned by applying ultrasonic waves

to the cleaning liquid supplied in a space between the surface to be cleaned and the vibration surface after the steps 1 to 4.

5

2. A cleaning method of a substrate for a mask blank, the method comprising:

a step 1 of supporting the substrate for a mask blank so that a surface to be cleaned directs
10 upward and is horizontal, one of two main surfaces of the substrate for a mask blank being assigned to the surface to be cleaned;

a step 2 of rotating the substrate for a mask blank around a rotation axis that is
15 perpendicular to the surface to be cleaned after the step 1;

a step 3 of supplying a cleaning liquid to the surface to be cleaned after the step 1;

a step 4 of bringing an ultrasonic
20 cleaning member into proximity of the surface to be cleaned to satisfy formula (2A),
[Math 2]

$$\frac{n\lambda}{2\cos\theta} - \frac{\lambda}{m\cos\theta} < D < \frac{n\lambda}{2\cos\theta} + \frac{\lambda}{m\cos\theta}, \quad \dots (2A)$$

25

where D is a distance between the surface to be cleaned and a vibration surface provided at an edge of the ultrasonic cleaning member, n is an integer greater than or equal to one, λ is a wavelength of
30 an ultrasonic wave propagating in the cleaning liquid applied from the vibration surface, m is an integer greater than or equal to 5, and θ is a value

satisfying formula (2B),
[Math 3]

$$\frac{\sin \theta}{\sin \Theta} = \frac{v_1}{v}, \quad \dots (2B)$$

5

where v is a velocity of an ultrasonic wave propagating in the cleaning liquid, v₁ is a velocity of an ultrasonic wave propagating in a vibration plate that forms the vibration surface and has an inclined surface relative to the vibration surface, a vibrator that applies vibration to the vibration plate being attached to the inclined surface, and θ is an angle formed by a line perpendicular to the inclined surface and a line perpendicular to the vibration surface, after the step 1; and

10 a step 5 of ultrasonically cleaning the surface to be cleaned by applying ultrasonic waves to the cleaning liquid supplied in a space between the surface to be cleaned and the vibration surface after the steps 1 to 4.

3. The cleaning method of a substrate for a mask blank according to claim 1 or 2,

25 wherein the substrate for a mask blank has any one of a configuration of:

a first configuration provided with a glass substrate having a first main surface having a rectangular shape, a second main surface having a rectangular shape opposite to the first main surface, and four end faces perpendicular to the first main surface and the second main surface;

a second configuration provided with the glass substrate, and a conductive film formed on the first main surface;

5 a third configuration provided with the glass substrate, the conductive film formed on the first main surface, and an extreme ultra-violet (EUV) light reflection film formed on the second main surface;

10 a fourth configuration provided with the glass substrate, the conductive film formed on the first main surface, the EUV light reflection film formed on the second main surface, and an EUV light absorption film formed on the EUV light reflection film;

15 a fifth configuration provided with the glass substrate, the conductive film formed on the first main surface, the EUV light reflection film formed on the second main surface, the EUV light absorption film formed on the EUV light reflection
20 film, and a hard mask film formed on the EUV light absorption film;

a sixth configuration provided with the glass substrate, and the EUV light reflection film formed on the second main surface;

25 a seventh configuration provided with the glass substrate, the EUV light reflection film formed on the second main surface, and the EUV light absorption film formed on the EUV light reflection film; and

30 an eighth configuration provided with the glass substrate, the EUV light reflection film formed on the second main surface, the EUV light absorption film formed on the EUV light reflection

film, and the hard mask film formed on the EUV light absorption film.

5 4. The cleaning method of a substrate for a mask blank according to claim 3,

 wherein glass of the glass substrate is quartz glass containing TiO_2 .

10

 5. The cleaning method of a substrate for a mask blank according to claim 1 further comprising:

 a step of measuring a relationship between
15 the distance (D) between the surface to be cleaned and the vibration surface and an ultrasonic intensity of the ultrasonic wave applied from the vibration surface in advance on substantially the same plane as the surface to be cleaned so that the
20 distance (D) satisfies the formula (1).

 6. The cleaning method of a substrate for a mask blank according to claim 2 further
25 comprising:

 a step of measuring a relationship between the distance (D) between the surface to be cleaned and the vibration surface and an ultrasonic intensity of the ultrasonic wave applied from the
30 vibration surface in advance on substantially the same plane as the surface to be cleaned so that the distance (D) satisfies the formula (2A).

7. The cleaning method of a substrate for
a mask blank according to any one of claims 1 to 6,
wherein the distance (D) between the
5 surface to be cleaned and the vibration surface
falls within a range from 0.1 mm to 5 mm.

8. The cleaning method of a substrate for
10 a mask blank according to any one of claims 1 to 7,
wherein a frequency of the ultrasonic wave
that is applied to the cleaning liquid falls within
a range from 0.4 MHz to 5.2 MHz.

15
9. The cleaning method of a substrate for
a mask blank according to any one of claims 1 to 8,
wherein an output power of the ultrasonic
wave that is applied to the cleaning liquid falls
20 within a range from 0.1 W to 100 W.

10. The cleaning method of a substrate for
a mask blank according to any one of claims 1 to 9,
25 wherein a flow rate of the cleaning liquid
falls within a range from 0.1 L/min to 5.0 L/min.

11. The cleaning method of a substrate for
30 a mask blank according to any one of claims 1 to 10,
wherein, as the cleaning liquid,
pure water;
a mixture of pure water and an ingredient

X that is at least one ingredient selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, formic acid, and acetic acid;

5 a mixture of pure water and an ingredient Y that is at least one ingredient selected from the group consisting of ammonia, tetramethylammonium hydroxide, triethanolamine, choline, sodium hydroxide, potassium hydroxide, and cesium
10 hydroxide;

 a mixture of pure water and an ingredient Z that is at least one ingredient selected from the group consisting of hydrogen peroxide, perchlorate ion, and periodate ion;

15 a mixture of pure water, the ingredient X, and the ingredient Z; or

 a mixture of pure water, the ingredient Y and the ingredient Z, is used.

20

12. The cleaning method of a substrate for a mask blank according to claim 11,

 wherein the cleaning liquid further dissolves at least one gas selected from the group
25 consisting of hydrogen (H₂), carbon dioxide (CO₂), nitrogen (N₂), oxygen (O₂), ozone (O₃), and argon (Ar).

30 13. A manufacturing method of a mask blank for EUVL, the method comprising:

 a step A of forming a conductive film on a first main surface of a glass substrate;

a step B of forming an EUV light reflection film on a second main surface that is opposite to the first main surface;

5 a step C of forming an EUV light absorption film on the EUV light reflection film; and

a step D of cleaning a substrate for a mask blank by the cleaning method according to any one of claims 1 to 10.

10