

DESCRIPTION

TITLE OF THE INVENTION

PROCESSING METHOD FOR GLASS PLATE, AND
5 PRODUCTION METHOD FOR MASK BLANK FOR EUVL

TECHNICAL FIELD

[0001]

The present disclosure relates to a
10 processing method for a glass plate, and a
production method for a mask blank for EUVL.

BACKGROUND ART

[0002]

15 Conventionally, photolithographic
techniques have been used to manufacture
semiconductor devices. In the photolithographic
techniques, a photomask pattern is irradiated with
light by an exposure apparatus, and the photomask
20 pattern is transferred to a resist film.

[0003]

In recent years, in order to make it
possible to transfer a fine pattern, use of exposure
light having a short wavelength, for example, ArF
25 excimer laser light or further EUV (Extreme Ultra-
Violet) light has been studied.

[0004]

Here, the EUV light includes soft X-ray
and vacuum ultraviolet light, and specifically
30 refers to light having a wavelength of about 0.2 nm
to 100 nm. At present, EUV light having a
wavelength of about 13.5 nm is mainly examined as
exposure light.

[0005]

Patent Document 1 discloses a production method for a mask blank for EUVL (Extreme Ultra-Violet Lithography). The mask blank for EUVL includes a glass plate, a reflection film formed on the glass plate, and an absorption film formed on the reflection film.

[0006]

The mask blank for EUVL is required to have a high flatness to improve a transfer accuracy for the fine pattern. Since the flatness of the mask blank for EUVL is mainly determined by a flatness of the glass plate as a substrate, a high flatness is required for the glass plate.

[0007]

The production method disclosed in Patent Document 1 includes a preliminary polishing step, a measurement step, and a correction polishing step. In the preliminary polishing step, both main surfaces of the glass plate are preliminarily polished. In the measurement step, the maximum plate thickness distribution and a flatness of the glass plate are measured. In the correction polishing step, the main surface of the glass plate is locally polished based on results of measurement of the measurement step.

PRIOR ART LITERATURE

PATENT LITERATURE

[0008]

Patent Document 1: WO 2011/115131

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0009]

For the local polishing of Patent Document
1, gas clusters or the like are used. The gas
5 clusters are ionized by collision of thermo
electrons and subsequently accelerated by an
electric field and radiated toward the first main
surface of the glass plate, to etch the first main
surface locally. As a result, the first main
10 surface can be made flat.

[0010]

The irradiation with the gas clusters is
performed inside a vacuum vessel. Since the glass
plate cannot be held by a vacuum chuck inside the
15 vacuum vessel, the glass plate is held by a clamp.
The clamp detachably holds the glass plate.
Accordingly, the clamp is brought into contact with
and separated from the glass plate.

[0011]

20 The glass plate is etched inside the
vacuum vessel and particles are generated. The
particles are produced when the gas clusters collide
with the glass plate or a peripheral member of the
glass plate. The material of the particles is, for
25 example, glass, metal, or resin. The generated
particles may stick to a clamp during standby. When
the clamp in this state approaches the glass plate,
the particles may get caught between the clamp and
the glass plate. As a result, defects may occur in
30 the glass plate.

[0012]

As the defects, concave scratches may
occur or convex deposits occur. These defects are

caused by particles. The scratches are contact traces of the particles, and the deposits are the particles themselves.

[0013]

5 One aspect of the present disclosure provides a technique that can suppress an occurrence of defects in the glass plate due to contact with the clamp.

10 MEANS FOR SOLVING THE PROBLEM

[0014]

 According to an aspect of the present disclosure, a processing method for a glass plate includes preparing a protective-layer equipped glass
15 plate that includes a glass plate, and a protective layer including a resin layer in contact with the glass plate; holding the protective-layer equipped glass plate by a clamp butted against the protective
20 plate by irradiating the first main surface with a beam-like gas cluster while holding the protective-layer equipped glass plate by the clamp.

EFFECT OF THE INVENTION

25 [0015]

 According to one aspect of the present disclosure, an occurrence of defects in the glass plate due to contact with the clamp can be suppressed.

30

BRIEF DESCRIPTION OF DRAWINGS

[0016]

[Figure 1] FIG. 1 is a flowchart showing a

production method for a mask blank for EUVL
according to an embodiment.

[Figure 2] FIG. 2 is a cross-sectional view
showing an example of a glass plate provided in S1
5 of FIG. 1.

[Figure 3] FIG. 3 is a plan view showing an
example of the glass plate in FIG. 2.

[Figure 4] FIG. 4 is a cross-sectional view
depicting the mask blank for EUVL according to the
10 embodiment.

[Figure 5] FIG. 5 is a cross-sectional view
showing an example of a photomask for EUVL.

[Figure 6] FIG. 6 is a cross-sectional view
depicting a processing apparatus according to the
15 embodiment.

[Figure 7] FIG. 7 is an enlarged cross-sectional
view of the glass plate of FIG. 6 and its peripheral
parts.

[Figure 8] FIG. 8 is a diagram showing the glass
20 plate and its peripheral parts as viewed in the
irradiation direction of a gas cluster in FIG. 7.

[Figure 9] FIG. 9 is a diagram depicting the
clamp and the spacer of FIG. 7 viewed from another
direction.

25 [Figure 10] FIG. 10 is a flowchart showing an
example of S3 in FIG. 1.

[Figure 11] FIG. 11 is a cross-sectional view
showing a clamp according to a first variation.

[Figure 12] FIG. 12 is a cross-sectional view
30 showing a clamp according to a second variation.

[Figure 13] FIG. 13 is a cross-sectional view
showing a clamp according to a third modification.

MODE FOR CARRYING OUT THE INVENTION

[0017]

In the following, embodiments of the present disclosure will be described with reference to the 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 "-" indicating a numerical value range means that numerical values before and after the symbol are included as a lower limit value and an upper limit value.

[0018]

As shown in FIG. 1, a production method for a mask blank for EUVL (Extreme Ultra-Violet Lithography) includes S1 to S7. A glass plate is used for producing the mask blank. The glass of the glass plate is preferably silica glass containing SiO_2 of 90 mass% or more. The upper limit of the content of SiO_2 in the silica glass is 100 mass%. The silica glass has a smaller linear expansion coefficient and a smaller dimensional change due to temperature change than a general soda lime glass. The silica glass may contain TiO_2 in addition to SiO_2 . The silica glass may contain SiO_2 of 90 to 95 mass% and TiO_2 of 5 to 10 mass%. When the content of TiO_2 is 5 mass% to 10 mass%, the linear expansion coefficient around the room temperature is substantially zero, and the dimensional change around the room temperature is unlikely to occur. The silica glass may contain a minor component other than SiO_2 and TiO_2 , but preferably does not contain a minor component.

[0019]

As shown in FIGS. 2 and 3, the glass plate 2 includes a first main surface 21, a second main surface 22, four end faces 23, four first chamfered surfaces 24, and four second chamfered surfaces 25. The first main surface 21 has a rectangular shape. In the present specification, the rectangular shape includes a shape in which chamfering is applied to corners. The rectangle includes a square. The second main surface 22 is opposite to the first main surface 21. The second main surface 22 is also rectangular in the same manner as the first main surface 21. The end face 23 is 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 boundary between the second main surface 22 and the end face 23. The first chamfered surface 24 and the second chamfered surface 25 are what is known as C-surfaces in this embodiment, but may be R-surfaces.

[0020]

The first main surface 21 of the glass plate 2 has a quality assurance region 26 shown by a dot pattern in FIG. 3. The quality assurance region 26 is a region processed to a desired flatness according to S1 to S4. The quality assurance region 26 is a region excluding a peripheral region 27 and is at a distance L of, for example, 5 mm or less from the end face 23 as viewed in a direction orthogonal to the first main surface 21. Although not shown, the second main surface 22 of the glass

plate 2 also has a quality assurance region and a peripheral region in the same manner as the first main surface 21.

[0021]

5 First, in S1 of FIG. 1, the first main surface 21 and the second main surface 22 of the glass plate 2 are polished. The first main surface 21 and the second main surface 22 may be simultaneously polished by a double-sided polishing apparatus or sequentially polished by a single-sided
10 polishing apparatus. In S1, the glass plate 2 is polished while a polishing slurry is supplied between a polishing pad and the glass plate 2. The polishing slurry contains an abrasive. The abrasive
15 is, for example, cerium oxide particles. The first main surface 21 and the second main surface 22 may be polished a plurality of times with abrasives of different materials or grain sizes.

[0022]

20 The abrasive used in S1 is not limited to cerium oxide particles. For example, the abrasive used in S1 may be silicon oxide particles, aluminum oxide particles, zirconium oxide particles, titanium oxide particles, diamond particles, or silicon
25 carbide particles.

[0023]

Next, in S2 of FIG. 1, surface shapes of the first main surface 21 and the second main surface 22 of the glass plate 2 are measured. For
30 the measurement of the surface shape, for example, a non-contact type measuring apparatus, such as a laser interference type, is used so as not to damage the surface. The measuring apparatus measures

surface shapes of the quality assurance region 26 of the first main surface 21 and the quality assurance region of the second main surface 22.

[0024]

5 Next, in S3 of FIG. 1, referring to the measurement result of S2, the first main surface 21 and the second main surface 22 of the glass plate 2 are processed with a beam-shaped gas cluster to improve the flatness. The first main surface 21 and
10 the second main surface 22 are etched in order by a gas cluster. Regarding the order, either of the surfaces may be polished first, and as such, the order is not particularly limited.

[0025]

15 The gas clusters are ionized by collision of thermal electrons, accelerated by an electric field, and radiated toward the first main surface 21 or the second main surface 22 after neutralization. By the collision of the gas clusters, the first main
20 surface 21 or the second main surface 22 is locally etched and flattened. Details of S3 will be described later.

[0026]

 Next, in S4 of FIG. 1, the first main
25 surface 21 and the second main surface 22 of the glass plate 2 are subjected to finishing polishing. The first main surface 21 and the second main surface 22 may be simultaneously polished by the double-sided polishing apparatus or sequentially
30 polished by the single-sided polishing apparatus. In S4, the glass plate 2 is polished while a polishing slurry is supplied between the polishing pad and the glass plate 2. The polishing slurry

contains an abrasive. The abrasive is, for example, colloidal silica particles.

[0027]

Next, in S5 of FIG. 1, a reflection film 3
5 shown in FIG. 4 is formed in the quality assurance region 26 of the first main surface 21 of the glass plate 2. The reflection film 3 reflects EUV light. The reflection film 3 may be, for example, a multilayer reflection film in which high refractive
10 index layers and low refractive index layers are alternately laminated. The high refractive index layer is formed of, for example, silicon (Si), and the low refractive index layer is formed of, for example, molybdenum (Mo). As the film forming
15 method of the reflection film 3, for example, a sputtering method such as an ion beam sputtering method or a magnetron sputtering method is used.
[0028]

Next, in S6 of FIG. 1, an absorption film
20 4 shown in FIG. 4 is formed on the reflection film 3 formed in S5. The absorption film 4 absorbs EUV light. The absorption film 4 is formed of, for example, a single metal, an alloy, a nitride, an oxide, or an oxynitride containing at least one
25 element selected from tantalum (Ta), chromium (Cr), and palladium (Pd). As the film forming method of the absorption film 4, the sputtering method is used, for example.
[0029]

30 Finally, in S7 of FIG. 1, a conductive film 5 shown in FIG. 4 is formed in the quality assurance region of the second main surface 22 of the glass plate 2. The conductive film 5 is used to

electrostatically suck a photomask by an electrostatic chuck of an exposure apparatus. The conductive film 5 is formed of, for example, chromium nitride (CrN). As the film forming method of the conductive film 5, for example, the sputtering method is used. Although S7 is executed after S5 and S6 in this embodiment, S7 may be executed before S5 and S6.

[0030]

The arrangement of the reflection film 3 and the conductive film 5 may be reversed. That is, the conductive film 5 may be formed in the quality assurance region 26 of the first main surface 21 of the glass plate 2, and the reflection film 3 may be formed in the quality assurance region of the second main surface 22 of the glass plate 2. The absorption film 4 is formed on the reflection film 3.

[0031]

According to the above-described S1 to S7, the mask blank for EUVL 1 shown in FIG. 4 is obtained. The mask blank for EUVL 1 includes the glass plate 2, the reflection film 3, the absorption film 4, and the conductive film 5. The mask blank for EUVL 1 may or may not include the conductive film 5. The mask blank for EUVL 1 may further include another film.

[0032]

For example, the mask blank for EUVL 1 may further include a low reflection film. The low reflection film is formed on the absorption film 4. The low reflection film is used for inspecting an opening pattern 41 of the absorption film 4 shown in

FIG. 5, and has a lower reflection characteristic with respect to the inspection light than the absorption film 4. The low reflection film is formed of, for example, TaON or TaO. As a method
5 for forming the low reflection film, for example, the sputtering method is used.

[0033]

The mask blank for EUVL 1 may further include a protection film. The protection film is
10 formed between the reflection film 3 and the absorption film 4. The protection film protects the reflection film 3 so that the reflection film 3 is not etched when the absorption film 4 is etched to form an opening pattern 41 in the absorption film 4.
15 The protection film is formed of, for example, Ru, Si, or TiO₂. As the method for forming the protection film, for example, the sputtering method is used.

[0034]

20 As shown in FIG. 5, the photomask for EUVL is obtained by forming the opening pattern 41 in the absorption film 4. A photolithography method and the etching method are used to form the opening pattern 41. Therefore, a resist film used for
25 forming the opening pattern 41 may be included in the mask blank for EUVL 1.

[0035]

Next, with reference to FIG. 6, a processing apparatus used in S3 of FIG. 1 will be
30 described. The processing apparatus 100 is what is known as a GCIB (Gas Cluster Ion Beam) processing apparatus.

[0036]

The processing apparatus 100 includes a vacuum vessel 101. The vacuum vessel 101 has a nozzle chamber 102, an ionization/acceleration chamber 103, and a processing chamber 104. The
5 three chambers 102, 103, and 104 are connected to each other to form a gas cluster passage. The three chambers 102, 103, and 104 are evacuated by three vacuum pumps 105, 106, and 107 to maintain a desired degree of vacuum. The number of chambers and the
10 number of vacuum pumps are not particularly limited.
[0037]

The processing apparatus 100 includes a generation unit 110. The generation unit 110 generates a gas cluster. The generation unit 110
15 includes, for example, a raw material tank 111, a pressure controller 113, a supply pipe 114, and a nozzle 116. The raw material tank 111 stores raw material gas (for example, CF_4 gas). The pressure controller 113 controls a supply pressure of the raw
20 material gas supplied from the raw material tank 111 to the nozzle 116 via the supply pipe 114. The nozzle 116 is provided in the nozzle chamber 102 and injects a raw material gas into a vacuum to form a supersonic gas jet 118.
25 [0038]

The raw material gas is cooled by adiabatic expansion in the gas jet 118. As a result, a portion of the gas jet 118 condenses into gas clusters, each of which is an aggregate of
30 several to several thousand atoms or molecules. Many gas clusters are contained near the center of the flow of the gas jet 118. Thus, the gas clusters can be efficiently delivered by passing only near

the center of the flow of the gas jet 118 through a schema 119.

[0039]

The raw material gas is not limited to CF₄ gas but may be SF₆ gas, Ar gas, O₂ gas, N₂ gas, NF₃ gas, N₂O gas, CHF₃ gas, C₂F₆ gas, C₃F₈ gas, C₄F₆ gas, SiF₄ gas, COF₂ gas, SeF₆ gas, TeF₆ gas, or WF₆ gas. A plurality of gases may be selected from these gases, and a mixed gas may be used as a raw material gas. The raw material gas is preferably a gas that can form a gas cluster of a large size and can etch at a high rate, more specifically, a gas that contains fluorine.

[0040]

The processing apparatus 100 includes an ionization unit 120. The ionization unit 120 ionizes at least a portion of the gas cluster in the gas jet 118. The ionization unit 120 includes, for example, one or more hot filaments 124 and a cylindrical electrode 126. The hot filament 124 generates heat by electric power (voltage V_F) from a power supply 125 and emits thermal electrons. The cylindrical electrode 126 accelerates the thermal electrons emitted from the hot filament 124 and collides the accelerated thermal electrons with the gas clusters. According to the collision of the electrons with the gas clusters, electrons are released from a portion of the gas clusters, and these gas clusters are positively ionized. Two or more electrons may be emitted, and polyvalent ionization may occur. A voltage V_A from a power supply 127 is applied between the cylindrical electrode 126 and the hot filament 124. The voltage

V_A (electric field) accelerates the thermal electrons and the electrons collide with the gas clusters.

[0041]

5 The processing apparatus 100 includes an acceleration unit 130. The acceleration unit 130 accelerates the gas cluster ionized by the ionization unit 120 to form a GCIB 128. The acceleration unit 130 includes, for example, a first
10 electrode 132 and a second electrode 134. The second electrode 134 is grounded, and a positive voltage V_s is applied to the first electrode 132 from a power supply 135. The first electrode 132 and the second electrode 134 form an electric field
15 for accelerating a positively ionized gas cluster. The accelerated gas cluster is extracted as a GCIB 128 from an opening of the second electrode 134. A power supply 136 supplies an acceleration voltage V_{Acc} for biasing the ionization unit 120 to the first
20 electrode 132 and the second electrode 134 so that the total GCIB acceleration potential becomes equal to V_{Acc} . V_{Acc} is, for example, 1 kV to 200 kV, and preferably 1 kV to 70 kV.

[0042]

25 The processing apparatus 100 may include a neutralization unit (not shown). The neutralization unit neutralizes the GCIB 128 formed by the acceleration unit 130 to form a neutral gas cluster. Since the glass plate 2 is irradiated with neutral
30 gas clusters, charging of the glass plate 2 can be prevented. The glass plate 2 also can be etched by irradiating the glass plate 2 with positively ionized gas clusters.

[0043]

The processing apparatus 100 includes an irradiation unit 150. The irradiation unit 150 irradiates the glass plate 2 with a beam-shaped gas cluster 129 to locally etch the glass plate 2. The diameter of the beam of the gas cluster 129 is, for example, 1 mm to 15 mm. The irradiation unit 150 includes, for example, a stage 151, a stage moving mechanism 152, and an aperture 153. The stage 151 is installed in the processing chamber 104 and holds the glass plate 2. The stage moving mechanism 152 moves the stage 151 two-dimensionally in the Y-axis direction and the Z-axis direction in order to move the irradiation point with the gas cluster 129 in the glass plate 2. By controlling the moving speed, the etching amount can be controlled, and the glass plate 2 can be flattened. The stage moving mechanism 152 can also move the stage 151 in the X-axis direction. The aperture 153 is provided in the middle of the passage of the gas cluster 129 to enhance the uniformity of intensity of the gas cluster 129. The gas cluster 129 passes through an opening of the aperture 153 and radiates the glass plate 2.

[0044]

Next, with reference to FIGS. 7 to 9, the irradiation unit 150 of the processing apparatus 100 will be described. In the present specification, the X-axis direction, the Y-axis direction, and the Z-axis direction are perpendicular to each other. The X-axis direction and Y-axis direction are horizontal, and the Z-axis direction is vertical. In the following description, the positive X-axis

direction is forward and the negative X-axis direction is backward. The irradiation direction of the gas cluster 129 shown by an arrow in FIG. 7 is the positive X-axis direction.

5 [0045]

As shown in FIG. 7, the irradiation unit 150 irradiates the beam-shaped gas cluster 129 forward and locally etches the first main surface 21 of the glass plate 2 with the irradiated gas cluster 129. The first main surface 21 is disposed rearward and inclined obliquely upward. Since the first main surface 21 faces obliquely upward, the stage 151 can stably hold the glass plate 2 from below. When an orientation of the glass plate 2 is reversed, local etching of the second main surface 22 of the glass plate 2 is naturally also possible.

15 [0046]

As shown in FIG. 9, the stage 151 is arranged to face the second main surface 22 of the glass plate 2. The stage 151 is arranged in front of the glass plate 2. The stage 151 may hold the glass plate 2 via, for example, a spacer 155. The spacer 155 forms a gap between the stage 151 and the glass plate 2. Compared with the case where the whole second main surface 22 of the glass plate 2 comes into contact with the stage 151, generation of a contact flaw on the second main surface 22 can be suppressed.

[0047]

30 The spacer 155 may have a tapered surface in a tapered shape. When the second chamfered surface 25 of the glass plate 2 is held by the tapered surface of the spacer 155, the second main

surface 22 is not brought into contact at all, so that the occurrence of a contact flaw on the second main surface 22 can be surely prevented. As shown in FIG. 8, a portion of the spacer 155 is disposed

5 outside the glass plate 2 as viewed in the irradiation direction of the gas cluster 129.

[0048]

In this embodiment, a portion of the spacer 155 is disposed outside the glass plate 2 as

10 viewed in the irradiation direction of the gas cluster 129, but the entire spacer 155 can be disposed inside the glass plate 2. In this case, the spacer 155 does not come into contact with the second chamfered surface 25 of the glass plate 2,

15 but comes contact with a peripheral region excluding the quality assurance region of the second main surface 22.

[0049]

The stage 151 may hold the glass plate 2

20 via a clamp 156. The glass plate 2 can be stably held in vacuum. The entire clamp 156 is disposed outside the glass plate 2 as viewed in the irradiation direction of the gas cluster 129. The clamp 156 presses, for example, the end face 23 of

25 the glass plate 2. A plurality of clamps 156 are provided along the peripheral edge of the glass plate 2 at intervals.

[0050]

Although the clamp 156 presses the end

30 face 23 of the glass plate 2 in this embodiment, it may press the peripheral region 27 of the first main surface 21 of the glass plate 2. The clamp 156 may press the first chamfered surface 24 of the glass

plate 2. In these cases as well, a portion of the clamp 156 is disposed outside the glass plate 2 as viewed in the irradiation direction of the gas cluster 129.

5 [0051]

The irradiation of the gas cluster 129 is performed inside the vacuum vessel 101. Since the glass plate 2 cannot be held by the vacuum chuck inside the vacuum vessel 101, the glass plate 2 is
10 held by the clamp 156. The clamp 156 detachably holds the glass plate 2. Therefore, the clamp 156 is brought into contact with and separated from the glass plate 2.

[0052]

15 The glass plate 2 is etched inside the vacuum vessel 101 to generate particles. The particles are generated when the gas cluster 129 collides with the glass plate 2 or a peripheral member of the glass plate 2. The material of the
20 particles is, for example, glass, metal, or resin. The generated particles may stick to the clamp 156 during standby. In this state, when the clamp 156 approaches the glass plate 2, particles are caught between the glass plate 2 and the clamp 156. As a
25 result, defects may occur in the glass plate 2.

[0053]

Therefore, in the present embodiment, a protective-layer equipped glass plate 7 is prepared. The protective-layer equipped glass plate 7 includes
30 a glass plate 2 and a protective layer 6. The protective layer 6 includes a resin layer 61 in contact with the glass plate 2. The resin layer 61 may be a single layer or a plurality of layers. The

resin layer 61 does not contain filler and powder at least on the contact surface with the glass plate 2. This is because filler and powder may cause dust or a scratch. The resin layer 61 preferably does not contain filler and powder not only on the contact surface with the glass plate 2 but also in the inside.

[0054]

As the resin of the resin layer 61, vinyl acetate resin, ethylene-vinyl acetate copolymer resin, isobutene-maleic anhydride copolymer resin, acrylic copolymer resin, styrene-butadiene rubber copolymer, vinyl chloride resin, chloroprene rubber, nitrile rubber, epoxy resin, modified epoxy resin, silicone resin, modified silicone resin, urethane resin, EVA resin, ABS resin, polypropylene, high-density polyethylene, low-density polyethylene, polystyrene, polyester, polyamide, polyvinyl chloride, polycarbonate, PET (Poly Ethylene Terephthalate), POM (Poly Oxy Methylene), PBT (Poly Butylene Terephthalate), polyvinylidene chloride, PVA (Poly Vinyl Alcohol), or fluororesin is used. Further, as the resin material of the shield plate 161, PPSU (Poly Phenyl Sulfone), PSU (Poly Sulfone), PAR (Poly Arylate), PEI (Poly Ether Imide), PEEK (Poly Ethel Ethel Keton), PPS (Poly Phenylene Sulfide), PES (Poly Ethel Sulfone), PAI (Poly Amide Imide), LCP (Liquid Crystal Polymer), PTFE (Poly Tetra Fluoro Ethylene), PCTFE (Poly Chroro TriFluoro Ethylene), or PVDF (Poly Vinylidene DiFluoride) are used. These resins can be removed by the RCA cleaning or scrub cleaning, which will be described later.

[0055]

Since the resin layer 61 is softer than the glass plate 2, it is softer than the particles generated by the etching of the glass plate 2 and serves as a buffer material. That is, when the particles are caught between the clamp 156 and the glass plate 2, the resin layer 61 deforms so as to absorb the particles. Therefore, an occurrence of defects in the glass plate 2 can be suppressed.

10 [0056]

The thickness of the resin layer 61 is not particularly limited, but is, for example, 0.001 mm to 10 mm, and preferably 0.001 mm to 1 mm. When the thickness of the resin layer 61 is 0.001 mm or more, the thickness of the resin layer 61 is greater than the particle diameter of the particles, so that a function as a buffer material can be obtained. In the case where the thickness of the resin layer 61 is 10 mm or less, when the clamp 156 presses the resin layer 61, the shear deformation of the resin layer 61 is small and the positional deviation of the glass plate 2 is small. When the thickness of the resin layer 61 is 1 mm or less, there is little influence on the machining accuracy.

25 [0057]

The protective layer 6 includes only the resin layer 61 in the present embodiment, but may include a metal layer or a ceramic layer in addition to the resin layer 61. The metal layer and the ceramic layer are arranged outside the resin layer 61, that is, on the side opposite to the glass plate 2 with respect to the resin layer 61. As the metal of the metal layer, aluminum, copper, iron, nickel,

zinc, titanium, stainless steel or brass is used. These metals can be removed by the RCA cleaning, described below. As the ceramic of the ceramic layer, alumina, zirconia, aluminum nitride, silicon carbide, silicon nitride, forsterite, steatite, cordierite, sialon, machinable ceramic, barium titanate, lead zirconate titanate, ferrite, or mullite is used.

[0058]

10 The protective layer 6 is formed, for example, on the end face 23 of the glass plate 2. The plurality of protective layers 6 are arranged along the peripheral edge of the glass plate 2 at intervals. The protective layers 6 can be removed
15 more easily than when the protective layer 6 is disposed over the entire periphery of the glass plate 2. The protective layer 6 may be disposed at a position in contact with the clamp 156.

[0059]

20 When the orientation of the glass plate 2 is reversed as described above, local etching of the second main surface 22 of the glass plate 2 is naturally also possible. In this case, the protective layer 6 also serves as a buffer material.
25 That is, when the particles are caught between the clamp 156 and the glass plate 2, the resin layer 61 deforms so as to absorb the particles. Therefore, an occurrence of defects in the glass plate 2 can be suppressed.

30 [0060]

Next, details of S3 in FIG. 1 will be described with reference to FIG. 10. S3 in FIG. 1 includes S31 through S36 shown in FIG. 10.

[0061]

First, in S31 of FIG. 10, a protective layer 6 is formed on the glass plate 2. For example, a liquid containing the material of the protective layer 6 is applied to the glass plate 2, and solidified to form the protective layer 6. Since the liquid has fluidity, a protective layer following the surface shape of the glass plate 2 can be formed. The material of the protective layer 6 includes, for example, a thermosetting resin, a thermoplastic resin or an ultraviolet curing resin.

[0062]

Instead of applying the liquid containing the material of the protective layer 6 to the glass plate 2 and solidifying the material, a tape-like protective layer 6 may be stuck to the glass plate 2. Since the protective layer 6 solidified beforehand is stuck to the glass plate 2, the working time can be shortened. The material of the tape-like protective layer 6 includes a thermosetting resin, a thermoplastic resin or an ultraviolet curing resin.

[0063]

Alternatively, instead of applying the liquid containing the material of the protective layer 6 to the glass plate 2 and solidifying the material, the glass plate 2 may be covered with a frame-shaped protective layer 6 shown in FIG. 13. The frame-shaped protective layer 6 includes, for example, a frame-shaped plate portion 65 and a rib portion 66 protruding from the entire peripheral edge of the plate portion 65. The plate portion 65 has an opening 65a larger than the quality assurance

region 26 of the first main surface 21 of the glass plate 2, and contacts the peripheral region 27. On the other hand, the rib portion 66 comes into contact with the end face 23 of the glass plate 2.

5 The frame-shaped protective layer 6 can be separated from the glass plate 2 as it is, and can be put on another glass plate 2 again.

[0064]

Although S31 in FIG. 10 is executed after
10 S2 in FIG. 1 in the present embodiment, it may be executed before S2 in FIG. 1, and further may be executed before S1 in FIG. 1. However, S32 in FIG. 10 is executed after S2 in FIG. 1.

[0065]

15 Next, at S32 in FIG. 10, a protective-layer equipped glass plate 7 is prepared. Specifically, for example, the protective-layer equipped glass plate 7 obtained in S31 is carried into the vacuum vessel 101 of the processing
20 apparatus 100 shown in FIG. 6 and placed on the stage 151.

[0066]

Next, in S33 of FIG. 10, as shown in FIGS. 7 to 9, the protective-layer equipped glass plate 7
25 is held by the clamp 156 butted against the protective layer 6. The protective layer 6 serves as a buffer material. That is, when the particles are caught between the clamp 156 and the glass plate 2, the resin layer 61 deforms so as to absorb the
30 particles. Therefore, an occurrence of defects in the glass plate 2 can be suppressed.

[0067]

Next, in S34 of FIG. 10, the first main

surface 21 of the glass plate 2 is irradiated with the beam-shaped gas cluster 129. In order to move the irradiation point, a stage moving mechanism 152 moves the stage 151 two-dimensionally in the Y-axis direction and the Z-axis direction. By controlling the moving speed, the etching amount can be controlled, and the first main surface 21 can be flattened.

[0068]

Next, at S35 in FIG. 10, the protective-layer equipped glass plate 7 is released by the clamp 156. Thereafter, the protective-layer equipped glass plate 7 is carried out from the vacuum vessel 101 of the processing apparatus 100 to the outside.

[0069]

Next, in S36 of FIG. 10, the protective-layer equipped glass plate 7 is cleaned with a cleaning liquid to remove the protective layer 6. The cleaning includes, for example, scrub cleaning. In the scrub cleaning, the protective-layer equipped glass plate 7 is rubbed and washed with a brush, a sponge, or the like. The resin layer 61 and thus the protective layer 6 can be efficiently removed.

In the scrub cleaning, an alkaline solution containing a surfactant may be used as the cleaning liquid. The removal efficiency can be improved by the action of alkali. The scrub cleaning and an ultrasonic cleaning may be used in combination. The scrub cleaning may also be used as a part of the RCA cleaning described below.

[0070]

The cleaning of the protective-layer

equipped glass plate 7 may include the RCA cleaning. The RCA cleaning includes, for example, a SC-1 cleaning, a dilute hydrofluoric acid cleaning, and a SC-2 cleaning in this order. In the SC-1 cleaning,
5 a mixed aqueous solution of ammonium hydroxide (NH_4OH) and hydrogen peroxide (H_2O_2) is used as a cleaning liquid. In the dilute hydrofluoric acid cleaning, dilute hydrofluoric acid is used as the cleaning liquid. In the SC-2 cleaning, a mixed
10 aqueous solution of hydrochloric acid (HCl) and hydrogen peroxide is used as the cleaning liquid. The RCA cleaning may further include the SPM cleaning. In the SPM cleaning, a mixed aqueous solution of sulfuric acid (H_2SO_4) and hydrogen
15 peroxide is used as the cleaning liquid.
[0071]

When the orientation of the glass plate 2 is reversed as described above, local etching of the second main surface 22 of the glass plate 2 is
20 naturally also possible. In this case as well, the resin layer 61 of the protective layer 6 serves as a buffer material. That is, when the particles are caught between the clamp 156 and the glass plate 2, the resin layer 61 deforms so as to absorb the
25 particles. Therefore, an occurrence of defects in the glass plate 2 can be suppressed.
[0072]

Next, the clamp 156 according to a first variation of the embodiment will be described with
30 reference to FIG. 11. The clamp 156 according to τ this variation presses the peripheral region 27 of the first main surface 21 of the glass plate 2. A protective layer 6 is formed in the peripheral

region 27. When the particles are caught between the clamp 156 and the glass plate 2, the resin layer 61 deforms so as to absorb the particles.

Therefore, an occurrence of defects in the glass
5 plate 2 can be suppressed.
[0073]

The clamp 156 presses the glass plate 2 against the spacer 155. Therefore, the protective layer 6 may be formed on the second chamfered
10 surface 25 of the glass plate 2 and pressed against the spacer 155. When the particles are caught between the spacer 155 and the glass plate 2, the resin layer 61 deforms so as to absorb the particles. Therefore, an occurrence of defects in
15 the glass plate 2 can be suppressed.
[0074]

The plurality of protective layers 6 are arranged along the peripheral edge of the glass plate 2 at intervals. The protective layers 6 can
20 be removed more easily than when the protective layer 6 is disposed over the entire periphery of the glass plate 2. The protective layer 6 may be disposed at a position in contact with the spacer 155 or the clamp 156.
25 [0075]

As described above, the spacer 155 may press the peripheral region of the second main surface 22 instead of the second chamfered surface 25 of the glass plate 2. In this case, the
30 protective layer 6 is formed in the peripheral region of the second main surface 22 of the glass plate 2, and pressed against the spacer 155.
[0076]

Next, the clamp 156 according to a second variation of the embodiment will be described with reference to FIG. 12. The clamp 156 according to the present variation presses the first chamfered
5 surface 24 of the glass plate 2. A protective layer 6 is formed on the first chamfered surface 24. When the particles are caught between the clamp 156 and the glass plate 2, the resin layer 61 deforms so as to absorb the particles. Therefore, an occurrence
10 of defects in the glass plate 2 can be suppressed.
[0077]

The clamp 156 presses the glass plate 2 against the spacer 155. Therefore, the protective layer 6 may be formed on the second chamfered
15 surface 25 of the glass plate 2 and pressed against the spacer 155. When the particles are caught between the spacer 155 and the glass plate 2, the resin layer 61 deforms so as to absorb the particles. Therefore, an occurrence of defects in
20 the glass plate 2 can be suppressed.
[0078]

The plurality of protective layers 6 are arranged along the peripheral edge of the glass plate 2 at intervals. The protective layer 6 can be
25 removed more easily than when the protective layer 6 is disposed over the entire periphery of the glass plate 2. The protective layer 6 may be disposed at a position in contact with the spacer 155 or the clamp 156.
30 [0079]

As described above, the spacer 155 may press the peripheral region of the second main surface 22 instead of the second chamfered surface

25 of the glass plate 2. In this case, the protective layer 6 is formed in the peripheral region of the second main surface 22 of the glass plate 2, and pressed against the spacer 155.

5

EXAMPLES

[0080]

Experimental data will be described below. Example 1 below is a practical example, and Example 2 below is a comparative example.

10

[0081]

In Example 1, the first main surface 21 of the glass plate 2 was processed by the beam-shaped gas cluster 129 by the processing apparatus 100 shown in FIG. 6. Processing conditions were as follows:

15

Material of the glass plate 2: Silica glass containing TiO_2

Raw material gas: CF_4 gas

20

Acceleration voltage V_{ACC} : 60 kV

Arrangement of the protective layer 6:

Arrangement in FIG. 8

Dimensions of the protective layer 6: 15 mm × 6 mm × 0.35 mm thickness

25

Material of the protective layer 6: silicone resin

Structure of the clamp 156: Structure in FIG. 9.

[0082]

30

In Example 1, since the clamp 156 pushed the end face 23 of the glass plate 2 through the protective layer 6, no defect was visually found in the portion of the end face 23 of the glass plate 2

pushed by the clamp 156, after the protective layer 6 was removed by the cleaning liquid. This is because the protective layer 6 deformed such that stress concentration did not occur when the
5 particles were caught between the clamp 156 and the glass plate 2.

[0083]

In Example 2, the first main surface 21 of the glass plate 2 was processed with the beam-shaped
10 gas cluster 129 under the same processing conditions as in Example 1 except that the protective layer 6 was not used. In Example 2, since the clamp 156 was brought into contact with the end face 23 of the glass plate 2, a defect was visually found in the
15 portion of the end face 23 of the glass plate 2 pressed by the clamp 156.

[0084]

From the results of Examples 1 and 2, it can be seen that when the clamp 156 pushes the end
20 face 23 of the glass plate 2 through the protective layer 6, an occurrence of defects in the glass plate 2 due to contact with the clamp 156 can be suppressed.

[0085]

25 As described above, the processing method for a glass plate and the production method for a mask blank for EUVL according to the present disclosure have been described. However, the present disclosure is not limited to the above-
30 described embodiments. Various variations, modifications, substitutions, additions, deletions, and combinations are possible within the scope recited in claims. They are also of course within

the technical scope of the present disclosure.

[0086]

For example, the application of the glass plate processed by the processing method of the present disclosure is not limited to EUVL. The application of the glass plate may be as long as high flatness is required, and may be, for example, a medical apparatus. The glass composition of the glass plate may be suitable for the use of the glass plate.

[0087]

This application claims priority based on Japanese Patent Application No. 2020-084730 filed with the Japan Patent Office on May 13, 2020, and the entire content of Japanese Patent Application No. 2020-084730 is incorporated herein by reference.

DESCRIPTION OF SIGNS

[0088]

- 1 Mask blank for EUVL
- 2 Glass plate
- 21 First main surface
- 22 Second main surface
- 23 End face
- 24 First chamfered surface
- 25 Second chamfered surface
- 3 Reflection film
- 4 Absorption film
- 6 Protective layer
- 61 Resin layer
- 7 Glass plate with protective layer
- 100 Processing apparatus
- 129 Gas cluster

151 Stage
155 Spacer
156 Clamp

CLAIMS

[Claim 1]

5 A processing method for a glass plate
comprising:
preparing a protective-layer equipped
glass plate that includes a glass plate and a
protective layer containing a resin layer in contact
with the glass plate;
10 holding the protective-layer equipped
glass plate by a clamp butted against the protective
layer; and
etching a first main surface of the glass
plate by irradiating the first main surface with a
15 beam-like gas cluster while holding the protective-
layer equipped glass plate by the clamp.

[Claim 2]

20 The processing method according to claim
1, wherein
the protective layer is formed on an end
face of the glass plate perpendicular to the first
main surface, on a first chamfered surface formed at
a boundary between the first main surface and the
25 end face, or in a peripheral region on the first
main surface of 5 mm or less from the end face.

[Claim 3]

30 The processing method according to claim
2, wherein
the glass plate further includes a second
main surface opposite to the first main surface, and
a second chamfered surface formed at a boundary

between the second main surface and the end face,

the protective layer is further formed in
a peripheral region on the second main surface of
the glass plate of 5 mm or less from the end face or
5 in the second chamfered surface, and is pressed
against a spacer by the clamp, and

the spacer forms a gap between the glass
plate and a stage disposed facing the second main
surface of the glass plate.

10

[Claim 4]

The processing method according to any one
of claims 1 to 3 further comprising:

removing the protective layer after
15 releasing the protective-layer equipped glass plate
by the clamp.

[Claim 5]

The processing method according to claim
20 4, wherein
the protective layer is removed by scrub
cleaning.

[Claim 6]

25 The processing method according to claim 4
or 5, wherein
the protective layer is removed with an
alkaline solution containing a surfactant.

30 [Claim 7]

The processing method according to any one
of claims 1 to 6 further comprising:

applying a liquid containing a material of

the protective layer to the glass plate, and
solidifying the liquid to form the protective layer.

[Claim 8]

5 The processing method according to any one
of claims 1 to 6 further comprising:

 sticking a protective layer in a form of
tape to the glass plate.

10 [Claim 9]

 The processing method according to any one
of claims 1 to 6 further comprising:

 covering the protective-layer equipped
glass plate in a form of a frame in a separable
15 manner.

[Claim 10]

 A production method for mask blank for
EUVL comprising:

20 flattening a first main surface of a glass
plate using the processing method according to any
one of claims 1 to 9;

 forming a reflection film that reflects
EUV light, the reflecting film being formed on the
25 first main surface of the glass plate; and

 forming an absorption film that absorbs
EUV light, the absorption film being formed on the
reflection film.