

SPECIFICATION

[TITLE OF INVENTION]

METHOD OF MANUFACTURING A MASK BLANK SUBSTRATE, METHOD OF MANUFACTURING A MASK BLANK, AND METHOD OF MANUFACTURING A TRANSFER MASK

[TECHNICAL FIELD]

[0 0 0 1]

This invention relates to a method of manufacturing a mask blank substrate, a method of manufacturing a mask blank using the mask blank substrate, and a method of manufacturing a transfer mask using the mask blank, more particularly, to a method of manufacturing a mask blank substrate, a method of manufacturing a mask blank, and a method of manufacturing a transfer mask with fewer defects.

[BACKGROUND]

[0 0 0 2]

Recently, there is an increasing need for reduction in defects on a mask blank substrate, a mask blank, and a transfer mask, since a defect on a mask blank substrate or a transfer mask causes transfer defects during wafer exposure. As a method for reducing defects, wet etching of a mask blank substrate is known in which a mask blank substrate is etched with alkali before forming a thin film for forming a transfer pattern on the mask blank substrate. The wet etching, which is a type of chemical etching, is conducted by wetting a surface of a glass substrate with an alkaline solution by dip method, paddle method, etc. In etching by means of paddle method, since fresh etching liquid is constantly supplied to each one of the glass substrate, the surface of the glass substrate can be kept clean, which is an advantage over dip method in view of cross contamination.

[0 0 0 3]

Publication 1 is cited as a technique employing paddle etching. Publication 1 discloses a method of paddle etching a glass substrate surface using 5% NaOH aqueous solution at 65°C.

As an example of applying paddle method in cases other than wet etching, Publication 2 describes a method of cleaning a substrate. Publication 2 describes an example of cleaning substrates such as a silicon wafer and a photomask.

[PRIOR ART PUBLICATIONS]

[PATENT PUBLICATIONS]

[0 0 0 4]

[Publication 1]

Japanese Patent Application Publication 2005-221928

[Publication 2]

Japanese Patent Application Publication 2005-251806

[SUMMARY OF THE INVENTION]

[PROBLEMS TO BE SOLVED BY THE INVENTION]

[0 0 0 5]

As described in Publication 1, when etching is carried out with a heated etching liquid, etching rate becomes significantly higher compared to an etching liquid at room temperature. On the other hand, in cases where the temperature of the etching liquid is higher than the temperature of a glass substrate, temperature of the etching liquid on the glass substrate becomes higher at a point where the etching liquid is supplied (dropped) and the temperature is lower at points farther therefrom. Namely, in cases where the temperature of the substrate is lower than that of the etching liquid, etching temperature at the point where the etching liquid is dropped is high, and the etching liquid temperature is lower at points farther away from the point where the liquid is dropped, causing low etching rate.

A glass substrate for a mask blank is normally rectangular. Therefore, at the edge of the glass substrate, especially at the corner, heat is released from the side surface of the glass substrate in addition to its main surface, so that the temperature of the substrate on that portion is likely to fall. Further, since a glass material has low heat conductivity, heat does not readily transfer to the region of lower temperature from other regions of the glass substrate, so that temperature distribution is likely to occur on the glass substrate. Therefore, when the glass substrate is not under a heated condition during etching process, a distribution may occur in lowering of the temperature (namely, temperature distribution occurs on the etching liquid on the substrate).

Generally, the higher the etching temperature, the faster the etching reaction proceeds, and the lower the etching temperature, the slower the etching reaction occurs. Therefore, when temperature distribution occurs on the etching liquid on the substrate, progression of etching reaction, namely, etching depth, differs on the substrate, causing distribution.

[0 0 0 6]

Wet etching is effective to remove foreign matters on a glass substrate surface by lift-off process. Therefore, the action of removing foreign matters correlates to etching depth. To achieve sufficient removal of foreign matters throughout the substrate, the entire region on the substrate should be etched to a certain etching depth. If distribution exists in etching temperature on the substrate, since etching depth should be aligned with a location with low etching temperature, namely, a location where etching reaction is slow, an excess etching depth is created at a location where etching temperature is high and etching reaction is fast. While etching is effective in removing foreign matters, it roughens the surface as etching reaction proceeds. Namely, if there is a distribution in etching temperature, a difference in surface texture (roughness) occurs between a region with low etching

temperature and slow etching rate, and a region with high etching temperature and fast etching reaction. Further, when a location loaded with foreign matters is etched, a difference in etching depth is created in the shadow portion of the foreign matters and the field, which may cause an apparent convex defect. Namely, a problem occurs where a process for removing foreign matter defect causes a defect associated with etching, which cannot lead to reduction of defects in a mask blank substrate.

[0007]

Further, since the etching reaction causes roughening of the surface of the mask blank substrate, it is preferable to minimize wet etching to minimize the increase of roughness on the surface of the mask blank substrate. Particularly, in the case of a mask blank substrate for EUV (Extreme Ultra Violet) lithography, a multi-component low-thermal expansion glass is used as a substrate. In the case of a glass made of a multi-component material, since reactivity with an etching liquid differs in each of the components, roughness is likely to occur compared to single-component synthetic quartz. Therefore, it is necessary to proceed with wet etching reaction in an in-plane uniform manner, and efficiently in a short time. Greater roughness on the surface of the mask blank substrate causes an increase in roughness on a multilayer film formed on the surface of the mask blank substrate. This roughness may change reflectance of the multilayer film to cause reduction in efficiency as a reflective mask. Further, more precise defect inspection sensitivity is required in an EUV lithography mask blank, since phase defects in particular cause significant problems, and there may be a problem where an increase in roughness becomes a source of background noise causing reduction in defect inspection sensitivity.

[0008]

In addition, in a spin table normally used in paddle etching, an etching liquid supplied to the surface of the glass substrate moves to the rear side of the glass substrate so that another cleaning step is required for the rear surface.

[0009]

Publication 2 discloses a technique of cleaning a substrate including the steps of supplying a cleaning liquid of normal temperature on a surface of the substrate of a silicon wafer, a photomask, etc., supplying pure water of normal temperature on the rear surface, and thereafter supplying pure water of high temperature.

Since the technique described in Publication 2 is a technique where the cleaning liquid dissolves or elutes foreign matters for removal, the technique may not be able to remove stable inorganic particles such as polishing grain. Therefore, particles such as silica, alumina, and ceria attached to the surface of the glass

substrate, etc. may not be removed.

Instead of not removing foreign matters such as the above mentioned particles, the technique of Publication 2 does not cause the problem of roughness as stated above. This is because of the premise that the cleaning liquid substantially has no etching action on the substrate. Namely, there is no need to consider generation of roughness and in-plane distribution of roughness, and it is sufficient if a certain foreign matter removing effect is obtained on the entire surface of the substrate, so that precise temperature control such as temperature distribution on the substrate in the cleaning step is unnecessary. Therefore, even in a glass substrate with large heat capacity, a process that may cause temperature distribution on the glass substrate, which may elevate the temperature of pure water supplied to the rear surface during cleaning step from room temperature to high temperature, can be selected.

On the other hand, in removing foreign matters by wet etching, foreign matters firmly attached to the substrate such as inorganic compounds can also be removed. However, to securely remove such foreign matters, generation of roughness due to etching and roughness distribution caused by variation in etching depth should be considered.

[0 0 1 0]

In view of the above, the object of this invention is to provide a method of manufacturing a mask blank substrate, a method of manufacturing a mask blank, and a method of manufacturing a transfer mask that can inhibit generation of distribution and variation in etching depth even if a heated wet etching liquid is used.

[MEANS FOR SOLVING THE PROBLEM]

[0 0 1 1]

To solve the above problems, this invention has the following structures.

[0 0 1 2]

(Structure 1)

A method of manufacturing a mask blank substrate comprising a step for wet etching a mask blank substrate having two main surfaces consisting of first and second main surfaces by introducing an etching liquid to the first main surface to cover the first main surface with the etching liquid, wherein the step for wet etching is conducted under a condition where the etching liquid adjusted to a temperature higher than a normal temperature is supplied to the first main surface, and a liquid adjusted to a temperature higher than the normal temperature is supplied to the second main surface.

[0 0 1 3]

(Structure 2)

A method of manufacturing a mask blank substrate according to Structure 1, wherein the wet etching is conducted by paddle etching.

[0014]

(Structure 3)

A method of manufacturing a mask blank substrate according to Structure 1 or 2, wherein the wet etching comprises at least one or more etchants, boiling point of the etchant being higher than a temperature of the etching liquid supplied to the first main surface.

[0015]

(Structure 4)

A method of manufacturing a mask blank substrate according to any one of Structure 1 to Structure 3, wherein supplying the liquid adjusted to a temperature higher than the normal temperature to the second main surface is carried out prior to commencement of introduction of the etching liquid.

[0016]

(Structure 5)

A method of manufacturing a mask blank substrate according to any one of Structure 1 to Structure 4, wherein temperature difference of the wet etching liquid and the liquid adjusted to a temperature higher than the normal temperature is within $\pm 10^{\circ}\text{C}$.

[0017]

(Structure 6)

A method of manufacturing a mask blank substrate according to any one of Structure 1 to Structure 5, wherein the liquid adjusted to a temperature higher than the normal temperature supplied to the second main surface is flowed.

[0018]

(Structure 7)

A method of manufacturing a mask blank substrate according to any one of Structure 1 to Structure 6 comprising a cleaning step using a cleaning liquid after the step for wet etching,

wherein at least a certain time during the cleaning step is conducted under a condition where the liquid adjusted to a temperature higher than the normal temperature is supplied to the second main surface.

[0019]

(Structure 8)

A method of manufacturing a mask blank substrate according to any one of Structure 1 to Structure 7, wherein the liquid adjusted to a temperature higher than the normal temperature is an aqueous solution.

[0020]

(Structure 9)

A method of manufacturing a mask blank comprising a step of

forming a transfer pattern thin film directly or via another layer on a first main surface of a mask blank substrate obtained from the method of manufacturing a mask blank substrate according to any one of Structure 1 to Structure 8.

[0021]

(Structure 10)

A method of manufacturing a transfer mask comprising a step of patterning a transfer pattern thin film of a mask blank obtained from the method of manufacturing a mask blank according to Structure 9 to form a transfer pattern.

[EFFECT OF THE INVENTION]

[0022]

According to this invention, a liquid adjusted to a temperature higher than a normal temperature is supplied to both of a first main surface and a second main surface, e.g., front and rear surfaces of the mask blank substrate, namely, an wet etching liquid adjusted to a temperature higher than a normal temperature and a liquid such as pure water adjusted to a temperature higher than a normal temperature are supplied to the first main face and the second main face, respectively, at the beginning of wet etching. This inhibits in-plane distribution of the glass substrate temperature. Regarding etching reaction, while the reaction rate differs due to contact temperature of the etching liquid and the glass substrate, according to this invention, etching reaction level can be made even by inhibiting in-plane distribution of glass substrate temperature.

The effect of wet etching of a mask blank substrate, a type of chemical etching, is the removal of foreign matters by lift-off effect, which is particularly effective for the removal of minute foreign matters. On the other hand, since etching is conducted on the surface of the mask blank substrate, roughness on the surface proceeds as etching reaction proceeds. Further, during lift-off process, a difference in etching depth of the shadow portion of the foreign matters and the field portion on the surface of the substrate causes irregularities. Thus, excess etching may cause an increase in roughness and generation of new defects. However, according to this invention, in-plane distribution of etching is made even to prevent partial excess etching to thereby inhibit the generation of defects caused by etching.

As stated above, according to the method of manufacturing the mask blank substrate, the method of manufacturing the mask blank, and the method of manufacturing the transfer mask of this invention, various problems caused by generation of distribution and variation in etching reaction can be inhibited.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[0023]

[FIG. 1] Fig. 1 is a plan view schematically showing a structure of the wet etching device used in this invention, (a) showing a top view, and (b) showing a bottom view;

[FIG. 2] Fig. 2 is a cross sectional view schematically showing a structure of the wet etching device used in this invention;

[FIG. 3] Fig. 3 is a flow diagram of a manufacturing step of the example.

[EMBODIMENTS FOR CARRYING OUT THE INVENTION]

[0024]

The embodiments of this invention are concretely described below with reference to the drawings. The embodiments are some of the cases for embodying this invention, and are not for limiting this invention within that scope.

[0025]

[Manufacture of Mask Blank Substrate]

1. Materials of Mask Blank Substrate

A mask blank substrate is not particularly limited as long as it has transparency to an exposure wavelength to be used. In this invention, synthetic quartz glass substrate and various other glass substrates (e.g., soda-lime glass, aluminosilicate glass, etc.) can be used, and, among them, synthetic quartz glass substrate is preferable as a phase shift mask blank glass substrate or a binary mask blank glass substrate used for forming a high-definition transfer pattern, for having high transmittance of UV radiation with short wavelength such as ArF excimer laser (wavelength 193nm).

[0026]

A low-thermal expansion glass used for an EUV mask is also applicable. Examples of EUV glass include, for example, $\text{SiO}_2\text{-TiO}_2$ glass (binary ($\text{SiO}_2\text{-TiO}_2$) and ternary ($\text{SiO}_2\text{-TiO}_2\text{-SnO}_2$, etc.)) having low thermal expansion property, e.g., $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Li}_2\text{O}$ crystallized glass, so-called multi-component glass.

[0027]

2. Polishing Step and Cleaning Step Before Etching

In the manufacturing step of the mask blank substrate, subsequent to polishing step, cleaning step is carried out to eliminate particles (e.g., foreign matters such as polishing grain attached to the surface of the glass substrate) present on the surface of the mask blank substrate.

[0028]

In the polishing step, a polishing pad is contacted on the surface of the mask blank substrate, a polishing liquid containing polishing grain is supplied to the surface of the mask blank substrate, the mask blank substrate and the polishing pad are moved relative to each other, and the surface of the mask blank substrate is polished. For example, a mask blank substrate is pressed onto a polishing surface plate having a polishing pad attached thereto, the polishing surface plate and the mask blank substrate are moved

relative to each other (i.e., the polishing pad and the mask blank substrate are moved relative to each other) while supplying a polishing liquid containing polishing grain, to thereby polish the surface of the mask blank substrate. As polishing grain, colloidal silica is preferably used at least in final polishing of precision polishing step, for favorable smoothness and flatness of the mask blank substrate can be obtained. In this polishing step, for example, a double side polishing device of a planetary gear can be used.

[0029]

After superprecision polishing step, cleaning is conducted to remove colloidal silica grain. Next, the main surface and an end surface of the mask blank substrate are brush cleaned, and spin cleaning is conducted with pure water. Instead of brush cleaning, the glass substrate can be subjected to dip washing where the glass substrate is immersed in a liquid bath of an aqueous solution of hydrofluoric acid, or subjected to cleaning using a detergent containing a surfactant.

[0030]

3. Wet Etching Step

The etching liquid used in the wet etching step for removing foreign matters on the mask blank substrate is not particularly limited, as long as the liquid is a chemical solution that can etch the materials forming the surface of the mask blank substrate. Some of the examples are acidic aqueous solution including hydrofluoric acid, and aqueous solution of an alkaline compound.

Preferably, an aqueous solution of strong alkaline compound is used. When an aqueous solution of an alkaline compound is used as the etching liquid, the etching liquid preferably has pH of 10 or more, more preferably 12 or more, and particularly 13 or more. An aqueous solution of alkaline compound renders zeta potential of the surface of the glass substrate negative. This causes foreign matters similarly having negative zeta potential to repulse the surface of the glass substrate, thereby preventing reattachment of the foreign matters. Therefore, the aqueous solution of alkaline compound is advantageous compared to acid solutions such as hydrofluoric acid in view of effect of removing foreign matters.

[0031]

As for the type of alkaline compound, any of inorganic alkaline compound and organic alkaline compound can be used.

Inorganic alkaline compounds include, for example, hydroxide of alkali metal such as KOH, NaOH, LiOH, RbOH, and CsOH, and hydroxide of alkali earth metal such as $\text{Ca}(\text{OH})_2$ and $\text{Sr}(\text{OH})_2$. Among the above, since Na ion (Na^+) and K ion (K^+) can stably coexist with silicon ion (SiO_3^{2-} , etc.) isolated from the glass substrate, aqueous solutions of KOH, NaOH with these ions dissociated are

particularly preferable in stably proceeding etching reaction. In the case of using other alkaline compounds as a solute, alkaline salt (e.g., carbonate) for adding Na ion (Na^+) or K ion (K^+) can be added to enhance etching efficiency.

[0 0 3 2]

Since concentration of etching liquid depends on concentration of hydroxy ion (OH^-) that contributes to the etching reaction, the concentration can be adjusted to the range of pH value given above. For example, in using strong alkaline compound with large dissociation constant such as KOH and NaOH, those having alkali concentration of 0.01mol/L or more are preferably used. The concentration is preferably 0.1mol/L or more, and particularly 1 mol/L or more. Since rinsing time after etching may take a long time when an etching liquid with solute of poor volatility such as NaOH and KOH is used, it is preferable to adjust the sum of concentration of inorganic alkaline components to 3mol/L or less. When an etching liquid containing an inorganic alkaline component alone is used, pH of 13 to 14 is preferable.

[0 0 3 3]

An aqueous solution of an organic alkaline compound can also be used as an etching liquid. In the case of an organic alkaline compound, the etching liquid has pH of 9 or more, preferably 10 or more, and more preferably 10.5 or more.

In using an organic alkaline compound as a solute of an etching liquid, quaternary ammonium hydroxide can be used, for example, tetraalkylammonium hydroxide can preferably be used.

Particularly preferably, tetraalkylammonium hydroxide having lower alkyl group with 1 to 4 carbons included in alkyl group is used. Concrete examples include tetramethylammonium hydroxide (TMAH), tetraethylammonium hydroxide (TEAH), tetrapropylammonium hydroxide (TPAH), and tetrabutylammonium hydroxide (TBAH).

Those having alkoxy group can be given as other examples of quaternary ammonium hydroxide. Concrete examples include trimethyl hydroxyethyl ammonium hydroxide, methyltri(hydroxyethyl) ammonium hydroxide, tetra(hydroxyethyl)ammonium hydroxide, and benzyl trimethyl ammonium hydroxide (BTMAH).

Among organic alkaline substances, for example, compounds such as tertiary alkylamine and ammonia with weak basic have poor capacity in glass etching. Therefore, they are inappropriate to be used alone as an etchant of an etching liquid for wet etching. Further, when ammonia is used as a component of the etching liquid, ammonia is adsorbed to the surface of the glass substrate, reacts with cleaning liquid components (e.g., sulfate ion) to be used in the following cleaning step, and the precipitated product (e.g., ammonium sulfate) causes haze, thus making it unpreferable.

[0 0 3 4]

Supply temperature of the wet etching liquid should be at

normal temperature or more, preferably 40°C or more, and particularly 60°C or more. When an inorganic alkaline compound having no volatility is used as a solute, temperature of etching liquid is preferably 95°C or less. A solute is concentrated due to volatilization of water as a solvent at locations farther away from the location where the etching liquid was supplied, which may cause concentration distribution of the etching liquid. The temperature is preferably 80°C or less. Normal temperature herein indicates the temperature of external environment when wet etching is conducted. When the wet etching device is placed inside a clean room or a clean booth, the normal temperature indicates the temperature within the clean room and the clean booth. In semiconductor relations, clean rooms and clean booths are often operated at 23°C, and in many cases, the environmental temperature is adjusted to 23°C around the semiconductor manufacturing device for determining processing condition and quality control. Optimization of properties and quality control of chemical solutions such as a resist and a developing solution are also conducted with 23°C as default. Thus, normal temperature is often set as 23°C, but without limitation.

[0035]

A wet etching liquid includes at least one or more etchants, with its boiling point preferably higher than the temperature of the etching liquid mentioned above. Since decrease in solubility due to temperature elevation and decrease in concentration due to volatilization of solute do not occur due to the boiling point of the etchant being higher than the supply temperature of the etching liquid, it is preferable for stability of the etching liquid. For example, when an inorganic strong alkaline component such as hydroxide of alkali metal is used as an etchant, due to its high boiling point and extremely low volatility (vapor pressure) in an environment of 100°C or less, decrease in concentration due to volatilization of solute is unlikely to occur, even if the wet etching liquid is used under a high temperature (basically 95°C or less as mentioned above).

In the case of using an organic alkaline compound as an etchant, four methyl groups among quaternary ammonium hydroxide are the substituent group, boiling point of low molecular weight/low boiling point tetramethylammonium hydroxide (TMAH) is 130°C or more, and reduction in concentration due to volatilization is unlikely to occur even if a wet etching liquid including a typical quaternary ammonium hydroxide as an etchant is used at high temperature.

[0036]

A rear surface supply liquid is supplied in the form of a liquid film flow covering the entire rear surface from the etching step to the cleaning step.

The temperature of the rear surface supply liquid is at normal

temperature or higher, the difference in temperature with the etching liquid is preferably 10°C or less, more preferably 5°C or less, and particularly 3°C or less. When the temperature difference with the etching liquid becomes 10°C or more, temperature distribution occurs on the glass substrate due to the temperature difference with the etching liquid so that variation occurs in etching rate and distribution occurs in the etching amount of the surface of the glass substrate. The variation and distribution in etching rate lead to variation in surface roughness of the surface of the mask blank substrate, size and number of defects caused by distribution and the wet etching, and distribution.

"Liquid film flow" herein indicates a condition where substantially the entire rear surface is wetted with the rear surface supply liquid accompanying flow, and temperature of the substrate can be controlled from the rear surface side by the rear surface supply liquid. Therefore, a region where wetting is not made locally due to bubbles, etc. formed in the rear surface supply liquid, and interruption of wetting due to temporary stop, etc. caused by change in supply level of the rear surface supply liquid are included in the concept of the liquid film flow herein.

[0037]

In a wet etching liquid that is highly temperature dependent (e.g., alkaline etching liquid), etching rate (elution rate) increases twice or more when temperature elevates by 10°C. For example, in the case of alkali etching, etching rate at 75°C becomes 2.5 times the etching rate of 65°C. Etching rate and temperature of a wet etching liquid are substantially proportional, and an increase of 5°C causes a roughly 1.5 times increase in the etching rate. Tolerable irregularity on the surface of the mask blank substrate caused by wet etching depends on the miniaturization generation and application layer of the transfer mask manufactured using the mask blank substrate. For example, tolerable irregularity on a gate layer (also referred to as poly layer) is small, and in a mask blank substrate for EUV lithography mask where a phase defect of a multilayer film is a significant problem, tolerable irregularity is extremely small at a level of 1 nm. Therefore, depending on the object to be applied, the temperature difference of the wet etching liquid and the rear surface supply liquid is preferably 5°C or less, and particularly 3°C or less.

[0038]

Component of the rear surface supply liquid is not particularly limited as long as the liquid does not react with the wet etching liquid and is stable at the temperature during wet etching, most preferably, water. Water herein indicates pure water such as ion exchange water, with resistivity of $1.0 \times 10^6 \Omega/\text{cm}$ or more, and preferably $1.0 \times 10^8 \Omega/\text{cm}$ or more.

It is preferable when water is used, since solvent of the

wet etching liquid is water, reactivity such as unexpected generation of heat and precipitation of the solute (alkaline component) of the etching liquid does not occur during mixture with the wet etching liquid and the liquid (water) to be supplied to the rear surface, and in addition, temperature control with the etching liquid is easy. Further, the rear surface can always be kept clean substantially without components other than water. What is also preferable, by using only pure water, is that residue does not remain after drying so that there is no need to conduct further cleaning of the rear surface. As stated above, it is preferable since unavoidable reaction with etching liquid and generation of heat can be inhibited by using water.

[0039]

Further, when a mixture of water and an organic solvent such as ethyl alcohol is used, viscosity of the liquid can be adjusted so that a stable supply of the liquid over the entire rear surface can be achieved. Other than the above, aqueous solutions where residues do not remain after cleaning can be used, such as hydrogen peroxide solution, ammonia solution, and carbonated water.

Wet etching liquid can be used as the rear surface supply liquid, by which etching on the rear surface can be conducted in synchronization.

[0040]

Supply of the rear surface liquid is not particularly limited, as long as a liquid film flow is formed on the rear surface. For example, a plurality of supply openings can be formed on a portion opposing the rear surface of the mask blank substrate, so that the entire rear surface is wetted by the rear surface supply liquid. Preferably, a hole can be created to form a radial liquid film flow on the rear surface. By constant liquid film flow in a radial manner, a flow from the center of the glass substrate towards the edge is created, so that the etching liquid dropped from the surface is inhibited from moving to the rear surface. Further, it is favorable that partial accumulation of the liquid film flow is prevented. Preferably, the rear surface supply liquid is supplied in a non-circulating manner without reuse of used liquid. Since fresh liquid constantly covers the rear surface, even if unavoidable particles are included in the rear surface supply liquid, the particles do not remain on the rear surface of the glass substrate and are flushed immediately.

[0041]

Methods of wet etching include paddle etching, spin etching, and spray etching, which are conducted by supplying an etching liquid on the surface to be etched, which can be carried out alone or in combination. Paddle etching and spin etching are particularly effective, which are preferably combined. By spinning during the spin etching, the mask blank substrate can be

quickly wetted with the etching liquid, and after wetting, subsequent paddle etching can prevent variation in etching progress due to the difference in contact time with the etching liquid, avoids risk of cross contamination, and also reduces the amount of the etching liquid to be used by employing paddle etching. Further, uniform etching reaction can be proceeded with a uniform temperature of the substrate surface and with the liquid film of the etching liquid formed on the substrate surface by paddle etching having substantially equal thickness as in this structure. Paddle etching is a method where etching is conducted with an etching liquid statically loaded entirely on the first main face of the substrate to be processed. Due to the rather long time period of the static condition, in-plane distribution and temporal change in wet etching liquid temperature are likely to occur by environmental influence. Since the mask blank substrate is normally rectangular in shape and the surface area per unit volume is not constant, in cases where the substrate is not under a heated condition, distribution may occur in lowering of the temperature (i.e., temperature distribution occurs in the etching liquid on the substrate).

[0 0 4 2]

After etching, a cleaning step is carried out for removing the etching liquid remaining on the mask blank substrate. Since the major purpose of the cleaning step is to remove the etching liquid, at least pure water cleaning should be carried out. An example of the cleaning method is spin cleaning. Preferably, a cleaning water with ultrasonic wave applied thereto (ultrasonic wave cleaning water) or warm water of about 40°C to 60°C is supplied on the mask blank substrate so that alkaline component adsorbed to the surface of the mask blank substrate can be efficiently removed. Particularly effective cleaning is made by a combination of spin cleaning and ultrasonic wave cleaning water or warm water. Wet etching step and cleaning after the wet etching is preferably conducted consecutively several times, e.g., three to five times.

[0 0 4 3]

Next, timing including commencement of supplying the wet etching liquid and the rear surface supply liquid is mentioned. As stated above, for the object of this invention (inhibiting in-plane distribution in etching reaction), it is important that etching is conducted in a manner where the wet etching liquid is supplied and held on the entire surface of the first main face (first main surface) of the mask blank substrate at a temperature higher than normal temperature and not to generate temperature distribution. Therefore, it is preferable to heat the first main face of the mask blank substrate to a temperature similar or close to that of the wet etching liquid before supplying the wet etching liquid to the mask blank substrate. One idea on the above is, for example, pure water adjusted to the same temperature as the wet

etching liquid is supplied to the first main face of the mask blank substrate for pre-heating before supplying the wet etching liquid. The mask blank substrate has low heat conductivity as seen in synthetic quartz glass as a typical example, and those with great heat capacity are the mainstream, and also have a certain thickness (e.g., thickness of 6.35mm). Conventionally, it was assumed that temperature control with sufficiently less in-plane distribution can be made on the wet etching liquid loaded on the first main face of the mask blank substrate by the above pre-heating step. However, when actually evaluated, inhibition of in-plane distribution of temperature was insufficient, resulting in low temperature at the outer peripheral portion of the mask blank substrate. To solve this problem, in this invention, the rear surface supply liquid with its temperature controlled to the temperature similar or close to (temperature higher than normal temperature) that of the wet etching liquid is supplied to the rear surface (second main surface) of the mask blank substrate. The timing to supply the rear surface supply liquid must be during at least a certain time during the wet etching step, and the timing to start supplying is preferably simultaneous with commencement of supplying the wet etching liquid or prior thereto, and more preferably, at the preheating step mentioned above. Further, the timing to stop supplying the rear surface supply liquid is preferably simultaneous with completion of the wet etching or thereafter. While a cleaning step using pure water, etc. is conducted after completion of the wet etching, in this cleaning step, it is further preferable that temperature control by the rear surface supply liquid is carried out until the wet etching is replaced by the cleaning liquid. While the mask blank substrate has low heat conductivity and great heat capacity, supplying the temperature-controlled rear surface liquid can carry out temperature control with sufficiently less in-plane distribution.

In this specification, "supplying rear surface supply liquid (liquid adjusted to a temperature higher than the normal temperature)" in a certain step indicates, unless particularly specified, that the liquid is supplied during at least a certain time during the step, regardless of whether intermittent or continuous.

[0 0 4 4]

[Manufacture of Mask Blank]

A thin film is formed on a mask blank substrate after completion of the cleaning step, and a light shielding film for use in a binary mask blank, a light-semitransmissive film for a half tone phase shift mask blank, or a multilayer reflecting film for reflective mask, and functional films additional thereto are formed in accordance with the types of the mask blank substrate and the purpose of the transfer mask to be manufactured.

[0 0 4 5]

(1) Binary Mask Blank

The binary mask blank is manufactured by forming a thin film including a light shielding film on a synthetic quartz glass substrate processed up to the wet etching step. The light shielding film (transfer pattern thin film) is formed from materials including a simple transition metal such as chromium, tantalum, ruthenium, tungsten, titanium, hafnium, molybdenum, nickel, vanadium, zirconium, niobium, palladium, and rhodium, or a compound thereof. One example is a light shielding film formed from chromium, or chromium compound including chromium and one or more elements selected from oxygen, nitrogen, carbon, etc. Another example is a light shielding film formed from a tantalum compound including tantalum and one or more elements selected from oxygen, nitrogen, boron, etc.

[0 0 4 6]

Such a binary mask blank includes a light shielding film configured as a double layer structure of a light shielding layer and a surface reflection preventing layer, and a three layer structure having a rear surface reflection preventing layer between the light shielding layer and the glass substrate. The composition of the light shielding film in the film thickness direction may be a composition gradient film that varies continuously or in stages.

[0 0 4 7]

(2) Phase Shift Mask Blank

For a phase shift mask blank, a half tone phase shift mask is manufactured that is configured to have a light-semitransmissive film (transfer pattern thin film) formed on a synthetic quartz glass substrate that has been processed up to the wet etching step, in which the light-semitransmissive film is patterned and provided with a shift portion.

In such a phase shift mask, to avoid pattern defects of the glass substrate to be transferred by the light-semitransmissive film pattern formed on the transfer region based on a light transmitted through the light-semitransmissive film, there is a configuration including a light-semitransmissive film on a glass substrate, and further a light shielding film (light shielding zone) thereon. In addition to the half tone phase shift mask blank, there are mask blanks for an enhancer-type phase shift mask and for a Levenson phase shift mask which is a glass substrate dug-down type where a glass substrate is dug by etching, etc. to provide a shift portion.

[0 0 4 8]

The light-semitransmissive film of the halftone phase shift mask blank is adapted to transmit light having an intensity that does not substantially contribute to exposure (e.g., 1% to 30%, and preferably 1% to 20% to exposure wavelength) and has a

predetermined phase difference (e.g., 180 degrees). By means of the light-semitransmissive portion onto which the light-semitransmissive film is patterned and a light-transmissive portion formed with no light-semitransmissive film and adapted to transmit light having an intensity that substantially contributes to exposure, there is provided a relationship in which the phase of the light transmitted through the light-semitransmissive portion is substantially inverted with respect to the phase of the light transmitted through the light-transmissive portion. As a consequence, the lights having passed near the boundaries between the light-semitransmissive portion and the light-transmissive portion and bent into the others' regions due to the diffraction phenomenon cancel each other out. This makes the light intensity at the boundaries approximately zero to thereby improve the contrast, i.e., the resolution, at the boundaries.

[0 0 4 9]

The light-semitransmissive film is formed from materials including, e.g., a compound of transition metal and silicon (including transition metal silicide), the material including, as primary components, both the transition metal and silicon, and at least one of oxygen, nitrogen, and carbon. The transition metals include molybdenum, tantalum, tungsten, titanium, hafnium, nickel, vanadium, zirconium, niobium, palladium, ruthenium, rhodium, chromium, or the like.

Further, in the case of a configuration where a light shielding film is formed on a light-semitransmissive film, since the materials for the light-semitransmissive film include transition metal and silicon, the material of the light shielding film preferably includes chromium, or chromium compound including chromium and elements such as oxygen, nitrogen, and carbon which has etching selectivity (has etching resistance) on the light-semitransmissive film.

[0 0 5 0]

Since a Levenson phase shift mask is manufactured from a mask blank having the structure similar to a binary mask blank, the structure of the pattern forming thin film is similar to the light shielding film of the binary mask blank. While the light-semitransmissive film of the mask blank for an enhancer type phase shift mask transmits light with intensity that does not substantially contribute to exposure (e.g., 1% to 30% to exposure wavelength), the phase difference of the film generated by the transmitting exposure light is small (e.g., phase difference of 30 degrees or less, and preferably 0 degree), which is the difference with the light-semitransmissive film of the half tone phase shift mask blank. While the material for the light-semitransmissive film includes elements similar to those of the light-semitransmissive film of the half tone phase shift mask blank, film thickness and composition ratio of each element are

adjusted to have a predetermined small phase difference and predetermined transmittance to the exposure light.

[0 0 5 1]

In the case where the thin film is a binary mask blank which is a light shielding film consisting of a material including transition metal and a compound of transition metal and silicon (including transition metal silicide, particularly molybdenum silicide), the material of the light shielding film includes a compound of transition metal and silicon, the material including, as primary components, both the transition metal and silicon, and one of or both of oxygen and nitrogen. Another example of the light shielding film is a material including, as primary components, transition metal, and at least one of oxygen, nitrogen, and boron. As a transition metal, molybdenum, tantalum, tungsten, titanium, hafnium, nickel, vanadium, zirconium, niobium, palladium, ruthenium, rhodium, chromium, etc. are applicable. Further, in forming a light shielding film from a compound of molybdenum silicide, there is a double layer structure of a light shielding layer (MoSi, etc.) and a surface reflection preventing layer (MoSiON, etc.), and a three layer structure including a rear surface reflection preventing layer (MoSiON, etc.) between the light shielding layer and the glass substrate. Moreover, the composition of the light shielding film in film thickness direction can be a composition gradient film that varies continuously or in stages.

[0 0 5 2]

For thinning the film thickness of a resist film to form a fine pattern, an etching mask film can be formed on the light shielding film. This etching mask film is preferably formed from materials including chromium, or chromium compound including chromium and elements such as oxygen, nitrogen, and carbon having etching selectivity (having etching resistance) on etching of the light shielding film including transition metal silicide. In this case, the mask blank can be manufactured with the etching mask film remaining on the light shielding film by providing the etching mask film with reflection preventing function.

[0 0 5 3]

In the case of a multi-level gradation mask blank which is a laminated structure of the semitransmissive film and the light shielding film, the materials of the semitransmissive film include elements similar to the light-semitransmissive film of the half tone phase shift mask blank, and in addition, include simple metals or alloys of chromium, tantalum, titanium, aluminium, etc., or compounds thereof. Film thickness and composition ratio of each element are adjusted to have a predetermined transmittance to exposure light. While the light shielding film of the binary mask blank can be applied as the materials of the light shielding film,

the composition and the film thickness of the light shielding film materials are adjusted to have a predetermined light shielding capacity (optical density) in a laminated structure with the semitransmissive film.

[0054]

In various thin films given above, an etching stopper film having etching resistance for a light shielding film and a light-semitransmissive film may be provided between the glass substrate and the light shielding film, or between the light-semitransmissive film and the light shielding film. The etching stopper film can be formed from a material that can simultaneously peel the etching mask film when etching the etching stopper film.

[0055]

(3) Reflective Mask Blank

In the case of a reflective mask blank, a low-thermal expansion glass (e.g., $\text{SiO}_2\text{-TiO}_2$ glass) that has gone through the wet etching step is used as a mask blank substrate. The thin film of the reflective mask has a structure in which a multilayer reflecting film reflecting exposure light is formed on a glass substrate, and an absorber film (transfer pattern thin film) absorbing exposure light is formed in a pattern on the multilayer reflecting film.

The multilayer reflecting film is formed by laminating a high refractive index layer and a low refractive index layer alternately.

Examples of the multilayer reflecting film include Mo/Si cycle laminated film in which Mo films and Si films are alternately laminated by about 40 cycles, Ru/Si cycle multilayer film, Mo/Be cycle multilayer film, Mo compound/Si compound cycle multilayer film, Si/Nb cycle multilayer film, Si/Mo/Ru cycle multilayer film, Si/Mo/Ru/Mo cycle multilayer film, and Si/Ru/Mo/Ru cycle multilayer film. Materials can be selected arbitrarily based on exposure wavelength. For the absorber film, materials having a function to absorb exposure light, e.g., EUV light, is preferably used, for example, tantalum (Ta) alone or those including Ta as a primary component.

[0056]

[Manufacture of Transfer Mask]

The method of manufacturing the transfer mask of this invention is characterized by including a step of forming a transfer pattern on the thin film of the mask blank manufactured in the method of manufacturing the mask blank. The step of manufacturing a transfer mask from a mask blank is described below. The mask blank used herein is the phase shift mask blank described above in (2), which is structured such that a light-semitransmissive film (thin film for forming a transfer pattern) and a light shielding film

are laminated, in that order, on a translucent substrate. This method of manufacturing the transfer mask (phase shift mask) is only an example, and the manufacture is possible by changing a part of the steps.

[0057]

First, a resist film is formed on a light shielding film of a phase shift mask blank by spin coating. A chemically amplified resist for electron beam exposure writing is preferably used for the resist film. Next, a transfer pattern to be formed on the light-semitransmissive film is exposed and drawn with an electron beam on the resist film, and predetermined process such as developing is conducted to thereby form a resist pattern having a transfer pattern. Subsequently, dry etching is conducted on the light shielding film using the resist pattern as a mask, and the transfer pattern to be formed on the light-semitransmissive film is formed on the light shielding film. After dry etching, the resist pattern is removed. Next, dry etching is conducted on the light-semitransmissive film using the light shielding film having the transfer pattern as a mask to form a transfer pattern on the light-semitransmissive film. Subsequently, a resist film is again formed, pattern to be formed on the light shielding film (pattern for light shielding zone, etc.) is exposed and drawn with an electron beam, and predetermined process such as developing is conducted to thereby form a resist pattern. Dry etching is conducted on the light shielding film using the resist pattern having a pattern such as a light shielding zone as a mask, and a pattern such as a light shielding zone is created on the light shielding film. Then, a predetermined cleaning process is conducted so that the transfer mask (phase shift mask) is formed.

[0058]

As stated above, according to the method of manufacturing the mask blank substrate, the method of manufacturing the mask blank, and the method of manufacturing the transfer mask of this embodiment, since distribution and variation occurring in etching reaction can be inhibited, generation of various problems associated therewith (a difference in etching depth on the substrate surface in the shadow portion of the foreign matters and the field causing irregularity, surface texture (roughness) being uneven, an increase in roughness, etc.) can be inhibited. Uneven roughness giving an adverse effect in adhesiveness of the thin film formed on the substrate can be inhibited by this embodiment. Further, in the case of an EUV mask blank substrate, the problem of surface texture (roughness) causing scattering of EUV light and forming a factor of decrease in reflectance can be reduced according to this embodiment.

In addition, efficiency in the step of wet etching is promoted due to uniform etching reaction rate (unnecessary etching where etching depth should be aligned to the location where etching

reaction is slow is inhibited).

[0059]

As another effect, by the rear surface (second main surface) of the glass substrate being covered with temperature controlled water, the etching liquid supplied to the surface (first main surface) can be inhibited from moving to the rear surface, by which contamination of the rear surface by the etching liquid (waste fluid) can be inhibited.

[0060]

[Example]

The embodiments of this invention are further concretely described below by means of examples.

[Manufacture of Mask Blank Substrate]

A. Preparation of mask blank substrate, polishing step

The mask blank substrate to be used is a synthetic quartz glass substrate (size 152.4mm×152.4mm, thickness 6.35mm). An end surface of the synthetic quartz glass substrate was chamfered and ground, and was further subjected to rough polishing and precision polishing with a polishing liquid containing cerium oxide grain. The glass substrate that went through the above process was set in a carrier of a double side polishing device, and was polished (superprecision polishing) under the following conditions.

polishing pad: soft polisher (suede type)

polishing liquid: colloidal silica grain (average particle size 100nm)+ water

processing pressure: 50 to 100g/cm²

processing time: 60 minutes

After completion of superprecision polishing, colloidal silica grain was removed, and the main surface and the end surface of the glass substrate were brush cleaned.

[0061]

B. Wet Etching Step

First, an outline of the wet etching device is described with reference to Fig. 1 showing a plan view of a major part and Fig. 2 showing a cross-sectional view. Fig. 1 (a) is a plan view seen from the top, and Fig. 1 (b) is a plan view seen from the bottom.

[0062]

Main structure of wet etching device 1 includes glass substrate holding portion 20 for holding mask blank substrate (glass substrate) 100, liquid film flow forming means 10 for forming a liquid film flow on rear surface 102 (second main surface) of glass substrate 100, and nozzles 34, 37, 42 supplying an etching liquid, temperature control water, and a cleaning liquid, respectively, to main surface 101 (first main surface) of the glass substrate.

[0063]

Nozzles 34, 37, 42 are provided on arms 32, 35, 40,

respectively, and the arms configured to move the position of each nozzle above glass substrate 100 or to retract from above glass substrate 100 by means of rotation mechanisms 33, 36, 41, respectively. Each arm is provided with an expandable mechanism, enabling each nozzle to be brought to a desired position in association with the rotation mechanism. Nozzle 42 is provided with an ultrasonic oscillator (not shown) so that a liquid to which an ultrasonic wave is applied can be provided on the glass substrate.

[0064]

Glass substrate holding portion 20 includes four holding portions 28 for holding glass substrate 100 with four corners of glass substrate 100, which is constructed by strut 29 supporting holding portion 28 fixed to a turntable (not shown). By horizontal rotation or horizontal fluctuation of the turntable, glass substrate 100 can be rotated horizontally or fluctuated horizontally. Further, strut 29 supporting holding portion 28 is provided with an expandable portion to adjust the height of glass substrate 100.

[0065]

Liquid film flow forming means 10 is constructed of a fixed portion (not shown), pillar 14, and stage 12 facing rear surface 102 of glass substrate 100. The fixed portion is to fix pillar 14 with respect to the turntable, allowing liquid film flow forming means 10 to maintain a static condition with respect to turntable 22 without being affected by the movement of turntable 22. Hole 18 opening into stage 12 is in communication with stage 12 and pillar 14, and is connected to pure water supply means (not shown). The pure water supply means is provided with a heater to control the temperature of pure water supplied to rear surface 102 (second main surface) of glass substrate 100.

[0066]

As shown in Fig. 2, in etching, glass substrate 100 is arranged such that stage 12 and rear surface 102 face each other, and the height is adjusted by glass substrate holding portion 20 so that they face each other at a predetermined interval. "Predetermined interval" is an interval allowing the rear surface supplying water (pure water) flowing out from hole 18 to form a liquid film flow contacting the rear surface of the glass substrate, for example, the interval ranging from 0.5mm to 5mm. If the interval is less than 0.5mm, the interval between glass substrate 100 and stage 12 becomes small enough that the flow resistance of the liquid film flow becomes too large. If the interval is greater than 5mm, it would be difficult to fill the rear surface 102 with the liquid. In this example, the interval of 1mm is applied.

[0067]

As a wet etching liquid, sodium hydroxide (NaOH) aqueous

solution of 5wt%(1.28mol/L) was used. The etching liquid has a pH of about 13.9. The etching liquid was supplied at 1L per minute.
[0 0 6 8]

In alkali etching, spin etching which supplies the etching liquid heated to 70°C to surface 101 of spin-rotating glass substrate 100, and paddle etching carried out by stopping the supply of the etching liquid and performed by a liquid film of the etching liquid formed on glass substrate 100 were conducted consecutively.
[0 0 6 9]

Fig. 3 shows the flow of the etching process.

First, scrub-cleaned glass substrate 100 is fixed to holding portion 28 of wet etching device 1 (Step S1). Next, the interval of rear surface 102 of glass substrate 100 and stage 12 is adjusted to 1mm (Step S2). 70°C pure water is supplied towards rear surface 102 from hole 18 of stage 12, and liquid film flow 202 is formed between rear surface 102 and stage 12 as shown in Fig. 2 (Step S3). Simultaneously, nozzle 37 is moved above glass substrate 100 by rotation mechanism 36 and the glass substrate is spin-rotated (Step S4). Thereafter, 70°C warm pure water is supplied through nozzle 37 to glass substrate surface 101 to sufficiently heat the substrate (Step S5).

[0 0 7 0]

Thereafter, position is adjusted using the rotation mechanism and the expandable mechanism so that a tip of nozzle 34 directs toward the center of glass substrate surface 101. On this occasion, position of nozzle 37 is properly adjusted so that nozzle 37 and arm 35 do not interrupt (contact) nozzle 34 and arm 32. Then, turntable 12 is rotated (10rpm), warm pure water from nozzle 37 is stopped, and alkali etching liquid is supplied through nozzle 34 to glass substrate surface 101 (Step S6). Next, rotation rate of the turntable is dropped and stopped to complete spin etching (Step S7), and supply of the alkali etching liquid is stopped (Step S8).

[0 0 7 1]

Thereafter, paddle etching was conducted with continued supply of the warm pure water to rear surface 102 and with the liquid film of the etching liquid formed on glass substrate surface 101 (Step S9). Next, pure water was supplied on surface 101 of glass substrate 100, and cleaning was made to replace the etching liquid on main surface 101 with warm pure water (Step S10). During this process, the liquid film flow of pure water was continuously formed on rear surface 102. The warm pure water was supplied through nozzle 37 and nozzle 42 to main surface 101. The temperature of the warm pure water used in the cleaning was initially 70°C, and was 40°C upon complete replacement with the alkali etching liquid. Nozzle 42 is provided with an ultrasonic oscillator, and the pure water supplied through nozzle 42 is ultrasonic wave applied water.

By using the ultrasonic wave applied water, chemical solution component and foreign matters lifted off from main surface 101 can be efficiently removed. Supplying was made through nozzle 42 on glass substrate 100 at 1L/min.

When the cleaning step is completed, the step goes back to the wet etching step (Step S4) (warm pure water supply to rear surface 102 is continued). The etching step and the cleaning step were repeated three times. When the final cleaning step was completed, glass substrate 100 was spin-dried.

[0072]

C. Evaluation

The above wet etching to glass substrate cleaning was conducted on ten glass substrates, and each glass substrate was evaluated on foreign matter distribution using defect inspection system M1350 (manufactured by Lasertec Co.).

As a result, in the glass substrate manufactured by the method described in the example, foreign matter removal rate after the etching was 98% or more in all regions of the surface to which etching was conducted, achieving a high level of foreign matter removal.

On the other hand, in Comparative Examples 1 and 2 mentioned below, while foreign matter removal rate at the central portion was 98% or more, gradual decrease in foreign matter removal rate was observed at locations farther away from the central portion. Particularly in Comparative Example 2, while foreign matter removal rate at the central portion was as high as 98%, removal rate of the peripheral portion did not reach 70%.

Further, the etching liquid moved to the rear surface in Comparative Example 1, requiring cleaning of the rear surface.

[0073]

Surface roughness distribution (roughness) on each of the ten glass substrates was measured on the surface roughness of ten points from the center in a radial manner using AFM (atomic force microscope).

In the glass substrate manufactured in the method of the example, the surface roughness after etching was $R_q=0.12\text{nm}$ (average), and range was 0.03nm . On the other hand, in Comparative Example 1 mentioned below, the surface roughness was $R_q=0.14\text{nm}$ and the range was 0.08nm , having variation in surface roughness compared to the example.

[0074]

As stated above, in the example, since the substrate temperature is controlled by supplying 70°C pure water from the rear surface side of the substrate, 98% or more foreign matter removal was achieved at all regions on the surface to which etching was conducted. In addition, since proceeding of the etching was in-plane uniform on the substrate, surface roughness distribution

occurring after the etching could be minimized. On the other hand, Comparative Example where temperature control is not performed on the rear surface resulted in in-plane variation of foreign matter removal and minute irregularity removal.

[0 0 7 5]

[Manufacture of Half Tone Phase Shift Mask Blank]

A half tone phase shift mask blank was manufactured using a glass substrate that went through the cleaning step in the method of manufacturing the mask blank substrate described in the example.

First, a light-semitransmissive film consisting of nitrided molybdenum and silicon was formed on the glass substrate. Concretely, a MoSiN film consisting of molybdenum, silicon, and nitrogen was formed at a film thickness of 69nm using a mixed target of molybdenum (Mo) and silicon (Si) (Mo:Si=10mol%:90mol%), under a mixed gas atmosphere of argon (Ar), nitrogen (N₂), and helium (He) (gas flow ratio Ar:N₂:He=5:49:46), with 0.3Pa gas pressure and 3.0kW electric power of DC power source, by reactive sputtering (DC sputtering). Next, the glass substrate with MoSiN film formed thereon was heated using a heating furnace under the condition of 450°C heating temperature within the atmosphere for one hour. The MoSiN film had 6.16% transmittance and 184.4 degree phase difference in ArF excimer laser light.

[0 0 7 6]

A light shielding film described below is formed on the light-semitransmissive film. Concretely, CrOCN layer with a film thickness of 30nm was formed using chromium (Cr) target as a sputtering target, under a mixed gas atmosphere of argon (Ar), carbon dioxide (CO₂), nitrogen (N₂), and helium (He) (0.2 Pa gas pressure, gas flow ratio Ar:CO₂:N₂:He=20:35:10:30) with 1.7kW electric power of DC power source, by reactive sputtering (DC sputtering). Subsequently, CrN layer having a film thickness of 4nm was formed under a mixed gas atmosphere of argon (Ar) and nitrogen (N₂) (0.1Pa gas pressure, gas flow ratio Ar:N₂=25:5), with 1.7kW electric power of DC power source, by reactive sputtering (DC sputtering). Finally, CrOCN layer with a film thickness of 14nm was formed under a mixed gas atmosphere of argon (Ar), carbon dioxide (CO₂), nitrogen (N₂), and helium (He) (0.2Pa gas pressure, gas flow ratio Ar:CO₂:N₂:He = 20:35:5:30), with 1.7kW electric power of DC power source, by reactive sputtering (DC sputtering). Thus, a chromium based light shielding film of a three layer laminated structure with a total film thickness of 48nm was formed.

This light shielding film is adjusted such that optical density (OD) is 3.0 in a laminated structure with the light-semitransmissive film at wavelength 193nm of ArF excimer laser exposure light. Further, surface reflectance of the light shielding film to the wavelength of the exposure light was 20%.

[0 0 7 7]

[Manufacture of Half Tone Phase Shift Mask]

Initially, a chemically amplified positive resist film for electron beam writing (PRL009 manufactured by FUJIFILM Electronic Materials Co., Ltd.) was formed on the mask blank as a resist film. The resist film was formed by using a spinner (spin coating device) for spin coating. After application of the resist film, a predetermined heat drying was conducted. The resist film has a film thickness of 150nm.

Next, a predetermined pattern was drawn on the resist film formed on the mask blank using an electron beam writing device, and developed using a predetermined developing solution to form a resist pattern.

Subsequently, etching of the light shielding film was conducted using the resist pattern as a mask. A mixed gas of Cl_2 and O_2 was used as a dry etching gas. Then, etching of the light-semitransmissive film (MoSiN film) was conducted to form a light-semitransmissive film pattern. A mixed gas of SF_6 and He was used as a dry etching gas.

Next, remaining resist pattern was peeled and a resist film similar to the above was again formed on the entire surface, a drawing was performed to form a light shielding zone at an outer circumference of the mask, and thereafter, the resist film was developed and a resist pattern was formed. Using this resist pattern as a mask, the light shielding film excluding light shielding zone region was removed by etching.

Next, remaining resist pattern was peeled and a phase shift mask was obtained.

The phase shift mask thus obtained was formed at a pattern precision having an excellent 45nm half pitch micropattern.

[0078]

[Manufacture of Binary Mask Blank]

Using the glass substrate obtained from the method of manufacturing the mask blank substrate described in the example, a binary mask blank was manufactured as described below. A MoSiN film (light shielding layer) and a MoSiN film (surface reflection preventing layer) were formed on the glass substrate as light shielding films. MoSiN film consisting of molybdenum, silicon, and nitrogen (film composition ratio Mo:9.9at%, Si:66.1at%, N:24.0at%) with a film thickness of 47nm was formed, using a mixed target of Mo and Si (Mo:Si=13at%:87at%), under a mixed gas atmosphere of Ar and N_2 .

Next, MoSiN film consisting of molybdenum, silicon, and nitrogen was formed at a film thickness of 13nm using a target of Mo:Si=13at%:87at% under a mixed gas atmosphere of Ar and N_2 . Total film thickness of the light shielding film was 60nm.

Optical density (OD) of the light shielding film (light shielding layer + surface reflection preventing layer) was 3.0 in ArF excimer laser exposure light wavelength 193nm.

Next, Cr based etching mask film described below was formed on the MoSi based light shielding film. Concretely, CrN film (film composition ratio Cr:75.3at%, N:24.7at%) having a film thickness of 5nm was formed using chromium (Cr) target as a sputtering target, under a mixed gas atmosphere of argon (Ar) and nitrogen (N₂), by reactive sputtering (DC sputtering). Element analysis of each layer of the light shielding film and the Cr based etching mask film was made by Rutherford Backscattering Spectrometry.

[0 0 7 9]

[Manufacture of Binary Mask]

A transfer binary mask was manufactured using the above binary mask blank.

Initially, a chemically amplified positive resist film for electron beam writing (PRL009 manufactured by FUJIFILM Electronic Materials Co., Ltd.) was formed on the mask blank as a resist film.

In forming the resist film, a spinner (spin coating device) was used for spin coating. After application of the resist film, a predetermined heat drying was conducted. Film thickness of the resist film was 100nm.

Next, a predetermined pattern was drawn on the resist film formed on the mask blank using an electron beam drawing device, developed with a predetermined developing solution to form a resist pattern.

Subsequently, etching of the etching mask film was conducted using the resist pattern as a mask. A mixed gas of Cl₂ and O₂ was used as a dry etching gas. Then, etching was conducted on the MoSi based light shielding film (MoSiN/MoSiN) using the pattern formed on the etching mask film as a mask to form a light shielding film pattern. A mixed gas of SF₆ and He was used as a dry etching gas.

Next, remaining resist pattern was peeled, and the etching mask film pattern was removed by etching.

The MoSi based binary mask thus obtained was formed at a pattern precision having an excellent 32nm half pitch micropattern.

[0 0 8 0]

[Comparative Example 1]

In Comparative Example 1, wet etching was conducted in the same method as the example (steps from spin etching to paddle etching and to pure water cleaning), except that temperature was not controlled on the mask blank substrate from the rear surface, and a liquid film flow was not formed on the rear surface.

The wet etching device used in Comparative Example 1 is a device in which an end surface of a glass substrate is fixed using a spin cup to thereby inhibit movement of the etching liquid to the rear surface of the glass substrate, the spin cup having no water bath including flowing water, and without temperature adjusting means. Other than the above, the structure is similar to the example.

In Comparative Example 1, as mentioned in the example, while foreign matter removal rate at the central portion of the manufactured mask blank substrate was 98% or more, a decrease in foreign matter removal rate was observed gradually at locations farther away from the central portion.

Further, since the etching liquid moved to the rear surface, cleaning of the rear surface was necessary. In addition, surface roughness of the mask blank substrate after wet etching was $R_q=0.14\text{nm}$, and the range was 0.08nm . Those of the example were $R_q=0.12\text{nm}$ (average), and range was 0.03nm . The surface roughness was greater compared to the example of this invention.

[0081]

[Comparative Example 2]

In Comparative Example 2, wet etching of the mask blank substrate was conducted with a method similar to the example, except for pure water at room temperature was used in supplying pure water to the rear surface in the wet etching device of the example.

As a result, as mentioned in the example, while foreign matter removal rate at the central portion of the mask blank substrate in Comparative Example 2 was 98% or more, a decrease in foreign matter removal rate was observed gradually at locations farther away from the central portion, with removal rate of the peripheral portion not reaching 70%. No such phenomenon was observed in the example of this invention. The reason for the significant variation in Comparative Example 2 in which pure water without temperature control was supplied to the rear surface is because of generation of a large temperature difference in the etching liquid on the etching surface caused by the difference in liquid temperature of the etching liquid and the water supplied to the rear surface, causing distribution in foreign matter removal capacity and in surface roughness.

[0082]

In the explanation of the embodiments above, while a liquid to be supplied to the rear surface of the substrate (liquid adjusted to a temperature higher than normal temperature) being supplied as a liquid film flow was given as an example, the liquid to be supplied to the rear surface side of the substrate is not limited to a fluid, but for example, a temperature controlled liquid can be kept in a pool, and the rear surface side of the substrate can be contacted thereto. However, the fluid as described in this embodiment is preferable, since fresh (clean) liquid is constantly provided. Further, while pure water supply means provided with a heater (not shown) was described as an example of means to control the temperature of the liquid to be supplied to the rear surface of the substrate, the point is to keep the temperature of the liquid to be supplied to the rear surface of the substrate at a predetermined temperature, for example, a structure in which a heater is provided on stage 12 is applicable.

[REFERENCE NUMERALS]

[0 0 8 3]

1...wet etching device, 10...fluid forming means, 12...stage,
14...pillar, 18...hole, 20...glass substrate holding mechanism,
28...holding portion, 32...arm, 33...rotation mechanism, 34...nozzle,
35...arm, 36...rotation mechanism, 37...nozzle, 40...arm, 41...rotation
mechanism, 42...nozzle, 100...glass substrate (mask blank substrate),
101...first main face (first main surface) of glass substrate,
102...second main face (second main surface) of glass substrate,
201...wet etching liquid, 202...warm pure water (liquid adjusted to
a temperature higher than normal temperature)

CLAIMS

1. A method of manufacturing a mask blank substrate made of a glass, comprising a step for wet etching a mask blank substrate having two main surfaces consisting of first and second main surfaces by introducing an etching liquid to the first main surface to cover the first main surface with the etching liquid,

wherein the step for wet etching is conducted under a condition where the etching liquid adjusted to a first temperature is supplied to the first main surface, and a liquid adjusted to a second temperature is supplied in the form of a radial liquid film flow covering the entire second main surface,

wherein the first temperature is in the range of 40° C to 95° C, and

wherein a temperature difference between the first temperature and the second temperature is within $\pm 5^{\circ}$ C.

2. A method of manufacturing a mask blank substrate according to claim 1, wherein the wet etching is conducted by paddle etching.

3. A method of manufacturing a mask blank substrate according to claim 1 or 2, wherein the wet etching comprises at least one or more etchants, boiling point of the etchant being higher than the first temperature of the etching liquid supplied to the first main surface.

4. A method of manufacturing a mask blank substrate according to any one of claim 1 to claim 3, wherein supplying the liquid adjusted to the second temperature to the second main surface is carried out prior to commencement of introduction of the etching liquid.

5. A method of manufacturing a mask blank substrate according to any one of claim 1 to claim 4, wherein the step for wet etching is conducted by arranging the mask blank substrate on a stage such that the

second main surface faces the stage at a predetermined interval and by forming the liquid film flow of the liquid between the second main surface and the stage.

6. A method of manufacturing a mask blank substrate according to claim 5, wherein the predetermined interval ranges from 0.5 mm to 5 mm.

7. A method of manufacturing a mask blank substrate according to any one of claim 1 to claim 6 comprising a cleaning step using a cleaning liquid after the step for wet etching,

wherein at least a certain time during the cleaning step is conducted under a condition where the liquid adjusted to the second temperature is supplied to the second main surface.

8. A method of manufacturing a mask blank substrate according to any one of claim 1 to claim 7, wherein the liquid adjusted to the second temperature is an aqueous solution.

9. A method of manufacturing a mask blank comprising:
the steps of manufacturing a mask blank substrate according to any one of claim 1 to claim 8; and
a step of forming a transfer pattern thin film directly or via another layer on the first main surface of the mask blank substrate.

10. A method of manufacturing a transfer mask comprising:
the steps of manufacturing a mask blank according to claim 9; and
a step of patterning the transfer pattern thin film of the mask blank.