

METHOD OF MANUFACTURING MASK BLANK WITH RESIST FILM,
METHOD OF MANUFACTURING TRANSFER MASK, MASK BLANK
WITH RESIST FILM, METHOD OF MANUFACTURING MASK BLANK,
AND MASK BLANK

Technical Field

[0001]

The present invention relates to a method of manufacturing a mask blank with a resist film, a method of manufacturing a transfer mask, a mask blank with a resist film, a method of manufacturing a mask blank, and a mask blank.

Description of Related Art

[0002]

In recent years, a pattern dimension required for a semiconductor device has been steadily finer. Along with such a finer dimension, the pattern dimension of a transfer mask has also been finer in manufacturing the semiconductor device.

[0003]

Since lithography is used for pattern formation of the transfer mask, dimensional accuracy of a resist pattern formed on the mask blank is directly linked to the dimensional accuracy of the pattern shape of the transfer mask. An electron beam exposure apparatus capable of forming a fine pattern is used for exposure of a resist in a lithography technique. In order to obtain a transfer pattern as designed, correction is performed while expecting a variation of dimensions due to various

factors. For example, patent document 1 discloses a technique of performing processing of correcting electron beam irradiation dose according to a film thickness of a resist film.

[0004]

Patent document 1: Japanese Patent Laid Open Publication No.2011-198922

[0005]

Request for dimensional accuracy of the resist pattern on the mask blank, has been increasingly strict in accordance with the fine structure of semiconductor devices. Specifically, a strict numerical value is requested as follows: CD uniformity (Critical Dimension Uniformity: CDU) which is an index of in-plane uniformity of a pattern, is 5nm or less and more strictly 3nm or less.

[0006]

As one approach to meet such a request, it can be considered that a resist film thickness is set to be constant in a plane. However, it becomes difficult to satisfy the abovementioned request only by such a constant film thickness. In order to solve such a circumstance, as shown in patent document 1, correction processing is conceivable in which the electron beam irradiation dose (exposure amount) is corrected according to the film thickness of the resist film. With this technique, even if the film thickness of the resist film is non-uniform in the plane, an exposure amount of each part can be set according to the film thickness of each part in the plane. As a result, exposure can be performed so that uniform pattern accuracy in the plane of the resist film.

[0007]

In patent document 1, a parameter (called “resist sensitivity” hereafter) showing a required exposure amount for pattern formation in the resist film, is associated with the film thickness of the resist film, to thereby correct the exposure amount according to the resist sensitivity.

[0008]

Here, the following problem is found by inventors of the present invention.

As described in patent document 1, the following case can be considered: namely, a film thickness distribution in the plane of the resist film is mapped as a resist sensitivity distribution view. If the resist sensitivity distribution view (called “in-plane sensitivity distribution information” hereafter) is obtained, mask blank is mounted on an exposure apparatus, and the exposure amount is corrected according to the in-plane sensitivity distribution information, to thereby expect the exposure capable of realizing uniform pattern accuracy in the plane of the resist film.

[0009]

However, there are many square mask blanks in plan view, depending on a case. In this case, upper/lower and right/left directions in plan view cannot be specified in the mask blank. Then, the inventors of the present invention is notified of the following fact: directions of the mask blank when the in-plane sensitivity distribution information is obtained, and directions of the mask blank when the mask blank is mounted on the exposure apparatus, are not matched with each other.

[0010]

Conventionally, there is no problem in forming the resist pattern, even if there is no matching between the abovementioned directions. Further, when spin-coating is used for coating of a resist liquid, the film thickness distribution is a distribution basically close to a symmetrical structure if a rotation center and a substrate center coincide with each other. In this case, there is no great influence even if the directions are not matched with each other.

[0011]

However, as described above, in recent years, the pattern dimension is steadily finer, which is requested for a semiconductor device. Then, a strict value such as CDU:5nm or less, and more strictly 3 nm or less, is requested. If such a strict pattern accuracy is requested, the abovementioned mismatch of the directions has a great influence on CDU.

[0012]

An object of the present invention is to provide a technique of improving the in-plane uniformity of the pattern.

Summary of the Invention

[0013]

In order to solve the above-described problem and as a result of strenuous efforts by the inventors of the present invention, it is found that when in-plane sensitivity distribution information is obtained, and when a mask blank is mounted on an exposure apparatus, the mask blank has a function of specifying upper/lower and right/left directions in a plan view.

The structure of the present invention formed based on the abovementioned knowledge is described as follows.

[0014]

<Structure 1>

First structure of the present invention is a method of manufacturing a mask blank with a resist film, including:

preparing a substrate having a thin film;

forming a resist film on a surface of the thin film; and

removing a peripheral edge portion of the resist film,

wherein in the removing, the peripheral edge portion of the resist film is removed so as to impart directions in plan view when the substrate is horizontally mounted, by a positional relation in plan view between the thin film and the resist film.

According to this structure, the directions of the mask blank with a resist film when in-plane sensitivity distribution information is obtained, and the directions of the mask blank with a resist film when the mask blank is mounted on the exposure apparatus, can be surely matched with each other. As a result, in-plane uniformity of the pattern can be improved even if a strict numerical value is requested, such as CDU: 5 nm or less, and more strictly 3 nm or less.

[0015]

<Structure 2>

Second structure of the present invention is the method of the first structure, wherein the substrate has a symmetrical shape in plan view.

When the substrate has the symmetrical shape in plan view,

asymmetrical property is newly given to an outer appearance of the substrate in plan view. Then, the effect described in structure 1 can be further enhanced.

[0016]

<Structure 3>

Third structure of the present invention is the method of the first or second structure, wherein in the removing, the peripheral edge portion of the resist film is entirely removed, and meanwhile the directions are imparted by setting a width of the removal margin of a specific peripheral edge portion to be larger or smaller than other peripheral edge portion.

If the resist film is removed in the peripheral edge portion of the mask blank with a resist film, a metal frame like a picture frame is formed in plan view. Usually, colors of the resist film and the thin film are completely different from each other. Therefore, if the peripheral edge portion of the resist film of an upper side is largely removed, a worker can easily recognize the directions. That is, by entirely removing the peripheral edge portion of the resist film, and meanwhile by setting the width of the removal margin of the specific peripheral edge portion to be larger or smaller than other peripheral edge portion, the directions are imparted, and in addition, the worker can easily recognize the directions.

[0017]

<Structure 4>

Fourth structure of the present invention is the method of the third structure, wherein the substrate has a rectangular shape in plan

view, and the given peripheral edge portion is a side of this rectangular shape.

In this case, the resist film can be easily removed using a chemical solution, and the width of the removal margin can be easily adjusted.

[0018]

<Structure 5>

Fifth structure of the present invention is a method of manufacturing a transfer mask.

The method includes:

preparing a substrate having a thin film;

acquiring in-plan sensitivity distribution information regarding a resist film;

forming a resist film on a surface of the thin film;

removing a peripheral edge portion of the resist film;

performing exposure to the resist film based on the in-plan sensitivity distribution information after the removing; and

performing development after the exposing, and forming a transfer pattern to the resist film,

wherein in the removing, the peripheral edge portion of the resist film is removed so as to impart directions in plan view when the substrate is horizontally mounted, by a positional relation in plan view between the thin film and the resist film, and in this state, the exposing is performed so that directions imparted by the removing, and directions in the in-plan sensitivity distribution information, are set in a matching state.

According to this structure, similarly to structure 1, the directions of the mask blank with a resist film when obtaining the in-plan sensitivity distribution information, and the directions of the mask blank with a resist film when the mask blank is mounted on the exposure apparatus, can be surely matched with each other. As a result, the in-plan uniformity of the pattern can be improved.

[0019]

<Structure 6>

Sixth structure of the present invention is a mask blank with a resist film provided with a substrate having a thin film and a resist film formed on a surface of the thin film, wherein the resist film is formed on the surface of the thin film so as to impart directions in plan view, when the substrate is horizontally mounted, by a positional relation between a thin film and the resist film in plan view.

According to this structure, similarly to structure 1, the directions of the mask blank with a resist film when obtaining in-plane sensitivity distribution information, and the directions of the mask blank with a resist film when the mask blank is mounted on the exposure apparatus, can be surely matched with each other. As a result, the in-plan the in-plan uniformity of the pattern can be improved.

[0020]

<Structure 7>

Seventh structure of the present invention is a method of manufacturing a mask blank provided with a substrate having a thin film, wherein marking is performed to a substrate or the thin film, to thereby impart directions in plan view when the substrate is

horizontally mounted.

According to this structure, the similar effect as described in structure 1 can be obtained.

[0021]

<Structure 8>

Eighth structure of the present invention is a method of manufacturing a transfer mask, including:

preparing a substrate having a thin film;

acquiring information of in-plan sensitivity distribution information regarding a resist film;

forming a resist film on a surface of the thin film;

performing exposure to the resist film based on the in-plan sensitivity distribution information; and

performing development after the exposure, and forming a transfer pattern to the resist film

wherein in the preparing a substrate, marking is performed to the substrate or the thin film, to thereby impart directions in plan view when the substrate is horizontally mounted, and thereafter in the exposure, the exposing is performed after directions imparted to the substrate in the preparing step and directions in the in-plan sensitivity information, are set in a matching state.

According to this structure, the similar effect as described in structure 1 can be obtained.

[0022]

<Structure 9>

Ninth structure of the present invention is a mask blank

provided with a substrate having a thin film, wherein an index for imparting directions in plan view when the substrate is horizontally mounted, is marked on the substrate or the thin film.

According to this structure, the similar effect as described in structure 1 can be obtained.

[0023]

According to the present invention, a technique of improving the in-plan uniformity of the pattern can be provided.

Brief description of the drawings

[0024]

FIG. 1 is a sectional view of the steps of manufacturing a mask blank, a mask blank with a resist film, and a transfer mask, according to an embodiment.

FIG. 2 is a schematic view showing an arrangement of a mask blank with a resist film, and chemical feeding nozzles for removing.

FIG. 3 is a photograph showing a result of an optical microscopic observation performed to the mask blank with a resist film according to an example.

FIG. 4 is a view showing in-plan sensitivity distribution information regarding the mask blank with a resist film used in examples and comparative examples, wherein (a) shows a two-dimensional graph and (b) is a three-dimensional graph.

FIG. 5 is a view showing in-plan sensitivity distribution information after the mask blank with a resist film is stored under a prescribed condition, according to examples and comparative examples,

wherein (a) shows a two-dimensional graph and (b) is a three-dimensional graph.

FIG. 6 is a view showing a result of the examples, and showing a degree of correcting exposure, in a case that directions when in-plan sensitivity distribution information is obtained after the mask blank with a resist film is stored under a prescribed condition, and directions when the mask blank with a resist film is mounted on an exposure apparatus, are set in a matching state, wherein (a) shows a two-dimensional graph and (b) is a three-dimensional graph.

FIG. 7 is a view showing a result of a comparative example, and showing a degree of correcting the exposure amount, when the directions when in-plan sensitivity distribution information is obtained in the mask blank with a resist film, and the directions when the mask blank with a resist film is mounted on the exposure apparatus, are set in a non-matching state (upside down), wherein (a) shows a two-dimensional graph and (b) is a three-dimensional graph.

FIG. 8 is a view showing the result of the comparative example, and showing a degree of correcting the exposure amount, in the case that the directions when in-plan sensitivity distribution information is obtained after the mask blank with a resist film is stored under a prescribed condition, and the directions when the mask blank with a resist film is mounted on the exposure apparatus, are set in a non-matching state (upside down), wherein (a) shows a two-dimensional graph and (b) is a three-dimensional graph.

Detailed description of the Invention

[0025]

[Embodiment 1]

Embodiments of the present invention will be described in detail hereafter.

In this embodiment, explanation is given in the following order.

1. Method of manufacturing a transfer mask

1-A) Preparing a substrate with a thin film (mask blank)

1-A-a) Preparing a substrate

1-A-b) Forming a thin film

1-B) Forming a resist film

1-C) Removing

1-D) Acquiring information

1-E) Exposure

1-F) Development

1-G) Etching

1-H) Others

2. Mask blank with a resist film

Regarding the structure not described hereunder, a publicly-known structure (for example, JPA 2013-210576 by this applicant) may be suitably employed. In this specification, for example, contents of the JPA 2013-210576 are employed, regarding the matter not particularly described, such as a structure of a thin film.

Further, [Embodiment 1] shows an example of devising a position of a resist film in plan view, to thereby imparting directions.

[Embodiment 2] shows an example of marking an index for imparting directions to a thin film or a substrate itself constituting a

mask blank.

[Embodiment 3] shows the other example.

[0026]

<1. Method of manufacturing a transfer mask>

A method of manufacturing a transfer mask 50 according to this embodiment will be described using FIG. 1. FIG. 1 is a sectional view of the steps of the method of manufacturing a mask blank 5, a mask blank 1 with a resist film and a transfer mask 50. This embodiment shows an example of preparing a substrate 10 and forming a thin film 11 on the substrate 10 in preparing a substrate with a thin film. However, an embodiment of preparing the mask blank 5 on which the thin film 11 is previously formed, and forming a resist film thereon, is also included in the embodiment of the present invention.

[0027]

1-A) Preparing a substrate with a thin film (mask blank)

1-A-a) Preparing a substrate

First, as shown in FIG. 1(a), the substrate 10 used for the transfer mask 50 is prepared. A glass substrate can be used as the substrate 10 of the transfer mask 50. In the case of a transmission type mask, a glass material having high transmissivity to an exposure light is used when a pattern is formed on a wafer. In the case of a reflective mask, a low thermal expansion glass is selected, which is capable of minimizing a thermal expansion of the substrate 10 caused by an energy of an exposure light.

Specifically, in the case of the transmission type mask (for example, a binary mask, a phase shift mask, and a gray-tone mask),

synthetic quartz glass, soda lime glass, aluminosilicate glass, borosilicate glass, and alkali-free glass, etc., can be given as the material of the substrate 10. As a specific example, the synthetic quartz glass having high transmissivity to a light with a wavelength of 300nm or less can be preferably used for the substrate 10 of the transfer mask, using ArF excimer laser with a wavelength of 193nm, and KrFexcimer laser with a wavelength of 254nm.

Further, in the case of the reflective mask, SiO₂-TiO₂ based mask can be preferably used, which is a glass material having a low thermal expansion coefficient in a range of about $0 \pm 1.0 \times 10^{-7}/^{\circ}\text{C}$, and more preferably in a range of about $0 \pm 0.3 \times 10^{-7}/^{\circ}\text{C}$.

[0028]

In this embodiment, the substrate 10 preferably has symmetry in plan view. The present invention is provided from a knowledge regarding a problem as follows: “under a circumstance that a pattern dimension requested for a semiconductor device has been steadily finer”, “upper/lower and right/left directions in plan view cannot be specified. In this case, directions of a mask blank 1 with a resist film when in-plan sensitivity distribution information is obtained, and directions of the mask blank 1 with a resist film when the mask blank 1 is mounted on the exposure apparatus, are set in non-matching state”. Although details are described later, in this embodiment, the directions in plan view are imparted when the substrate 10 is horizontally mounted, by a positional relation between the thin film 11 and the resist film 12 in plan view. That is, non-symmetry is caused by an arrangement of the resist film 12 which is provided on the substrate 10 having symmetry in

plan view.

Therefore, when the substrate 10 has a symmetric shape in plan view, an outer appearance in plan view is “symmetry → non-symmetry”. Then, an effect of this embodiment is particularly exhibited. However, even if the substrate 10 does not have symmetry, it is still easy to specify the upper/lower and right/left directions in plan view. In this case as well, it is possible to reduce the problem of non-matching state between the directions of the mask blank 1 with a resist film when in-plan sensitivity distribution information is obtained, and the directions of the mask blank 1 with a resist film when the exposure apparatus is mounted. As a result, it is possible to exhibit the effect of this embodiment as follows: namely, in-plan uniformity of the pattern can be improved.

[0029]

Preferably, the substrate 10 is rectangular in plan view, and a prescribed peripheral edge portion is preferably one side of this rectangle. Of course, the substrate 10 may have a polygonal shape, or may be a circular shape, a circular shape with partially straight line, or the other symmetric shape or asymmetric shape. However, in the above case, 1-C) the resist film 12 can be easily removed using a chemical liquid described later in the removing step, and a width of a removal margin can be easily adjusted. Particularly, in the case of a square in plan view, this is a situation that upper/lower and right/left directions cannot be specified at all. In such a circumstance, by performing 1-C) removing step, the upper/lower and right/left directions can be specified.

[0030]

1-A-b) Forming a thin film

Next, as shown in FIG. 1(b), the thin film 11 is formed on a main surface of the substrate 10. The thin film 11 formed on the surface of the substrate 10, and under the resist film 12, is the thin film selected according to a purpose of use of the transfer mask 50 to be manufactured. For example, the following (1) to (5) can be given.

[0031]

(1) Thin film of a binary mask

When a binary mask is fabricated, the thin film 11 having a light-shielding film is formed on the substrate 10 having light-transmitting properties to a light with an exposure wavelength.

Such a light-shielding film is made of a material containing a transition metal simple substance such as chromium, tantalum, ruthenium, tungsten, titanium, hafnium, molybdenum, nickel, vanadium, zirconium, niobium, palladium, and rhodium, etc., or a compound of them. For example, the light-shielding film composed of chromium or a chromium compound obtained by adding one kind or more elements selected from oxygen, nitrogen, and carbon, to chromium, can be given. Also, for example, the light-shielding film composed of a tantalum compound obtained by adding to tantalum one or more elements selected from oxygen, nitrogen, and boron, can be given.

Further, the thin film 11 has a structure of the light-shielding film such as a double-layer structure including a light-shielding film and a surface anti-reflection layer, or a three-layer structure including a rear surface anti-reflection layer between the light-shielding layer and the substrate 10. Further, the light-shielding film may be a

composition gradient film containing a continuously or gradually different composition in a film thickness direction of the light-shielding film.

Further, the thin film 11 may have a structure having an etching mask film on the light-shielding film. This etching mask film is preferably made of a material composed of particularly chromium, or a chromium compound obtained by adding to chromium the element such as oxygen, nitrogen, and carbon having etching selectivity (has etching resistance) to the etching applied to the light-shielding film containing transition metal silicide. In this case, the transfer mask 50 may be fabricated while leaving the etching mask film on the light-shielding film, by providing an antireflection function to the etching mask film.

[0032]

(2) Thin film of a binary mask having other structure

As other example of the thin film 11 of the binary mask, there is a structure having a light-shielding film made of a material containing a transition metal and silicon (transition metal silicide, particularly containing molybdenum silicide).

This light-shielding film is made of a material containing a compound of the transition metal and silicon, which is the material mainly composed of these transition metal and silicon, oxygen and/or nitrogen. Further, the light-shielding film is made of a material mainly composed of the transition metal, oxygen, nitrogen, and/or boron. As the transition metal, molybdenum, tantalum, tungsten, titanium, hafnium, nickel, vanadium, zirconium, niobium, palladium, ruthenium, rhodium, chromium, etc. can be used.

Particularly, in the case of forming the light-shielding film by a compound of molybdenum silicide, there is a double layer structure including a light-shielding layer (MoSi, etc.) and a surface antireflection layer (MoSiON, etc.), and there is a three-layer structure further including a rear surface antireflection layer (MoSiON, etc.) between the light-shielding layer and the substrate 10.

Further, the light-shielding film may be a composition gradient film containing a continuously or gradually different composition in a film thickness direction of the light-shielding film.

[0033]

(3) Thin film of a halftone type phase shift mask

When a halftone type phase shift mask is fabricated, the thin film 11 is formed, having a light semi-transmitting film made of a material containing a compound of the transmission metal and silicon (containing transition metal silicide and particularly molybdenum silicide) on the substrate 10 having light-transmitting properties to the wavelength of the exposure light used for transfer.

By the light semi-transmitting film included in the thin film 11, a light with an intensity of not substantially contributing to the exposure (for example, 1% to 30% of the wavelength of the exposure light), is transmitted, and such a light semi-transmitting film has a prescribed phase difference (for example, 180 degrees). The halftone type phase shift mask is configured to have a light semi-transmitting portion in which the light semi-transmitting film is patterned and a light transmitting portion in which the light with an intensity of contributing to the exposure is allowed to pass and having no light semi-transmitting

film formed thereon, so that the phase of the light transmitting through the light semi-transmitting portion has substantially an inverted relation with the phase of the light transmitting through the light transmitting portion, to thereby mutually cancel the lights that pass through the vicinity of a border portion between the light semi-transmitting portion and the light transmitting portion by a diffraction phenomenon so that a light intensity on the border portion becomes almost zero, and a contrast, namely, a resolution on the border portion can be improved.

Such a light semi-transmitting film is made of a material containing for example the transition metal and silicon (including transition metal silicide), which is the material mainly composed of these transition metals and silicon, oxygen and/or nitrogen. As the transition metal, molybdenum, tantalum, tungsten, titanium, hafnium, nickel, vanadium, zirconium, niobium, palladium, ruthenium, rhodium, chromium, etc., can be used.

Further, when the light-shielding film is formed on the light semi-transmitting film, particularly chromium, and a chromium compound obtained by adding elements such as oxygen, nitrogen, or carbon to chromium having etching selectivity (having etching resistance) to the light semi-transmitting film, is preferably used as the material of the light-shielding film, because the material of the light semi-transmitting film contains the transition metal and silicon.

[0034]

(4) Thin film of a multi-tone mask

The thin film 11 of a multi-tone mask has a lamination structure

of one or more semi-transmitting film and light-shielding film.

Regarding the material of the light semi-transmitting film, a metal simple body such as chromium, tantalum, or aluminum and alloy of them, or a compound of them is also included, in addition to the element similar to the element of the light semi-transmitting film of the halftone type phase shift mask blank.

A film thickness or a composition ratio of each element, is adjusted to a specific transmissivity to the exposure light. Regarding the light-shielding film as well, the light-shielding film of the binary mask blank can be used, and the composition and the film thickness of the material of the light-shielding film are adjusted to obtain a specific light-shielding performance (optical density) in a lamination structure of the light semi-transmitting film and the light-shielding film.

[0035]

(5) Thin film of a reflective mask

The thin film 11 of a reflective mask has a structure as follows: a multilayer reflection film is formed on the substrate 10 to reflect the exposure light, and an absorber film is formed into a pattern-like shape on the multilayer reflection film to absorb the exposure light. The light (EUV light) incident on the reflective mask mounted on an exposure machine (pattern transfer device), is absorbed in a certain portion of the absorber film, and at a portion without the absorber film, an optical image reflected by the multilayer reflection film is transferred on a semiconductor substrate 10 through a reflective optical system.

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

As an example of the multilayer reflection film, Mo / Si cycled lamination film in which Mo film and Si film are alternately laminated by about 40 cycles, Ru/Si cycled multilayer film, Mo/Be cycled multilayer film, Mo compound/Si compound cycled multilayer film, Si/Nb cycled multilayer film, Si/Mo/Ru cycled multilayer film, Si/Mo/RU/Mo cycled multilayer film, and Si/Ru/Mo/Ru cycled multilayer film, etc., are given. The material of them can be suitably selected depending on the wavelength of the exposure light.

Further, the absorber film has a function of absorbing the EUV light for example, which is the exposure light, and for example, tantalum (Ta) simple body or the material mainly composed of Ta can be preferably used. A crystalline state of such an absorber film is preferably an amorphous or microcrystalline structure from a viewpoint of smoothness and flatness.

[0036]

1-B) Forming a resist film

Next, as shown in FIG. 1(c), a resist film 12 is formed on the thin film 11 of the mask blank 5. The resist film 12 is formed by a resist liquid. A publicly-known liquid may be used as the resist liquid. A publicly-known technique may be used as a specific formation method of the resist film 12. For example, the surface of the mask blank 5 is spin-coated with the resist liquid, and thereafter, baking may be applied thereto.

[0037]

As described above, the mask blank with a resist film is fabricated, which is used for manufacturing the transfer mask 50.

[0038]

1-C) Removing

In this step, as shown in FIG. 1(d), the peripheral edge portion of the resist film 12 is removed. More specifically, the peripheral edge portion of the resist film 12 is removed so as to impart directions when the substrate 10 is horizontally mounted, by the positional relation between the thin film 11 and the resist film 12 in plan view.

A specific example of this step will be described hereafter, using FIG. 2. FIG. 2 is a schematic view showing the mask blank 1 with a resist film and the arrangement of chemical feeding nozzles 20 for removing in plan view, in the removing step according to this embodiment. Note that the shape of the substrate 10 in plan view is a square. Further, the chemical feeding nozzles 20 for removing (simply called nozzles 20 hereafter) provided in an upper direction viewed from the mask blank 1 with a resist film, are expressed by dot lines.

[0039]

First, the mask blank 1 with a resist film is mounted so that the resist film is position in the upper direction, and the substrate 10 is positioned in a lower direction. That is, the main surface of the resist film 12 is directed upward, and the rear surface of the substrate 10 (opposite surface to the surface on which the thin film 11 is formed) is directed downward. Then, a plurality of nozzles 20 are arranged in the upper direction viewed from the peripheral edge portion of the resist film 12, for feeding a chemical liquid to remove the resist film 12. Discharge ports of the nozzles 20 are directed to the peripheral edge portion of the resist film 12.

[0040]

Here, in order to impart directions in plan view when the substrate 10 is horizontally mounted, by the positional relation between the thin film 11 and the resist film 12 in plan view, the arrangement of the nozzles 20 is devised. Specifically, the nozzles 20 corresponding to one side (called an upper side) in a direction which is a reference direction in plan view (although not limited, for example upper direction), are arranged so as to be closer to a peripheral edge (outside) of the substrate 10. In this state, the chemical liquid is discharged from the nozzles 20, for removing the resist film 12. Thus, as shown in FIG. 2, in this embodiment, the peripheral edge portion of the resist film 12 in one side (called an upper side) in the direction (upper direction) which is a reference direction in plan view, can be removed by a small portion, compared with the peripheral edge portion of other side.

[0041]

The peripheral edge portion of the resist film 12 is removed and the thin film 11 is exposed. The thin film 11 in this embodiment is a metal film. Therefore, a metal frame like a picture frame in plan view is formed on the peripheral edge portion of the mask blank 1 with a resist film. Usually, colors of the resist film 12 and the thin film 11 are different from each other. Therefore, if the peripheral edge portion of the resist film 12 of the upper side is largely removed, a worker can easily recognize the directions. That is, directions are imparted by entirely removing the peripheral edge portion of the resist film 12, and meanwhile by making the width of the removal margin smaller than the peripheral edge portion at a prescribed peripheral edge portion. In

addition, the worker can easily recognize the directions.

Further, when the shape of the substrate 10 in plan view is a rectangular (particularly square) as shown in this embodiment, the width of the removal margin of the resist film can be easily changed, and workability is remarkably improved, by moving every rows of a plurality of nozzles arranged in a row, in a central direction or an outside direction of the substrate.

[0042]

Here, directions are imparted by setting the width of the removal margin to be small. However, conversely, it is also possible to impart directions by setting the width of the removal to be larger than other peripheral edge portion. In this case, the nozzles 20 corresponding to the upper side are arranged closer to the substrate 10. However, if directions can be consequently imparted to the mask blank 1 with a resist film, there is no limit in the size of the removal margin of the resist film 12, and there is no limit in the shape of the removal margin. Further, the width of the removal margin of the resist film 12 of the side other than the upper side may be the same or may be different from each other. After all, there is no limit in the removal margin if the worker can specify the upper side.

[0043]

If the resist film 12 is formed by coating the surface of the thin film 11 with the resist liquid, the resist film 12 is formed so as to rise in the peripheral edge portion of the thin film 11. If other member (member, etc., in the apparatus) is brought into contact with the risen portion at the time of carrying the mask blank 1 with a resist film,

particles are generated from the resist film 12. As described above, a strict numerical value of CDU is requested, such as 5 nm or less, and more strictly 3 nm or less. In such a circumstance, generation of the particles causes a remarkable reduction of the in-plan uniformity. However, by entirely removing the peripheral edge portion of the resist film 12 as shown in this embodiment, generation of the particles from the resist film 12 can be suppressed. Of course, even if not entirely removing the peripheral edge portion, directions can be imparted by removing a specific peripheral edge portion. However, if the reason of abovementioned particles is taken into consideration, it is preferable that the peripheral edge portion of the resist film 12 is entirely removed. In this state, the width of the removal margin at a specific peripheral edge portion is preferably set to be larger or smaller than other peripheral edge portion.

[0044]

These steps provide the method of manufacturing the mask blank 1 with a resist film. In these steps, directions can be imparted to the mask blank 1 with a resist film, and as a result, the in-plan uniformity of the pattern can be improved.

The method of manufacturing the transfer mask 50 is provided by adding the following step to the abovementioned steps. Explanation is given hereafter.

[0045]

1-D) Acquiring information & 1-E) Exposure

As shown in FIG. 1(e), exposure is performed to formed resist film 12 in a prescribed shape. At this time, exposure is performed to

the resist film 12 based on the in-plane sensitivity distribution information. The in-plane sensitivity distribution information is the information showing a sensitivity distribution in the exposure when the resist film 12 is viewed in plane. This information may be numerical value information or may be visual information like a resist sensitivity distribution diagram. A publicly-known technique may be used as an acquisition technique of the in-plane sensitivity distribution information. For example, as described in patent document 1, a film thickness distribution is mapped in the plane of the resist film 12, which is then used as the resist sensitivity distribution diagram. If the film thickness of the resist film 12 is large, there is a possibility that the resist film 12 is not sufficiently reacted, even if the resist film 12 is exposed to a specific exposure amount. On the other hand, if the film thickness of the resist film 12 is small, the resist film 12 is sufficiently reacted. The resist sensitivity distribution diagram is created based on this information. Then, the mask blank 5 is mounted on the exposure device, and the exposure amount is corrected according to its in-plane sensitivity distribution information, to thereby perform exposure to obtain a uniform pattern accuracy in the plane of the resist film 12.

1-D) Acquiring information, may be performed before actually performing exposure in the exposing step.

[0046]

As described in the problem of the present invention, there are a plurality of square mask blanks 5 in plan view, depending on a case. In this case, upper/lower and right/left directions cannot be specified in plan view in the mask blank 5. Then, there is a possibility that

directions of the mask blank 1 with a resist film when in-plane sensitivity distribution information is obtained, and directions of the mask blank 1 with a resist film when the mask blank 1 is mounting on the exposure device, are not matched with each other. However, in this embodiment, directions are imparted to the mask blank 1 with a resist film, and exposure can be performed by setting the directions imparted by the removing step, and the directions in the in-plane sensitivity distribution information, to be matched with each other.

[0047]

Regarding a specific exposure technique and the technique of correcting the exposure amount, the publicly-known technique may be used. For example, electron beam lithography may be used, or the exposure method used for each mask given in the 1-A-b) Forming a thin film, may be used.

[0048]

1-F) Development

As shown in FIG. 1(f), the resist pattern is formed by development. A publicly-known method may be used as a specific operation and developer in the developing step.

[0049]

1-G) Etching step

The resist pattern can be formed through the abovementioned steps. A specific pattern is formed on the thin film 11 under the resist pattern, utilizing the resist pattern. As shown in FIG. 1(g), etching is applied to the thin film 11 using the resist film 12 as a mask, the resist film 12 having a specific resist pattern formed thereon. By etching, a

specific transfer pattern is formed on the thin film 11.

[0050]

A publicly-known technique may be used as the technique of etching. As a preferable example, dry etching is used in etching the thin film 11, using a reactive gas as an etchant. By utilizing the resist pattern of this embodiment, an accurate transfer pattern can be formed even if an isotropic etching gas is contained in the reactive gas.

[0051]

Further, in the etching method, chromium is contained in the composition of a surface layer of the thin film 11, and the reactive gas is a mixed gas containing at least oxygen and chlorine, and such an etching method is preferably used in the present invention.

[0052]

1-H) Others

Then, as shown in FIG. 1(h), the transfer mask 50 of this embodiment is manufactured by suitably performing the processing of removing the resist pattern and cleaning and others. The publicly-known technique may be used as these techniques.

Further, another film may be suitably provided other than the abovementioned structure. For example, a resist underlying film may be provided between the thin film 11 and the resist film 12.

[0053]

<2. Mask blank 1 with a resist film>

In the abovementioned technique, the mask blank 1 itself with a resist film manufactured through the steps from the first to 1-C) Removing, has a great characteristic as well. The mask blank 1 with a

resist film of this embodiment includes the substrate 10 having the thin film 11, and the resist film 12 formed on the surface of the thin film 11. Then, the resist film 12 is formed on the surface of the thin film 11, so as to impart directions when the substrate 10 is horizontally mounted, by the positional relation in plan view between the thin film 11 and the resist film 12.

[0054]

When the resist film 12 is removed at the peripheral edge portion of the mask blank 1 with a resist film, a metal frame like a picture frame is formed in plan view. Usually, the resist film 12 and the thin film 11 have completely different colors. Therefore, if the peripheral edge portion of the upper side resist film 12 is largely removed, it is not easy for the worker to recognize the directions. That is, the directions are imparted by setting the width of the removal margin to be larger or smaller than other peripheral edge portion at a specific peripheral edge portion, while entirely removing the peripheral edge portion of the resist film 12, and it is easy for the worker to recognize the directions.

[0055]

Thus, a sensitivity map can be created, in which a distribution state of the resist sensitivity is fixed. An exposure condition (for example, electron beam lithography condition) for correcting dimensions at the time of drawing, is created based on the abovementioned sensitivity map, to thereby set the longitude and latitude of both maps in a matching state, and prevent confusion from occurring in recognizing up/down, and left/right (in other words, confusion in recognizing north, south, east, and west). Thus, the resist pattern having excellent

dimension accuracy (CDU) can be formed, and therefore the transfer mask 50 having excellent dimension accuracy can be manufactured as a result.

[0056]

[Embodiment 2]

This embodiment shows an example of marking an index for imparting directions to the thin film 11 or the substrate 10 constituting the mask blank 5. Note that contents not particularly specified, is the same as [Embodiment 1].

[0057]

First, in 1-A-a) Preparing a substrate, marking is applied to the substrate 10 or the thin film 11, to thereby impart directions to the mask blank 5 when the mask blank 5 is horizontally mounted. The marking here, shows that the index is given to the mask blank 5. The index is not particularly limited, if it can impart directions when the mask blank 5 is horizontally mounted. For example, processing may be performed to drop a corner of an intersection between a side which is an upper side when substrate 10 is viewed horizontally and other side, or an index showing directions such as arrow may be applied to the substrate 10 or the thin film 11 as a mark. The position of the marking may be arbitrary selected, and for example, marking of the index may be applied to an end face of the substrate 10, or an upper side portion of the intersection between the end face and a main surface of the substrate 10 may be chamfered, and marking of the index may be applied to the chamfered surface. When marking of the index is applied to the main surface of the substrate 10, the index is marked at a visible position

even after applying a resist liquid thereto. For example, the following structure may also be acceptable, that is, by entirely removing the peripheral edge portion of the resist film 12 by the step of 1-C) Removing, the index is exposed, which is marked on the peripheral edge portion of the thin film 11.

Further, in the steps after the step of 1-D Acquiring information & 1-E) Exposing, the technique similar to the technique of [Example 1] may be used.

In this embodiment, the mask blank 5 itself has characteristics. First, the mask blank 5 has the substrate 10 having the thin film 11. In this state, marking of the index is applied to the substrate 10 or the thin film 11 for imparting directions when the mask blank 5 is horizontally mounted. Thus, the resist pattern having excellent dimension accuracy (CDU) can be formed, and as a result, the transfer mask 50 having excellent dimension accuracy can be manufactured.

[0058]

[Embodiment 3]

This embodiment shows the other example.

In the abovementioned embodiment, each step is provided. However, a technical concept of the present invention is summarized as follows.

“The resist film is formed on a base body, so as to determine directions when the base body is mounted horizontally, by a positional relation in plan view between the base body and the resist film formed on the base body.”

“Marking is applied to the base body, to impart directions when

the base body is mounted horizontally.”

Of course, the above contents may be applied to the method of manufacturing a transfer mask 50 or the mask blank 1 itself with a resist film.

[0059]

The “base body” called here, is an object to be coated with the resist liquid, and indicates the substrate 10 having the thin film 11 in the above embodiment. Of course, the technique of the above embodiment can be applied, even in a case that the base body is interpreted as the substrate 10 itself and the substrate 10 is coated with the resist film 12. In this case, for example, there is a case that imprint mold is fabricated from the mask blank 5. Since the imprint mold is a pattern transfer system used by directly pressing it to the resist film 12 which is applied on a transfer object. Therefore, the imprint mold has a great influence on the shape of a fine pattern formed on the surface of the mold for imprint.

[0060]

Particularly, the master mold which is an original mold for fabricating the imprint mold, is manufactured by a technique of forming a chromium thin film 11 or a Ta-based thin film 11, etc., on the surface of the substrate 10 such as a synthetic quartz glass, etc., and forming the resist film 12 thereon. In this case, the resist film 12 is patterned by lithography, and etching is applied to a lower thin film 11 or the substrate 10 using the resist pattern as a mask, so that an uneven pattern of the mold for imprint is formed.

That is, even in a case that the imprint mold is fabricated,

in-plane uniformity of the pattern is a great problem. In order to improve the in-plane uniformity, it is important to obtain in-plane sensitivity distribution information and correct the exposure amount according to the information. In this case, similarly to the method of manufacturing the transfer mask 50, it is important to make the directions matched with each other, between the case when in-plane sensitivity distribution information is obtained and the case when the mask blank is mounted on the exposure device.

As a result, each of the abovementioned steps is performed, even in a case that the imprint mold is fabricated, and therefore the concept of the present invention can be sufficiently used.

[0061]

As described above, according to each of the abovementioned embodiments, the technique of improving the in-plan uniformity of the pattern can be provided.

Example

[0062]

The present invention will be specifically described hereafter, while showing examples. Of course, the present invention is not limited to the following example.

[0063]

<Example>

In this example, an effect was examined regarding the matching between “the directions of the mask blank 1 with a resist film when in-plane sensitivity distribution information was obtained, and the directions of the mask blank 1 when the mask blank 1 was mounted on

the exposure device”. Therefore, the process immediately before actual exposure was performed in the step of 1-E) Exposing. That is, a result of correcting the exposure amount based on the in-plane sensitivity distribution information was examined. If such a correction result shows that the in-plane uniformity can be maintained satisfactorily, uniformity of a finally obtained pattern can also be maintained satisfactorily. Based on this concept, the difference of the in-plane uniformity was examined in the result of correcting the exposure amount, between the cases when the directions are matched with each other (example) and the case when the directions are not matched with each other (comparative example), for obtaining the in-plane sensitivity distribution information and for mounting the mask blank on the exposure device.

[0064]

1-A) Preparing a substrate (mask blank) with a thin film

1-A-a) Preparing a substrate

A substrate 10 (called a transmitting substrate 10) was prepared, having a transmitting property and made of synthetic quartz glass in which a main surface dimension was about 152 mm × about 152 mm and a thickness was about 6.25 mm.

[0065]

1-A-b) Forming a thin film

First, a light semi-transmitting (lower layer) was formed on the transmitting substrate 10.

MoSiN film (lower layer) was formed by a film thickness of 69 nm on the substrate 10 made of synthetic quartz glass by a reactive

sputtering (DC sputtering), using a single-wafer sputtering device and a mixed target of molybdenum (Mo) and silicon (Si) (atomic% ratio of Mo : Si = 13 : 87) as a sputter target, and in a mixed gas atmosphere of argon and nitrogen. Transmittance was 6.04% ($\lambda = 193$ nm) and a phase difference was 179.5°.

[0066]

Next, a transmitting film (upper layer) of a three-layer structure was formed on the light semi-transmitting film.

A chromium-rich CrOCN film was formed by a film thickness of 30 nm by a reactive sputtering (DC sputtering: DC power of 1.9kW), using a chromium (Cr) target and a single-DC sputtering device, and using a mixed gas of argon (Ar), carbon dioxide (CO₂), nitrogen (N₂), and helium (He) (flow rate ratio of Ar : CO₂ : N₂ : He = 22 : 39 : 6 : 33, Pressure = 0.2 pa) as a sputtering gas.

CrN film was formed thereon by a thickness of 4 nm, by a reactive sputtering (DC sputtering), using a single-wafer sputtering device and using a mixed target of molybdenum (Mo) and silicon (Si) (atomic% ratio of Mo : Si = 13 : 87) as a sputter target.

A chromium-rich CrOCN film was formed thereon by a film thickness of 14nm, using the same chromium (Cr) target, and by a reactive sputtering (DC sputtering: DC power of 1.9kW), and using a mixed gas of argon (Ar), carbon dioxide (CO₂), nitrogen (N₂), and helium (He) (flow rate ratio of Ar : CO₂ : N₂ : He = 21 : 37 : 11 : 31, and pressure = 0.2Pa) of argon (Ar).

By the above-described procedure, a light-shielding film 3 made of a chromium-based material including a lowermost layer made of

CrOCN, a lower layer made of CrN, and an upper layer made of CrOCN, was formed from the phase shift film side.

By the above-described procedure, the substrate 10 with a thin film 11 was obtained. An optical concentration of the light semi-transmitting film and the light shielding film was 3.0 ($\lambda = 193$ nm).

[0067]

1-B) Forming a resist film

First, HMDS processing was performed to the light-shielding film which was the upper layer of the thin film 11, for improving adhesion to the resist film 12. Thereafter, the surface of the thin film 11 was coated with a chemically amplified positive resist for electron beam lithography (PRL009: by Fujifilm Electronic Materials Co., Inc.) by spin coating, and heat treatment was applied thereto for 600 seconds at 130°C, to thereby form a resist film 12 (film thickness of 120 nm).

[0068]

1-C) Removing

The mask blank 1 with a resist film was placed in an apparatus shown in FIG. 2. Then, nozzles 30 for discharging a chemical liquid to remove the resist film 12, were arranged so that the width of the removal margin of the resist film 12 was small in one side (upper side) of a square substrate 10 in plan view. Then, the chemical liquid was discharged and the entire peripheral edge portion of the resist film 12 was removed, and the width of the removal margin of the resist film 12 was set to be smaller than the width of other side, compared with the width of the removal margin of other side. This state is shown in FIG. 3. FIG. 3 is a photograph showing a result of an optical microscope

observation performed to the mask blank 1 with a resist film. As shown in FIG. 3, the present invention achieves a point that the width of the removal margin of the resist film 12 was 1.1 mm on the upper side, and the width of the removal margin was 1.5mm on the other side (for example left side).

[0069]

1-D) Acquiring information

First, the in-plan sensitivity distribution information regarding the resist film 12 was visualized by measuring the film thickness of the resist film 12 (441 points (21 points $\times$ 21 points) in a substrate center 4.2 inches square area), using a spectral interferometric film thickness measuring apparatus (manufactured by Nanometrics Inc.). FIG. 4 shows the result of this visualization.

FIG. 4 is a view showing the in-plane sensitivity distribution information of the mask blank 1 with a resist film, according to examples and comparative examples, wherein (a) is a two-dimensional graph, and (b) is a three-dimensional graph.

Incidentally, FIG. 5 is a view showing the in-plane sensitivity distribution information after the mask blank 1 with a resist film of examples and comparative examples is stored under specific conditions, wherein (a) is a two-dimensional graph, and (b) is a three-dimensional graph.

[0070]

1-E Exposing

Next, an exposure amount was corrected based on the in-plane sensitivity distribution information so that the pattern formed on the

resist film 12 was uniform, using an electron beam lithography system produced by Elionix Co. The result is shown in FIG. 6. FIG. 6 is a view showing the result of the example, wherein the mask blank 1 with a resist film is housed in a casing having an opening in an upper part so as to be opened and closed, and showing a degree of correcting the exposure amount in the case of the directions when in-plane sensitivity distribution information after the mask blank 1 is stored under specific conditions (23°C and 30h), and the directions when the mask blank 1 with a resist film is mounted on the exposure device, are matched with each other, wherein (a) is a two-dimensional graph, and (b) is a three-dimensional graph.

When FIG. 6 is referenced, it is found that correction of the exposure amount is normally performed. By performing exposure in this state, it is possible to obtain a more excellent in-plane uniformity of the pattern formed on the resist film 12. Also, it is possible to obtain an excellent in-plane uniformity of the pattern formed on the transfer mask 50 or the imprint mold.

[0071]

<Comparative example>

In comparative example, the directions of the mask blank 1 with a resist film when in-plane sensitivity distribution information is obtained, and the directions of the mask blank 1 with a resist film when the mask blank 1 is mounted on the exposure device, are set in a non-matching state (upside-down). The other points are the same as examples. The result is shown in FIG. 7. FIG. 7 is a view showing the result of the comparative example, and is a view showing the degree of

correcting the exposure amount in the case that the directions when the in-plane sensitivity distribution information of the mask blank 1 with a resist film is obtained, and the directions when the mask blank 1 with a resist film is mounted on the exposure device are non-matching state (upside-down), wherein (a) is a two-dimensional graph, and (b) is a three-dimensional graph.

When FIG. 7 is referenced, it is found that the correction of the exposure amount is not normally performed. If the exposure is performed in this state, the in-plane uniformity of the pattern formed on the resist film 12 cannot be maintained. It is also found that the in-plane uniformity of the pattern formed on the transfer mask 50 or the imprint mold cannot be maintained.

[0072]

A similar test was performed to the mask blank 1 with a resist film after being stored under specific conditions. FIG. 8 is a view showing the result of the comparative example, and is a view showing the degree of correcting the exposure amount in the case that the directions when the in-plane sensitivity distribution information of the mask blank 1 with a resist film is obtained, and the directions when the mask blank 1 with a resist film is mounted on the exposure device are non-matching state (upside-down), wherein (a) is a two-dimensional graph, and (b) is a three-dimensional graph.

When FIG. 8 is referenced, it is found that correction of the exposure amount is not normally performed. If the exposure is performed in this state, the in-plane uniformity of the pattern formed on the resist film 12 cannot be maintained. It is also found that the

in-plane uniformity of the pattern formed on the transfer mask 50 or the imprint mold cannot be maintained.

[0073]

As a result, according to this example, the in-plane uniformity of the pattern can be improved.

Description of Signs and Numerals

1	Mask blank with a resist film
5	Mask blank
10	Substrate
11	Thin film
12	Resist film
20	Nozzle
50	Transfer mask

What is claimed is:

1. A method of manufacturing a mask blank with a resist film, comprising:
preparing a substrate having a thin film, and having a rectangular shape in plan view;

forming a resist film on a surface of the thin film; and
entirely removing a peripheral edge portion of the rectangular shape in the resist film,

wherein in the removing, three sides of the peripheral edge portion of the rectangular shape in the resist film are removed with the same removal width, and meanwhile a remaining one side is removed with a removal amount larger or smaller than the other three sides, so as to impart directions in plan view when the substrate is horizontally mounted, by a positional relation in plan view between the thin film and the resist film.

2. The method according to claim 1, wherein the substrate has a symmetrical shape in plan view.

3. The method according to claim 1 or 2, wherein in the removing, the remaining one side of the peripheral edge portion of the rectangular shape in the resist film is removed with a removal amount smaller than the other three sides.

4. A method of manufacturing a transfer mask using the mask blank with a resist film manufactured by the method of any one of claims 1 to 3, comprising:

acquiring in-plan sensitivity distribution information regarding a resist film of the mask blank with a resist film;

performing exposure to the resist film based on the in-plan sensitivity distribution information after the removing; and

performing development after the exposing, and forming a transfer pattern to the resist film,

wherein in the performing exposure, the exposing is performed to the resist film so that directions imparted to the mask blank with a resist film, and directions in the in-plan sensitivity distribution information, are set in a matching state.

5. A mask blank with a resist film provided with a substrate having a thin film and a rectangular shape in plan view, and a resist film formed on a surface of the thin film, wherein a peripheral edge portion of the rectangular shape is entirely

removed in the resist film, and three sides of the peripheral edge portion of the rectangular shape in the resist film are removed with the same removal width, and meanwhile a remaining one side is removed with a removal amount larger or smaller than the other three sides, so as to impart directions in plan view when the substrate is horizontally mounted, by a positional relation in plan view between the thin film and the resist film.

6. The mask blank with a resist film according to claim 5, wherein the remaining one side of the peripheral edge portion of the rectangular shape in the resist film is removed with a removal amount smaller than the other three sides.

7. A method of manufacturing a transfer mask using the mask blank with a resist film of claim 5 or 6, comprising:

- acquiring in-plan sensitivity distribution information regarding a resist film of the mask blank with a resist film;

- performing exposure to the resist film based on the in-plan sensitivity distribution information after the removing; and

- performing a pattern formation of performing development after the exposing, and forming a transfer pattern to the resist film,

- wherein in the performing exposure, the exposing is performed to the resist film so that directions imparted to the mask blank with a resist film, and directions in the in-plan sensitivity distribution information, are set in a matching state.