

[DESCRIPTION]

[TITLE OF INVENTION]

METHOD OF MANUFACTURING MASK BLANK, MASK BLANK, METHOD OF
MANUFACTURING PHOTOMASK, AND PHOTOMASK

5 [TECHNICAL FIELD]

[0001]

The present invention relates to a method of manufacturing a mask blank, a
mask blank, a method of manufacturing a photomask, and a photomask. Particularly,
the invention relates to a preferred technique used for a photo-mask blank including a
10 mask layer containing silicon.

This application claims priority from Japanese Patent Application No. 2020-
113378 filed on June 30, 2020, the contents of which are incorporated herein by
reference in their entirety.

[BACKGROUND ART]

15 [0002]

In order to form a photomask used in a photolithography process of manufacture
of an FPD (Flat Panel Display), a semiconductor device, or the like, a photo mask blank
(mask blank) is used. The mask blank has a configuration in which a mask layer is
stacked on one of main surfaces of a transparent substrate such as a glass substrate, or the
20 like.

[0003]

In the manufacturing a mask blank, a film serving as a mask layer having
predetermined optical characteristics such as a light-shielding layer or the like is formed
on the transparent substrate. The mask layer formed of a single layer or a plurality of
25 layers may be stacked. A resist pattern is formed on the mask layer, the resist pattern is

used as a mask, the mask layer is removed by selectively etching, a predetermined mask pattern is formed, and therefore a photomask is manufactured.

[0004]

As the mask layer formed on the mask blank, a mask layer or the like formed of
5 a film containing silicon or a film containing silicon and molybdenum is known (Patent Literatures 1 to 3).

Additionally, in recent years, there has been a demand for a mask blank used for a photolithography process in which high-definition patterning is possible.

[CITATION LIST]

10 [PATENT LITERATURE]

[0005]

[Patent Literature 1] Japanese Unexamined Patent Application, First Publication
No. 2015-111246

[Patent Literature 2] Japanese Patent No. 6418035

15 [Patent Literature 3] Japanese Patent No. 6579219

[SUMMARY OF THE INVENTION]

[PROBLEMS TO BE SOLVED BY THE INVENTION]

[0006]

However, in a case in which the mask layer contains molybdenum, when laser
20 irradiation is carried out in an exposure step, a film thickness of an oxide layer formed as a superficial layer becomes larger, that is, there is a problem in that accuracy in shape of the formed pattern is degraded.

Furthermore, for the achievement of high-definition patterning, it is necessary to further increase an etching rate of the mask layer in a pattern formation step.

25 [0007]

Additionally, in a case of using sputtering when forming a mask layer, a target containing silicon serving as a film-forming material is used; however, since the specific resistance of the target is high, there are problems with plasma generation, and there is a case in which a mask layer having desired film characteristics may be not obtained.

5 Moreover, in a case of using RF sputtering with a target having a high resistance when forming a mask layer, a state in which plasma is generated varies due to a decrease in an anode, and there is a problem in that a mask layer having desired film characteristics is not obtained.

[0008]

10 The invention was conceived in view of the above-described circumstances and achieves the following objects.

1. To provide a mask blank used for a photolithography process in which high-definition patterning is possible.

2. To provide a mask blank that can achieve accurate patterning.

15 3. To increase an etching rate of a mask layer.

4. To stabilize plasma and to form a mask layer having desired film characteristics.

[MEANS FOR SOLVING THE PROBLEMS]

[0009]

20 A method of manufacturing a mask blank according to one aspect of the invention is a method of manufacturing a mask blank in which a mask layer containing silicon is stacked on a transparent substrate and forms the mask layer by sputtering using a target containing a dopant reducing a specific resistance.

25 In the method of manufacturing a mask blank according to one aspect of the invention, the specific resistance of the target may be from 0.001 Ωcm to 0.1 Ωcm .

In the method of manufacturing a mask blank according to one aspect of the invention, the dopant may be one or more selected from the group consisting of boron, phosphorus, and arsenic.

5 In the method of manufacturing a mask blank according to one aspect of the invention, the dopant may be boron in the target, and a dopant concentration thereof may be in a range of 1×10^{18} atm/cm³ to 1×10^{20} atm/cm³.

In the method of manufacturing a mask blank according to one aspect of the invention, the target may be silicon single crystal or polycrystalline silicon.

10 In the method of manufacturing a mask blank according to one aspect of the invention, an atmosphere gas used in the sputtering may contain nitrogen.

In the method of manufacturing a mask blank according to one aspect of the invention, an atmosphere gas used in the sputtering may contain oxygen.

In the method of manufacturing a mask blank according to one aspect of the invention, the sputtering may be DC sputtering.

15 A mask blank according to one aspect of the invention is a mask blank manufactured by the aforementioned method of manufacturing a mask blank, the mask layer containing boron as the dopant, wherein a dopant concentration of the mask layer is in a range of 1×10^{18} atm/cm³ to 1×10^{20} atm/cm³.

20 In the mask blank according to one aspect of the invention, an etching rate of the mask layer in dry etching may be 1.05 to 1.5 times an etching rate of a layer formed by using a non-doped target.

In the mask blank according to one aspect of the invention, the mask layer may contain nitrogen or oxygen.

25 In the mask blank according to one aspect of the invention, a compositional ratio of nitrogen or oxygen in the mask layer may be changed in a film thickness direction.

In the mask blank according to one aspect of the invention, the mask layer may contain a phase-shift layer.

A method of manufacturing a photomask according to one aspect of the invention is a method of manufacturing a photomask from the above-mentioned mask blank, the method includes forming a resist pattern on a surface of the mask layer (resist-pattern formation step), and forming a mask pattern by patterning the mask layer using the resist pattern as a mask (mask-pattern formation step). When the mask pattern is formed (in the mask-pattern formation step), the mask layer is dry-etched.

A photomask according to one aspect of the invention is manufactured by the above-described method of manufacturing the photomask.
[0010]

The method of manufacturing a mask blank according to one aspect of the invention is a method of manufacturing a mask blank in which a mask layer containing silicon is stacked on a transparent substrate and forms the mask layer by sputtering using a target containing a dopant reducing a specific resistance.

Consequently, when forming the mask layer by sputtering, since a specific resistance of the target is reduced, electric power for forming plasma is stabilized, plasma in a state of forming a film is stabilized, and the mask layer can be formed. As a result, an abnormal electrical discharge phenomenon, for example, arc is prevented from being generated during sputtering, factors which cause characteristics and defects of a thin film to occur are reduced, and the film formation characteristics can be improved.

Additionally, it is possible to cause dopants to be contained in the mask layer, and it is possible to improve the film characteristics of the mask layer.

Here, specifically, regarding the improvable film characteristics of the mask layer, the selection ratio of the mask layer to the substrate increases with an increase in

the etching rate, and it is easy to determine an end point for determining completion of etching by a light-emission monitor. Accordingly, for example, it means that a depth at which the transparent substrate is excessively etched can be minimally reduced. Since the film characteristics can be improved as stated above, a degree of accuracy in shape of the mask layer during pattern formation increases, and it is possible to provide the mask blank that realizes high-definition patterning.

[0011]

In the method of manufacturing a mask blank according to one aspect of the invention, the specific resistance of the target may be from 0.001 Ωcm to 0.1 Ωcm .

Because of this, electric power for forming plasma is stabilized, plasma in a state of forming a film is stabilized, and the mask layer can be formed. As a result, the film formation characteristics can be improved.

[0012]

In the method of manufacturing a mask blank according to one aspect of the invention, the dopant may be one or more selected from the group consisting of boron, phosphorus, and arsenic.

Therefore, the range of the aforementioned specific resistance is achieved in the target, electric power for forming plasma is stabilized, plasma in a state of forming a film is stabilized, and the mask layer can be formed. As a result, an abnormal electrical discharge phenomenon, for example, arc is prevented from being generated during sputtering, factors which cause characteristics and defects of a thin film to occur are reduced, and the film formation characteristics can be improved.

Here, it is possible to form a P-type semiconductor in a case of using boron as dopants, it is possible to form an N-type semiconductor in a case of using phosphorus or arsenic as dopants, and it is possible to reduce the specific resistance of the target.

[0013]

In the method of manufacturing a mask blank according to one aspect of the invention, the dopant may be boron in the target, and a dopant concentration thereof may be in a range of 1×10^{18} atm/cm³ to 1×10^{20} atm/cm³.

5 Consequently, the range of the specific resistance of the above-described target is achieved, electric power for forming plasma is stabilized, plasma in a state of forming a film is stabilized, and the mask layer can be formed. As a result, an abnormal electrical discharge phenomenon, for example, arc is prevented from being generated during sputtering, factors which cause characteristics and defects of a thin film to occur
10 are reduced, and the film formation characteristics can be improved. Particularly, an electric discharge impedance can be reduced by reducing the specific resistance of the target, and therefore stabilization of plasma is possible.

Here, specifically, stabilization of plasma means that reproducibility of a cathode current value is high in a case in which the cathode current value varies during
15 film formation, and in a case in which film formation is carried out multiple times under the same conditions, means that reproducibility of film thickness is high in the case of forming a film by time control.

Furthermore, uniformity of the film thickness on the formed mask layer and uniformization of the film characteristics at a plurality of positions different from each
20 other on the surface of the formed mask layer are achieved, and a CD profile can be reduced when a wafer is exposed.

Additionally, improvement in the dry etching rate on the formed mask layer is achieved, and therefore it is possible to improve a cross-sectional configuration.

[0014]

25 In the method of manufacturing a mask blank according to one aspect of the

invention, the target may be silicon single crystal or polycrystalline silicon.

Accordingly, the uniformity of a state in which the target contains the dopants is maintained, the uniformity of a dopant concentration is maintained even in an atmosphere in which plasma is generated, and the uniformity of the dopant concentration
5 in the formed mask layer can be maintained.

The target can be formed by an FZ method, a CZ method, or a cast growth method.

[0015]

In the method of manufacturing a mask blank according to one aspect of the
10 invention, an atmosphere gas used in the sputtering may contain nitrogen.

For this reason, it is possible to form, as the mask layer, a nitrided silicon coating such as SiN, SiON, or the like. Alternatively, it is possible to form a silicon coating as a part of the mask layer.

[0016]

15 In the method of manufacturing a mask blank according to one aspect of the invention, an atmosphere gas used in the sputtering may contain oxygen.

For this reason, it is possible to form, as the mask layer, an oxidized silicon coating such as SiON, SiO, or the like. Alternatively, it is possible to form a silicon coating as a part of the mask layer.

20 [0017]

In the method of manufacturing a mask blank according to one aspect of the invention, the sputtering may be DC sputtering.

Therefore, it is possible to improve a film thickness, the film characteristics, and reproducibility of the characteristics profile as compared with a case of forming a mask
25 layer by RF sputtering.

[0018]

A mask blank according to one aspect of the invention is a mask blank manufactured by the aforementioned method of manufacturing a mask blank, the mask layer containing boron as the dopant, wherein a dopant concentration of the mask layer is
5 in a range of 1×10^{18} atm/cm³ to 1×10^{20} atm/cm³.

Consequently, the etching rate with respect to the mask layer increases, and it is possible to reduce the etching time with respect to the mask layer during pattern formation. Therefore, the selection ratio of the mask layer to the transparent substrate increases, and it is easy to determine an end point for determining completion of etching
10 by a light-emission monitor. Accordingly, it is possible to minimally reduce a depth at which the transparent substrate is excessively etched. Furthermore, since it is possible to suppress side etching with respect to the mask layer, it is possible to further improve the cross-sectional configuration.

[0019]

15 In the mask blank according to one aspect of the invention, an etching rate of the mask layer in dry etching may be 1.05 to 1.5 times an etching rate of a layer formed by using a non-doped target.

Consequently, as compared with a mask layer formed by using a silicon target not containing dopants, accuracy in shape by patterning is improved at a higher etching
20 rate while shortening the etching time, and it is possible to realize further high-definition patterning.

[0020]

In the mask blank according to one aspect of the invention, the mask layer may contain nitrogen or oxygen.

25 Accordingly, it is possible to form, as the mask layer, a nitrided or oxidized

silicon coating such as SiN, SiON, SiO, or the like. Alternatively, it is possible to form a silicon coating as a part of the mask layer. As a result, transmissivity is controlled, and it is possible to obtain a mask blank having predetermined optical characteristics such as a low degree of reflectance.

5 [0021]

In the mask blank according to one aspect of the invention, a compositional ratio of nitrogen or oxygen in the mask layer may be changed in a film thickness direction.

Consequently, variations in transmissivity and reflectance with respect to a wavelength of the transmitted light are small, and variation in an etching rate at a boundary face between layers is gradual. Therefore, the mask blank having an excellent cross-sectional configuration can be realized.

[0022]

In the mask blank according to one aspect of the invention, the mask layer may contain a phase-shift layer.

15 Accordingly, a mask blank can be realized which allows a phase-shift mask to be manufactured in which high-definition patterning is possible.

[0023]

A method of manufacturing a photomask according to one aspect of the invention is a method of manufacturing a photomask from the above-mentioned mask blank, the method includes forming a resist pattern on a surface of the mask layer (resist-pattern formation step), and forming a mask pattern by patterning the mask layer using the resist pattern as a mask (mask-pattern formation step). When the mask pattern is formed (in the mask-pattern formation step), the mask layer is dry-etched.

Consequently, the selection ratio of the mask layer to the transparent substrate increases with an increase in the etching rate, and it is easy to determine an end point by

25

a light-emission monitor used for determining completion of etching. Accordingly, a depth at which the transparent substrate is excessively etched can be minimally reduced. Furthermore, the thickness of the resist layer is reduced, and it is possible to shorten a length of operation time required for the resist-pattern formation step. The etching rate
5 with respect to the mask layer increases, and it is possible to reduce the etching time with respect to the mask layer during pattern formation. Damage to the resist layer is reduced, and it is possible to maintain the accuracy in shape by etching. It is possible to manufacture the photomask applicable to high-definition patterning.

[0024]

10 A photomask according to one aspect of the invention is manufactured by the above-described method of manufacturing the photomask. Consequently, it is possible to realize high-definition patterning.

[Effects of the Invention]

[0025]

15 According to the invention, an effect is obtained in that it is possible to provide the mask blank that can manufacture a phase-shift mask applicable to high-definition patterning.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[0026]

20 FIG. 1 is a flowchart showing a method of manufacturing a mask blank according to an embodiment of the invention.

FIG. 2 is a cross-sectional view explaining a step of the method of manufacturing the mask blank according to the embodiment of the invention.

FIG. 3 is a cross-sectional view explaining a step of the method of
25 manufacturing the mask blank according to the embodiment of the invention.

FIG. 4 is a cross-sectional view explaining a step of the method of manufacturing the mask blank according to the embodiment of the invention.

FIG. 5 is a cross-sectional view explaining a step of the method of manufacturing the mask blank according to the embodiment of the invention.

5 FIG. 6 is a schematic view showing a film formation apparatus in the method of manufacturing the mask blank according to the embodiment of the invention.

FIG. 7 is a schematic view showing a vacuum chamber of the film formation apparatus in the method of manufacturing the mask blank according to the embodiment of the invention.

10 FIG. 8 is a schematic view showing the vacuum chamber of the film formation apparatus in the method of manufacturing the mask blank according to the embodiment of the invention.

FIG. 9 is a flowchart showing a method of manufacturing a photomask by use of the mask blank according to the embodiment of the invention.

15 FIG. 10 is a cross-sectional view explaining a step of the method of manufacturing the photomask by use of the mask blank according to the embodiment of the invention.

FIG. 11 is a cross-sectional view explaining a step of the method of manufacturing the photomask by use of the mask blank according to the embodiment of
20 the invention.

FIG. 12 is a cross-sectional view explaining a step of the method of manufacturing the photomask by use of the mask blank according to the embodiment of the invention.

FIG. 13 is a graph showing mask blank according to Examples of the invention.

25 FIG. 14 is an image showing the mask blank according to Example of the

invention.

FIG. 15 is an image showing the mask blank according to Example of the invention.

[EMBODIMENTS FOR CARRYING OUT THE INVENTION]

5 [0027]

Hereinafter, a mask blank, a phase-shift mask (photomask), and manufacturing methods thereof according to an embodiment of the invention will be described with reference to the drawings.

FIG. 1 is a flowchart showing the mask blank according to the embodiment.

10 FIGS. 2 to 5 are cross-sectional views explaining steps of the method of manufacturing the mask blank according to the embodiment. In FIGS. 1 to 5, reference numerals 10A and 10B represent the mask blank.

[0028]

The mask blank 10B according to the embodiment is used for light with a
15 wavelength of 200 nm or less, particularly, exposure light of ArF excimer laser light (wavelength of 193 nm) used in photolithography using a phase-shift mask.

Alternatively, the mask blank 10B according to the embodiment is used for a phase-shift mask (photomask) used in an exposure light wavelength range of approximately 248 nm to 436 nm.

20 As shown in FIG. 5, the mask blank 10B according to the embodiment includes: a glass substrate (transparent substrate) 11; the mask layer (a phase-shift layer 12 and an antireflection layer 13) that is formed on the glass substrate 11 and has predetermined optical characteristics; and a resist layer 15 formed on the mask layer.

[0029]

25 The mask layer includes the phase-shift layer 12 formed on the glass substrate

11 and the antireflection layer 13 formed on the phase-shift layer 12. That is, the antireflection layer 13 is provided at a position further from the glass substrate 11 than the phase-shift layer 12.

In the phase-shift layer 12 and the antireflection layer 13, a refractive index, an extinction coefficient, a transmissivity, a reflectance, a film thickness, or the like are set as the optical characteristics required for the photomask, and they form the mask layer serving as a phase-shift film.

[0030]

As a configuration of the mask blank 10B according to the embodiment, as shown in FIG. 5, a configuration may be adopted in which the resist layer (photoresist layer) 15 is previously formed on the mask layer having the phase-shift layer 12 and the antireflection layer 13 stacked in layers. Note that, as the mask blank 10B according to the embodiment, a configuration may be adopted in which the antireflection layer 13 is not stacked.

[0031]

Note that, in the mask blank 10B according to the embodiment, other than the mask layer configured of the phase-shift layer 12 and the antireflection layer 13, a configuration may be adopted in which an adhesion layer, a chemical resistance layer, a passivation layer, a light-shielding layer, an etching stopper layer, or the like are stacked. As a material of the light-shielding layer, various materials are applicable, but it is preferable use a film formed of a chromium-based material available to an auxiliary film used for etching processing.

Furthermore, as shown in FIG. 5, the resist layer 15 may be formed on the aforementioned multi-layered film.

[0032]

As the glass substrate 11, a material having a high degree of transparency and optical isotropy is used, and for example, a quartz glass substrate can be used. The size of the glass substrate 11 is not particularly limited and is adequately selected depending on a substrate to be exposed by use of the mask (for example, a substrate for an FPD, or
5 the like such as a semiconductor, an LCD (liquid crystal display), a plasma display, an organic EL (electro luminescence) display, or the like).

[0033]

In the embodiment, a substrate formed in a rectangular shape having a length of approximately 100 mm or a substrate formed in a rectangular shape having a length of
10 250 mm or more is applicable as the glass substrate 11. Furthermore, a substrate with a thickness of 1 mm or less, a substrate with a thickness of several mm, or a substrate with a thickness of 10 mm or more can be used.

[0034]

Moreover, the flatness of the glass substrate 11 may be reduced by polishing a
15 surface of the glass substrate 11. The flatness of the glass substrate 11 can be less than or equal to, for example, 5 μm . As a result, the depth of focus of the mask becomes deep, and it significantly contributes to forming a fine pattern with a high level of accuracy. Furthermore, it is preferable that the value of the flatness be a small value, for example, be less than or equal to 0.5 μm .

20 [0035]

The phase-shift layer 12 contains Si (silicon) as a main component. The phase-shift layer 12 contains a predetermined dopant. The phase-shift layer 12 may further contain O (oxygen), N (nitrogen), and C (carbon).

As the kind of the dopant, a material (element) is selected which reduces a
25 specific resistance by doping in a state in which a compositional ratio (atm%) of Si, N, O,

or the like does not vary. Specifically, one or more materials selected from the group consisting of B (boron), P (phosphorus), As (arsenic), or the like are adopted.

[0036]

Additionally, a configuration may be adopted such that the composition of the phase-shift layer 12 varies in the thickness direction in the phase-shift layer 12. In this case, the phase-shift layer 12 can be configured by stacking one, two, or more kinds selected from the group consisting of a simple body of Si, oxide, nitride, carbide, oxynitride, carbonitride, and carbon-oxynitride of Si.

As described hereinbelow, in the phase-shift layer 12, a thickness of the phase-shift layer 12, a compositional ratio (atm%) of Si, N, O, or the like, and a content rate of a dopant (atm%) are set so as to obtain predetermined optical characteristics, an etching rate, a specific resistance, or the like.

[0037]

The film thickness of the phase-shift layer 12 is set depending on the optical characteristics required for the phase-shift layer 12 and varies depending on a compositional ratio of Si, N, O, or the like. The film thickness of the phase-shift layer 12 can be from 40 nm to 150 nm.

[0038]

Furthermore, the phase-shift layer 12 may be configured by a single layer so as to satisfy a phase difference and a transmissivity required for a phase-shift film. For example, the phase-shift layer 12 may include a layer having an antireflection function in order to satisfy a predetermined surface reflectance. In the entirety of the phase-shift layer 12, the phase-shift layer 12 may be configured by a multi-layer so as to satisfy a phase difference and a transmissivity required for a phase-shift film.

25 [0039]

Even in the case in which the phase-shift layer 12 is configured by a single layer and in the case in which the phase-shift layer 12 is configured by a multi-layer, the phase-shift layer 12 may be formed such that a compositional ratio of each of the layers constituting the phase-shift layer 12 continuously varies in the thickness direction.

- 5 Moreover, in the case in which the phase-shift layer 12 is configured by a multi-layer, the phase-shift layer 12 may be configured by combination of two or more layers, each of which is selected from: a layer having constituent elements different from each other; and a layer having constituent elements which are the same as each other and have compositional ratios different from each other. In the case in which the phase-shift
- 10 layer 12 is configured so as to include three or more multi-layered films, as long as the same layers are not disposed so as to be adjacent to each other, the phase-shift layer 12 may be formed by combination including the same layers.

[0040]

- The phase-shift layer 12 is a film providing a predetermined phase-shift value
- 15 and a predetermined transmissivity with respect to light with a wavelength of 200 nm or less, particularly, exposure light of ArF excimer laser light (wavelength of 193 nm) used in photolithography using a phase-shift mask.

[0041]

- For example, it is preferable that the phase-shift layer 12 be configured to
- 20 include a portion formed of a silicon-based material represented as SiN or SiON in the thickness direction of the phase-shift layer 12. Consequently, a predetermined transmissivity is provided and chemical resistance is improved while ensuring a predetermined phase difference.

[0042]

- 25 Regarding the phase difference of the phase-shift layer 12, it is sufficient if the

phase difference of the phase-shift layer 12 is 150 to 200°, approximately 180±10°, or 175 to 185° at the boundary between a region where a phase-shift film is present and a region where a phase-shift film is not present.

For example, it is preferable that the transmissivity of the phase-shift layer 12 with respect to the exposure light be in a range of 3% to 40%, and furthermore be in a range of 5% to 10%.

[0043]

The thickness of the phase-shift layer 12 is 40 nm to 70 nm or 50 nm to 65 nm. The larger the thickness of the pattern of the mask layer, the smaller the three-dimensional effect of the phase-shift layer 12. Additionally, the thickness of the phase-shift layer 12 is set in a thickness range such that predetermined optical characteristics are obtained with respect to light with a wavelength of 200 nm or less. The thinner the phase-shift layer 12, the easier the micro pattern is formed.

[0044]

As described above, the phase-shift layer 12 is formed of a silicon-based material. Specifically, the phase-shift layer 12 is SiN (silicon nitride) or SiON (silicon oxynitride). The phase-shift layer 12 may contain other elements. In this case, dopants serving as impurities are contained in the phase-shift layer 12.

[0045]

By increasing a contained amount of nitrogen contained in the phase-shift layer 12 as much as possible, the transmissivity thereof increases. The deficient amount of the transmissivity is compensated by adding a bare minimum of oxygen to the phase-shift layer 12, and the thickness of the phase-shift layer 12 can be reduced by reducing a contained amount of oxygen to be low. Accordingly, it is preferable that a contained amount of oxygen contained in a silicon-based material be 1/3 or less (compositional

ratio) of a contained amount of nitrogen, and particularly be 1/5 or less (compositional ratio) thereof.

[0046]

5 The phase-shift layer 12 may include a layer formed of Si and N. Furthermore, the phase-shift layer 12 may be formed of two or more multi-layers having compositional ratios of Si and N different from each other. Moreover, the phase-shift layer 12 may be formed such that a compositional ratio of Si and N step-by-step or continuously varies in the thickness direction of the phase-shift layer 12.

[0047]

10 The phase-shift layer 12 contains a predetermined dopant, specifically, one selected from the group consisting of B (boron), P (phosphorus), As (arsenic), or the like.

The dopant contained in the phase-shift layer 12 is boron, and a dopant concentration is in a range of 1×10^{18} atm/cm³ to 1×10^{20} atm/cm³.

[0048]

15 The antireflection layer 13 contains Cr (chromium) and O (oxygen) as main components. Also, the phase-shift layer 12 contains C (carbon) and N (nitrogen).

In this case, the antireflection layer 13 can be configured by stacking one, two, or more kinds selected from the group consisting of oxide, nitride, carbide, oxynitride, carbonitride, and carbon-oxynitride of Cr. Additionally, a configuration may be adopted such that the composition of the antireflection layer 13 varies in the thickness direction in the antireflection layer 13. As described hereinbelow, the thickness of the antireflection layer 13 and a compositional ratio (atm%) of Cr, N, C, O, Si, or the like are set such that a predetermined adherence property (hydrophobicity) and predetermined optical characteristics are obtained.

25 [0049]

In the antireflection layer 13, an oxygen content (oxygen concentration) can be set in a range of 6.7 atm% to 63.2 atm% and a nitrogen content (nitrogen concentration) can be set in a range of 4.6 atm% to 39.3 atm%.

It is possible to reduce a refractive index and a value of an extinction coefficient of the antireflection layer 13 by setting the nitrogen concentration and the oxygen concentration of the antireflection layer 13. Particularly, it is possible to significantly reduce a refractive index and a value of an extinction coefficient of the antireflection layer 13 by increasing the oxygen concentration of the antireflection layer 13.

[0050]

Furthermore, by setting the film thickness of the antireflection layer 13 to be in a range of 30 nm to 60 nm, it is possible to reduce the reflectance with respect to light with a wavelength of 200 nm or less, particularly, exposure light of ArF excimer laser light (wavelength of 193 nm) used in photolithography using a phase-shift mask. Note that, the compositional ratio of the constituent materials of the antireflection layer 13 is not limited to the above-mentioned value. The aforementioned compositional ratio is an example of the invention.

[0051]

As shown in FIG. 1, the mask blank according to the embodiment includes: a substrate preparation step S11, a mask-layer formation step S12, and a resist formation step S13.

[0052]

In the substrate preparation step S11 shown in FIG. 1, the glass substrate 11 formed of a quartz glass having, for example, a predetermined size is prepared as shown in FIG. 2.

In the substrate preparation step S11, a surface processing such as polishing, HF

cleaning, or the like can be carried out with respect to the glass substrate 11 having a high degree of transparency and optical isotropy.

[0053]

In the mask-layer formation step S12 shown in FIG. 1, the phase-shift layer 12
5 and the antireflection layer 13 which constitute the mask layer are formed in order on the glass substrate 11.

[0054]

FIG. 6 is a schematic view showing a manufacturing apparatus of the mask blank according to the embodiment.

10 The phase-shift layer 12 and the antireflection layer 13 of the mask blank 10A are manufactured by a manufacturing apparatus 100 shown in FIG. 6 in the mask-layer formation step S12 according to the embodiment.

[0055]

The manufacturing apparatus 100 is a single-wafer DC sputtering apparatus.

15 As shown in FIG. 6, the manufacturing apparatus 100 includes a load chamber 101a, an unload chamber 101b, a transfer chamber 101c connected to the load chamber 101a and the unload chamber 101b via a hermetical sealing mechanism, vacuum chambers (a first vacuum chamber and a first vacuum processing chamber) 102, and vacuum chambers (a second vacuum chamber and a second vacuum processing chamber)
20 103. The vacuum chambers 102 and 103 include film formation mechanisms corresponding to the respective two film formation treatments. The vacuum chambers 102 and 103 are film formation chambers connected to the transfer chamber 101c.

[0056]

The transfer chamber 101c includes: a transfer mechanism 101d that transfers
25 the glass substrate 11 transferred from outside of the manufacturing apparatus 100 via the

load chamber 101a to the vacuum chamber 102 and the vacuum chamber 103; and a pumping mechanism such as a rotary pump, a turbo-molecular pump, or the like, which depressurizes the inside of the transfer chamber 101c.

[0057]

5 FIG. 7 is a schematic view showing a vacuum chamber of the manufacturing apparatus of the mask blank according to the embodiment. FIG. 8 is a schematic view showing a vacuum chamber of the manufacturing apparatus of the mask blank according to the embodiment.

 In the vacuum chamber 102, a material film used for a mask blank is formed
10 using a long-slow sputtering (LTS) method.

[0058]

 As shown in FIG. 7, the vacuum chamber 102 has a film formation space 102K. A reaction-gas introduction hole 114a and an inert-gas introduction hole 114b are connected to the film formation space 102K. Moreover, a vacuum exhaust hole 114d
15 and a vacuum exhaust hole 114e are connected to the film formation space 102K. Furthermore, the vacuum chamber 102 includes a cathode electrode (backing plate) 105A (105) and a substrate holder 107.

[0059]

 The substrate holder 107 includes a substrate-holding mechanism. The
20 substrate holder 107 is configured to cause the glass substrate 11 transferred to the vacuum chamber 102 by the transfer mechanism 101d to face a target 104A to be inclined with respect thereto and to hold the glass substrate 11 during film formation. A heater 111 is provided inside the substrate holder 107.

[0060]

25 In the film formation space 102K, the target 104A that functions as a first film

formation mechanism of two film formation mechanisms and supplies a film-forming material thereto is provided.

The film formation mechanism of the vacuum chamber 102 includes the target 104A, the cathode electrode 105A that holds the target 104A, and a power supply 112A that applies a sputtering voltage with negative electrical potential to the cathode electrode 105A. The power supply 112A can apply a high-frequency voltage or a DC voltage.

[0061]

The target 104A serving as a base material of a film material and being formed in a flat plate-shape is provided on a surface of the cathode electrode 105A. The cathode electrode 105A is disposed along a ceiling 102a having a dome shape and forming the vacuum chamber 102. That is, the vacuum chamber 102 has a configuration in which the target 104A serving as a base material of a film material and being formed in a flat plate-shape is inclined in a single film formation space 102K.

The target 104A corresponding to formation of the phase-shift layer (mask layer) 12 is used in the vacuum chamber 102.

[0062]

Inside the vacuum chamber 102, sputtered particles scattered from the target 104A travel to a rotating processing-target surface of the rectangular-shaped glass substrate 11 (R: rotation direction). A tilt angle ΔA (Δ), which is formed between: a vertical direction T11 (an arrow of a dotted line) with respect to a sputtering surface 104As of the target 104A; and a line segment TSA (TS: an arrow of a solid line) connecting a center of the sputtering surface 104As of the target 104A and a center of the processing-target surface of the glass substrate 11, is different from the vertical direction T11. Here, the line segment TSA (TS) is a so-called distance between the target 104A and the glass substrate 11.

[0063]

A vacuum pump not shown in the drawings is connected to the vacuum exhaust hole 114d and the vacuum exhaust hole 114e. A magnet plate 109A (109) including magnets 110A (110) doubly-concentrically disposed thereon is provided on a back surface of the cathode electrode 105A. A sputtering power supply (power supply) 112A (112) is electrically connected to the cathode electrode 105A.

[0064]

The film formation mechanism of the vacuum chamber 102 has the inert-gas introduction hole 114b, the reaction-gas introduction hole 114a, the vacuum exhaust hole 114d, and the vacuum exhaust hole 114e. The inert-gas introduction hole 114b is connected to a gas introduction mechanism that introduces a gas into a space close to the cathode electrode 105A in the film formation space 102K. The reaction-gas introduction hole 114a introduces a reactive gas into a space close to the glass substrate 11. The vacuum exhaust hole 114d is connected to a high-vacuum pumping mechanism such as a turbo-molecular pump or the like that depressurizes the inside of the film formation space 102K so as to obtain high vacuum. The vacuum exhaust hole 114d discharges the gas inside the film formation space 102K from the position close to the cathode electrode 105A. The vacuum exhaust hole 114e discharges the gas inside the film formation space 102K from the position close to the glass substrate 11.

[0065]

Furthermore, the vacuum chamber 103 that is a film formation chamber serving as a chamber different from the vacuum chamber 102 includes a second film formation mechanism of the two film formation mechanisms, which supplies a film-forming material. The vacuum chamber 103 includes a mechanism that is substantially the same as the film formation mechanism of the vacuum chamber 102.

The vacuum chamber 103 has a configuration that is substantially the same as that of the vacuum chamber 102. In the vacuum chamber 103, a material film used for a mask blank is formed using a long-slow sputtering (LTS) method.

[0066]

5 As shown in FIG. 8, the vacuum chamber 103 has a film formation space 103K. A reaction-gas introduction hole 114a and an inert-gas introduction hole 114b are connected to the film formation space 103K. Moreover, a vacuum exhaust hole 114d and a vacuum exhaust hole 114e are connected to the film formation space 103K. Furthermore, the vacuum chamber 103 includes a cathode electrode (backing plate) 105B
10 (105) and the substrate holder 107.

[0067]

The substrate holder 107 includes a substrate-holding mechanism. The substrate holder 107 is configured to cause the glass substrate 11 transferred to the vacuum chamber 103 by the transfer mechanism 101d to face a target 104B to be
15 inclined with respect thereto and to hold the glass substrate 11 during film formation. A heater 111 is provided inside the substrate holder 107.

[0068]

In the film formation space 103K, the target 104B that functions as a second film formation mechanism of the two film formation mechanisms and supplies a film-
20 forming material thereto is provided.

The film formation mechanism of the vacuum chamber 103 includes the target 104B, the cathode electrode 105B that holds the target 104B, and a power supply 112B that applies a sputtering voltage with negative electrical potential to the cathode electrode 105B. The power supply 112B can apply a high-frequency voltage or a DC voltage.

25 [0069]

The target 104B serving as a base material of a film material and being formed in a flat plate-shape is provided on a surface of the cathode electrode 105B. The cathode electrode 105B is disposed along a ceiling 103a having a dome shape and forming the vacuum chamber 103. That is, the vacuum chamber 103 has a configuration in which the target 104B serving as a base material of a film material and being formed in a flat plate-shape is inclined in a single film formation space 103K.

The target 104B corresponding to formation of the antireflection layer (mask layer) 13 is used in the vacuum chamber 103.

[0070]

Inside the vacuum chamber 103, sputtered particles scattered from the target 104B travel to a rotating processing-target surface of the rectangular-shaped glass substrate 11 (R: rotation direction). A tilt angle ΔB (Δ), which is formed between: a vertical direction T11 (an arrow of a dotted line) with respect to a sputtering surface 104Bs of the target 104B; and a line segment TSB (TS: an arrow of a solid line) connecting a center of the sputtering surface 104Bs of the target 104B and a center of the processing-target surface of the glass substrate 11, is different from the vertical direction T11. Here, the line segment TSB (TS) is a so-called distance between the target 104B and the glass substrate 11.

[0071]

A vacuum pump not shown in the drawings is connected to the vacuum exhaust hole 114d and the vacuum exhaust hole 114e. A magnet plate 109B (109) including magnets 110B (110) doubly-concentrically disposed thereon is provided on a back surface of the cathode electrode 105B. The sputtering power supply (power supply) 112B (112) is electrically connected to the cathode electrode 105B.

[0072]

The film formation mechanism of the vacuum chamber 103 has the inert-gas introduction hole 114b, the reaction-gas introduction hole 114a, the vacuum exhaust hole 114d, and the vacuum exhaust hole 114e. The inert-gas introduction hole 114b is connected to a gas introduction mechanism that introduces a gas into a space close to the cathode electrode 105B in the film formation space 103K. The reaction-gas introduction hole 114a introduces a reactive gas into a space close to the glass substrate 11. The vacuum exhaust hole 114d is connected to a high-vacuum pumping mechanism such as a turbo-molecular pump or the like that depressurizes the inside of the film formation space 103K so as to obtain high vacuum. The vacuum exhaust hole 114d discharges the gas inside the film formation space 103K from the position close to the cathode electrode 105B. The vacuum exhaust hole 114e discharges the gas inside the film formation space 103K from the position close to the glass substrate 11.

[0073]

The above-mentioned two film formation mechanisms are controlled such that necessary compositions or conditions for film formation are obtained to form the phase-shift layer 12 and the antireflection layer 13 on the glass substrate 11 in order.

In the embodiment, the first film formation mechanism of the vacuum chamber 102 corresponds to film formation of the phase-shift layer 12, and the second film formation mechanism of the vacuum chamber 103 corresponds to film formation of the antireflection layer 13.

[0074]

Specifically, in the first film formation mechanism of the vacuum chamber 102, the target 104A is formed of a material containing silicon and a predetermined dopant which serve as a composition necessary to form the phase-shift layer 12 on the glass substrate 11.

[0075]

The target 104A contains dopants reducing a specific resistance of silicon. The dopant of the target 104A is boron. The dopant concentration of the target 104A is in a range of 1×10^{18} atm/cm³ to 1×10^{20} atm/cm³.

5 The specific resistance of the target 104A is 0.001 Ωcm to 0.1 Ωcm.

[0076]

The specific resistance of the target 104A decreases by adding the dopant thereto. Accordingly, electric power for forming plasma is stabilized, plasma in a state of forming a film is stabilized, and the phase-shift layer 12 can be formed. As a result,
10 an abnormal electrical discharge phenomenon, for example, arc is prevented from being generated during sputtering, factors which cause characteristics and defects of a thin film to occur are reduced, and the film formation characteristics can be improved. Additionally, it is possible to cause dopants to be contained in the phase-shift layer 12, and it is possible to improve the film characteristics of the mask layer including the
15 phase-shift layer 12.

[0077]

Moreover, the etching rate with respect to the mask layer increases, and it is possible to reduce the etching time with respect to the mask layer during pattern formation. Thus, it is possible to reduce the film thickness of the resist.

20 [0078]

The target 104A is single crystal or polycrystal of silicon and is formed by an FZ method, a CZ method, or a cast growth method. The target 104A maintains the uniformity of a state in which the target 104A contains the dopants therein, maintains the uniformity of a dopant concentration even in an atmosphere in which plasma is
25 generated, and can maintain the uniformity of the dopant concentration in the formed

mask layer.

[0079]

Here, specifically, improvable film characteristics of the mask layer means an increase in the etching rate or the like. Since the film characteristics can be improved as mentioned above, a degree of accuracy in shape of the mask layer during the formation of the mask pattern increases, and it is possible to provide the mask blank 10B that realizes high-definition patterning.

[0080]

Moreover, in the first vacuum chamber 102, pumping through the vacuum exhaust hole 114d connected to the high-vacuum pumping mechanism and pumping through the vacuum exhaust hole 114e are carried out in accordance with the conditions for film formation.

Furthermore, in the first film formation mechanism of the vacuum chamber 102, a sputtering voltage applied from the power supply 112A to the cathode electrode 105A is set corresponding to the film formation of the phase-shift layer 12.

[0081]

Additionally, in the second film formation mechanism of the vacuum chamber 103, the target 104B is formed of a material containing, for example, chromium which serves as a composition necessary to form the antireflection layer 13 on the phase-shift layer 12.

[0082]

At the same time, in the second film formation mechanism of the vacuum chamber 103, the gas supplied from the inert-gas introduction hole 114b and the reaction-gas introduction hole 114a to the film formation space 103 is set corresponding to the film formation of the antireflection layer 13. The above-described gas contains a

processing gas and a sputtering gas. The processing gas contains nitrogen, oxygen, or the like. The sputtering gas contains argon, nitrogen gas, or the like. The gas containing the processing gas and the sputtering gas is set so as to obtain a predetermined gas partial pressure.

5 Here, as the atmosphere gas in the film formation of the antireflection layer 13, He, Ar, Ne, N₂, NO, NO₂, O₂, CO₂, and CH₄ are applicable.

[0083]

Moreover, in the second vacuum chamber 103, pumping through the vacuum exhaust hole 114d connected to the high-vacuum pumping mechanism and pumping
10 through the vacuum exhaust hole 114e are carried out in accordance with the conditions for film formation.

Furthermore, in the second film formation mechanism of the vacuum chamber 103, a sputtering voltage applied from the power supply 112B to the cathode electrode 105B is set corresponding to the film formation of the antireflection layer 13.

15 [0084]

In the manufacturing apparatus 100 shown in FIG. 6, the glass substrate 11 transferred from the load chamber 101a to the transfer chamber 101c is loaded to the vacuum chamber 102 by the transfer mechanism 101d. Subsequently, first sputtering film formation is carried out with respect to the glass substrate 11 in the vacuum chamber
20 102. Thereafter, the glass substrate 11 is transferred from the vacuum chamber 102 to the vacuum chamber 103 through the transfer chamber 101c by the transfer mechanism 101d. After that, second sputtering film formation is carried out in the vacuum chamber 103. Next, the film-formation-completed glass substrate 11 is transferred to the unload chamber 101b through the transfer chamber 101c by the transfer mechanism 101d and is
25 furthermore transferred from the unload chamber 101b to the outside of the

manufacturing apparatus 100.

[0085]

In a phase-shift-layer formation step, a sputtering gas serving as a supply gas is supplied from the inert-gas introduction hole 114b to a space close to the backing plate 105A of the vacuum chamber 102 in the first film formation mechanism of the vacuum chamber 102. Furthermore, a reactive gas serving as a supply gas is supplied from the reaction-gas introduction hole 114a to a space close to the backing plate 105A of the vacuum chamber 102. In this state, a sputtering voltage is applied from the power supply 112A to the cathode electrode 105A. Moreover, a predetermined magnetic field may be formed on the target 104A by a magnetron magnetic circuit of the magnet plate 109A.

[0086]

Ions excited by plasma generated in the space close to the cathode electrode 105A inside the vacuum chamber 102 collide with the target 104A of the cathode electrode 105A and sputter particles of a film-forming material thereof. Because of this, the sputtered particles and the reactive gas are attached to the glass substrate 11 after being bonded. Consequently, as shown in FIG. 3, the phase-shift layer 12 having a predetermined composition is formed on the surface of the glass substrate 11.

[0087]

At this time, the reactive gas containing nitrogen gas, an oxygen-containing gas, or the like and having a predetermined partial pressure is supplied to the inside of the vacuum chamber 102 from the inert-gas introduction hole 114b and the reaction-gas introduction hole 114a during the film formation of the phase-shift layer 12. The composition of the phase-shift layer 12 is in a set range by switching operations of the gas introduction mechanism so as to control the partial pressure.

[0088]

Here, a nitrogen gas (N_2 gas), an oxygen gas (O_2 gas), a nitrogen oxide gas (N_2O gas, NO gas, NO_2 gas), a carbon dioxide gas (CO_2), or the like may be used as the reactive gas. A helium gas, a neon gas, an argon gas, or the like which is a noble gas
5 may also be used as the sputtering gas.

[0089]

Similarly, in an antireflection-layer formation step, a sputtering gas serving as a supply gas is supplied from the inert-gas introduction hole 114b to a space close to the cathode electrode 105B of the vacuum chamber 103 in the second film formation
10 mechanism of the vacuum chamber 103. Furthermore, a reactive gas serving as a supply gas is supplied from the reaction-gas introduction hole 114a to a space close to the backing plate 105B of the vacuum chamber 103. In this state, a sputtering voltage is applied from the power supply 112B to the cathode electrode 105B. Moreover, a predetermined magnetic field may be formed on the target 104B by a magnetron
15 magnetic circuit of the magnet plate 109B.

[0090]

Ions excited by plasma generated in the space close to the cathode electrode 105B inside the vacuum chamber 103 collide with the target 104B of the cathode electrode 105B and sputter particles of a film-forming material thereof. Because of this,
20 the sputtered particles and the reactive gas are attached to the glass substrate 11 after being bonded. Consequently, the antireflection layer 13 having a predetermined composition is formed on the surface of the glass substrate 11.

[0091]

Additionally, a nitrogen gas, an oxygen-containing gas, or the like is supplied to
25 the inside of the vacuum chamber 103 from the inert-gas introduction hole 114b and the

reaction-gas introduction hole 114a so as to obtain a predetermined partial pressure during the film formation of the antireflection layer 13. The composition of the antireflection layer 13 is in a set range by switching operations of the gas introduction mechanism so as to control the partial pressure.

5 [0092]

Here, CO₂ (carbon dioxide), O₂ (oxygen), N₂O (dinitrogen oxide), NO (nitrogen monoxide), CO (carbon monoxide), or the like can be adopted as the oxygen-containing gas.

Moreover, CO₂ (carbon dioxide), CH₄ (methane), C₂H₆ (ethane), CO (carbon
10 monoxide), or the like can be adopted as a carbon-containing gas.

[0093]

Moreover, in addition to the phase-shift layer 12 and the film formation of the antireflection layer 13 mentioned above, another coating may be stacked in layers on the mask layer. In this case, for example, a method of preparing a target corresponding to
15 another coating and forming a film by sputtering based on sputtering conditions such as gas or the like is adopted. Additionally, the mask blank 10A not having the resist layer 15 may be manufactured by stacking a coating on the mask layer using a film formation method other than sputtering. Note that, an inter-back type or an in-line type film formation apparatus or the like can be used instead of the manufacturing apparatus 100
20 for carrying out single-wafer film formation.

[0094]

In the resist formation step S13 shown in FIG. 1, the resist layer 15 is formed on the uppermost surface of the mask blank 10A formed on the mask layer. The resist layer 15 may be positive or may be negative. As the resist layer 15, a resist layer
25 applicable to etching with respect to a so-called chromium-based material and etching

with respect to a silicon-based material is adopted. A liquid resist is used as the resist layer 15. A chemical amplification type resist may be used as the resist liquid.

[0095]

In the resist formation step S13 according to the embodiment, application of the resist layer 15 to the mask blank 10A is carried out using a coating applicator, for example, a known spin coater or the like. The coating applicator can be used in manufacture of a photoresist-film-attached mask blank and applies a resist liquid onto the mask blank 10A.

[0096]

In the resist formation step S13, after the resist layer 15 is applied and formed onto the uppermost surface of the mask blank 10A, a baking treatment or the like is carried out, the resist formation step S13 is completed, and the mask blank 10B is manufactured as shown in FIG. 5.

[0097]

Note that, in the method of manufacturing the mask blank, other than the phase-shift layer 12, the antireflection layer 13, and the resist layer 15, an adhesion layer, a passivation layer, a light-shielding layer, a chemical resistance layer, an etching stopper layer, or the like, which serves as the mask layer, may be stacked on the glass substrate 11. In this case, a step of stacking the aforementioned layer on the glass substrate 11 can be provided before formation of the resist layer 15.

[0098]

FIG. 9 is a flowchart showing a method of manufacturing a photomask by use of the mask blank according to the embodiment of the invention. FIGS. 10 to 12 are cross-sectional views explaining a step of the method of manufacturing the photomask by use of the mask blank according to the embodiment of the invention.

As shown in FIG. 12, the phase-shift mask (photomask) 10 according to the embodiment is obtained by forming an exposed pattern on the mask blank 10B including the phase-shift layer 12, the antireflection layer 13, and the resist layer 15 which are stacked in layers.

5 [0099]

Hereinbelow, a manufacturing method of manufacturing the phase-shift mask 10 from the mask blank 10B according to the embodiment will be described.

As shown in FIG. 9, the method of manufacturing the photomask using the mask blank according to the embodiment includes a resist-pattern formation step S21 and a
10 mask-pattern formation step S22.

[0100]

In the resist-pattern formation step S21 shown in FIG. 9, as the resist layer 15 is subjected to exposure and development as shown in FIG. 10, a resist pattern 15P is formed outside the mask layer. The resist pattern 15P functions as an etching mask
15 with respect to the phase-shift layer 12 and the antireflection layer 13.

[0101]

In the resist-pattern formation step S21, a selective exposure processing is carried out to the chemical amplification type resist layer 15, and a latent image is formed. The exposure processing can also be carried out by irradiation of actinic rays.

20 Here, laser or electron beam can be adopted as the actinic rays of the exposure processing.

[0102]

Next, the resist layer 15 on which the latent image is formed by the light irradiation is subjected to PEB processing. The PEB processing is generally carried out
25 at a temperature of approximately 70 to 150°C for 30 seconds to 150 seconds.

Subsequently, in a development process, the resist layer 15 that is heated after being subjected to exposure is in contact with a developing solution used for lithography, and the resist pattern 15P corresponding to the latent image appears.

[0103]

- 5 The shape of the resist pattern 15P is adequately set in accordance with the etching patterns of the phase-shift layer 12 and the antireflection layer 13. For example, a shape having an open width corresponding to an open width of a phase-shift pattern to be formed is set on a phase-shift region.

[0104]

- 10 After that, as a first step of the mask-pattern formation step S22, an antireflection pattern formation step is carried out. In this step, dry etching is carried out via the resist pattern 15P, the antireflection layer 13 is etched, and an antireflection pattern 13P is formed.

[0105]

- 15 Chlorine-based dry etching containing oxygen can be used as etching of the antireflection pattern formation step.

[0106]

- Next, as a second step of the mask-pattern formation step S22, a phase-shift pattern formation step is carried out. In this step, the phase-shift layer 12 is subjected to
20 dry etching via the antireflection pattern 13P and the resist pattern 15P which are patterned. Accordingly, as shown in FIG. 12, a phase-shift pattern 12P is formed.

[0107]

 Fluorine-based dry etching can be used as etching of the phase-shift pattern formation step.

- 25 [0108]

In the embodiment, the target 104A used when forming the phase-shift layer 12 contains dopants reducing a specific resistance of silicon. As the boron concentration is set in the above-mentioned range, the specific resistance of the target 104A can be set in the aforementioned range. Therefore, electric power for forming plasma is stabilized, plasma in a state of forming a film is stabilized, and it is possible to form the phase-shift layer 12. As a result, the film formation characteristics can be improved. Additionally, it is possible to cause dopants to be contained in the phase-shift layer 12, and it is possible to improve the film characteristics of the mask layer including the phase-shift layer 12.

10 [0109]

Additionally, the etching rate with respect to the mask layer increases, and it is possible to reduce the etching time with respect to the mask layer during pattern formation. Furthermore, since the etching rate of the mask layer with respect to the glass substrate increases, etching processing can be easily controlled in accordance with determination of an end point for determining completion of etching. Consequently, a depth at which the glass substrate 11 is excessively etched can be minimally reduced.

[0110]

Moreover, the target 104A is silicon single crystal or polycrystalline silicon and is formed by an FZ method, a CZ method, or a cast method. The uniformity of a state in which the target 104A contains the dopants is maintained, the uniformity of a dopant concentration is maintained even in an atmosphere in which plasma is generated, and the uniformity of the dopant concentration in the formed mask layer can be maintained.

[0111]

Furthermore, in the method of manufacturing the mask blank according to the embodiment, since the DC sputtering is used as the sputtering of the mask-layer

25

formation step S12, it is possible to improve the reproducibility of the film characteristics as compared with a case of forming a mask layer by RF sputtering.

[0112]

Accordingly, in the mask blank 10B according to the embodiment, the phase-
5 shift layer 12 formed of SiN or SiON includes, for example, B (boron). Furthermore, the concentration of boron is in a range of 1×10^{18} atm/cm³ to 1×10^{20} atm/cm³.

Therefore, it is possible to increase the etching rate of the dry etching to be 1.05 to 1.5 times an etching rate of a layer formed by use of a non-doped target.

[0113]

10 Consequently, as compared with a case of not containing dopants, accuracy in shape by patterning is improved at a higher etching rate while shortening the etching time, it is applicable to further high-definition patterning.

Thus, the etching time with respect to the mask layer during pattern formation is reduced, damage to the surface of the resist layer 15 is suppressed, accuracy in shape by
15 etching is maintained, and it is possible to manufacture the phase-shift mask 10 applicable to high-definition patterning.

[0114]

Although the case has been described in which boron is used as the dopant in the embodiment, it is possible to increase the etching rate even in a case of using phosphorus
20 or arsenic as the dopant.

[0115]

Furthermore, a plurality of configurations described in the aforementioned embodiment can be used individually or in combination therewith.

Examples

25 [0116]

Hereinafter, Examples of the invention will be described.

[0117]

Firstly, as a specific example of the mask blank according to the invention, DC sputtering test will be described.

5 [0118]

<Experimental Example 1>

Reactive sputtering was carried out using a target made of silicon containing dopants doped thereto, and therefore the mask layer was formed on a transparent substrate. Additionally, DC sputtering film formation was carried out by application of
10 a DC voltage serving as a sputtering voltage supplied from the power supply to the target.

At this time, conditions for film formation and film thickness were optimized as stated below.

[0119]

15 Phase difference in a wavelength of 193 nm: 180 deg

Transmissivity: 5.8%

[0120]

Items of the sputtering are shown below.

Substrate: quartz

20 Sputtering power: DC 1.5 kW

Target: silicon

Dopant: boron (B)

Dopant concentration: 1×10^{19} atm/cm³

Film-forming gas: Ar: 10 sccm, N₂: 8 sccm

25 [0121]

<Experimental Example 2>

Similarly to Experimental Example 1, reactive sputtering was carried out using a target made of non-doped silicon that does not contain boron or the like doped thereto, and therefore the mask layer was formed on a transparent substrate.

5 At this time, conditions for film formation and film thickness were optimized as stated below.

[0122]

Phase difference in a wavelength of 193 nm: 180 deg

Transmissivity: 5.8%

10 [0123]

Items of the sputtering are shown below.

Substrate: quartz

Sputtering power: DC 1.5 kW

Target: silicon

15 Dopant: none

Dopant concentration of: 0 atm/cm³

Film-forming gas: Ar: 10 sccm, N₂: 7 sccm

[0124]

<Experimental Example 3>

20 Similarly to Experimental Example 2, reactive sputtering was carried out using a target made of non-doped silicon that does not contain boron or the like doped thereto, and therefore the mask layer was formed on a transparent substrate.

At this time, conditions for film formation and film thickness were optimized as stated below.

25 [0125]

Phase difference in a wavelength of 193 nm: 180 deg

Transmissivity: 5.8%

[0126]

Items of the sputtering are shown below.

5

Substrate: quartz

RF frequency of Sputtering: 13.56 MHz

Sputtering power: 1.5 kW

Target: silicon

Dopant: none

10

Dopant concentration of: 0 atm/cm³

Film-forming gas: Ar: 10 sccm, N₂: 5 sccm

[0127]

In Experimental Examples 1 to 3, a length of time (film formation time) of forming a film until a predetermined film thickness is obtained, the number of defects of 0.5 μm or more observed on a film surface per unit area, and reproducibility of phase difference in a case of continuously forming films 10 times (deg) were measured.

15

Here, the reproducibility of phase difference (deg) means a difference between the maximum value and the minimum value of a monitoring value in a case in which an average phase difference for each substrate is the monitoring value.

20

The reproducibility of phase difference (deg) is the index showing the stability of the film thickness and the optical constant.

The results are shown in Table 1.

[0128]

(Table 1)

	FILM FORMATION TIME (sec)	TOTAL NUMBER OF DEFECTS GREATER THAN OR EQUAL TO 0.5 μm	REPRODUCIBILITY OF PHASE DIFFERENCE IN CASE OF CONTINUOUSLY FORMING FILMS 10 TIMES (deg)
EXPERIMENTAL EXAMPLE 1	850	3	2
EXPERIMENTAL EXAMPLE 2	980	33.9	3.9
EXPERIMENTAL EXAMPLE 3	1750	5.5	6.1

[0129]

Here, since it is necessary to induce a voltage to the surface of the target in a case of carrying out reactive sputtering, it is necessary to reduce the electrical resistance of the target for DC sputtering. However, in order to cause a high resistance target such as non-doped silicon to be subjected to sputtering, it was necessary to apply a high-frequency thereto and RF sputtering was thereby required.

From the above-described results, DC sputtering was possible by adding dopants to Si, and it was understood that the film formation time, defects, and the reproducibility were improved.

[0130]

Particularly, as compared with the case of carrying out DC sputtering using the non-doped silicon target such as Experimental Example 2, in the case of carrying out DC sputtering using the high-concentrated B-doped silicon target in Experimental Example 3, the reproducibility of the phase difference was higher, and it was possible to carry out film formation in a state in which the number of defects was extremely low.

Furthermore, as compared with the case of carrying out RF sputtering using the non-doped silicon target such as Experimental Example 1, in the case of the DC sputtering using the high-concentrated B-doped silicon target in Experimental Example 3, it was understood that the reproducibility of the phase difference was extremely

higher, and the number of defects was low.

[0131]

<Experimental Example 4>

The mask layer obtained by Experimental Example 1 and the quartz substrate on
5 which the mask layer was formed were subjected to dry etching treatment, and each
etching rate (Etching Rate) was evaluated. Furthermore, the selection ratio (selectivity)
at this time was measured.

The results are shown in FIG. 13.

[0132]

10 Items of the dry etching are shown below.

Plasma source: ICP (Inductively Coupled Plasma: inductively-coupled plasma)

Antenna power: 1.5 kW

Bias power: 0 to 200 W

Pressure of dry etching atmosphere: 1.36 Pa

15 Supply gas: CF₄: 150 sccm, O₂: 8 sccm

[0133]

<Experimental Example 5>

Similarly to Experimental Example 4, the mask layer obtained by Experimental
Example 3 and the quartz substrate on which the mask layer was formed were subjected
20 to dry etching treatment, and each etching rate (Etching Rate) was evaluated.
Furthermore, the selection ratio (selectivity) at this time was measured.

The results are shown in FIG. 13.

[0134]

From the results shown in FIG. 13, as compared with non-doped Experimental
25 Example 5, in Experimental Example 4 in which film formation was carried out using the

boron-doped (B-doped) target, it was understood that the etching rate was higher under the same bias value. Moreover, it was understood that the selection ratio of the boron-doped (B-doped) target was improved.

[0135]

5 <Experimental Example 6>

A light-shielding layer containing Cr as a main component and an antireflection layer were stacked on the mask layer obtained by Experimental Example 1 in layers, and a resist layer was formed on the antireflection layer.

Next, the aforementioned multi-layered body was subjected to dry etching under
10 the same conditions as those of Experimental Examples 4 and 5. Thereafter, the cross-sectional configuration of the multi-layered body was observed.

Here, the bias power was 100 W.

A SEM image of Experimental Example 6 is shown in FIG. 14. Note that, in
FIG. 14, the surface of the quartz substrate close to the mask layer on which a pattern
15 was formed is represented by a solid line.

[0136]

<Experimental Example 7>

Similarly to Experimental Example 6, a light-shielding layer containing Cr as a
main component and an antireflection layer were stacked on the mask layer obtained by
20 Experimental Example 3 in layers, and a resist layer was formed on the antireflection
layer.

Next, the aforementioned multi-layered body was subjected to dry etching under
the same conditions as those of Experimental Examples 4 and 5. Thereafter, the cross-sectional configuration of the multi-layered body was observed.

25 Here, the bias power was 100 W.

A SEM image of Experimental Example 7 is shown in FIG. 15. Note that, in FIG. 15, the surface of the quartz substrate close to the mask layer on which a pattern was formed is represented by a solid line.

[0137]

5 From the results shown in FIG. 15, in Experimental Example 7 in which film formation was carried out using a non-doped target, it was understood that, since the selection ratio was low, a degree of over etching of the quartz substrate increased. Accordingly, since displacement of phase difference occurred in Experimental Example 7, it was understood that the optical characteristics of a photomask became degraded.

10 [0138]

In contrast, from the results shown in FIG. 15, in Experimental Example 6 in which film formation was carried out using the boron-doped (B-doped) target, it was understood that, since the selection ratio was large, a degree of over etching of the quartz substrate decreased. For this reason, in Experimental Example 6, it was understood that
15 the displacement of phase difference was reduced and the optical characteristics of the photomask were improved.

[0139]

In the method of manufacturing the mask blank according to the invention, the sputtering may be carried out under conditions in which DC input power is set to be 0.1
20 to 0.2 to 4.0 kW and film formation pressure is set to be 0.05 to 0.6 to 0.7 Pa.

Consequently, it is possible to stabilize electric discharge.

[0140]

In the method of manufacturing the photomask according to the invention, the plasma forming power may be set to be 0.2 to 1.0 kW, the bias power may be set to be 10
25 to 80 W, and CF₄ may be set to be 100 to 200 sccm in the dry etching conditions of the

mask-pattern formation step.

Accordingly, the etching time with respect to the mask layer during pattern formation is reduced, damage to the surface of the resist layer is suppressed, accuracy in shape by etching is maintained, and it is possible to manufacture the photomask

5 applicable to high-definition patterning.

[DESCRIPTION OF REFERENCE NUMERALS]

[0141]

10...phase-shift mask (photomask)

10A and 10B...mask blank

10 11...glass substrate (transparent substrate)

12...phase-shift layer (mask layer)

12P...phase-shift pattern (mask pattern)

13...antireflection layer (mask layer)

13P...antireflection pattern (mask pattern)

15 15...resist layer (photoresist layer)

15P...resist pattern

100...manufacturing apparatus

104A, 104B...target

[CLAIMS]

1. A method of manufacturing a mask blank in which a mask layer containing silicon is stacked on a transparent substrate, the method comprising:
forming the mask layer by sputtering using a target containing a dopant reducing
5 a specific resistance.
2. The method of manufacturing a mask blank, according to claim 1, wherein the specific resistance of the target is from 0.001 Ωcm to 0.1 Ωcm .
- 10 3. The method of manufacturing a mask blank according to claim 1 or claim 2, wherein
the dopant is one or more selected from the group consisting of boron, phosphorus, and arsenic.
- 15 4. The method of manufacturing a mask blank according to claim 3, wherein the dopant is boron in the target, and
a dopant concentration thereof is in a range of $1 \times 10^{18} \text{ atm/cm}^3$ to $1 \times 10^{20} \text{ atm/cm}^3$.
- 20 5. The method of manufacturing a mask blank according to claim 4, wherein the target is silicon single crystal or polycrystalline silicon.
6. The method of manufacturing a mask blank according to any one of claims 1 to 5, wherein
25 an atmosphere gas used in the sputtering contains nitrogen.

7. The method of manufacturing a mask blank according to any one of claims 1 to 5, wherein

an atmosphere gas used in the sputtering contains oxygen.

5

8. The method of manufacturing a mask blank according to any one of claims 1 to 7, wherein

the sputtering is DC sputtering.

10 9. A mask blank manufactured by the manufacturing method according to any one of claims 1 to 8, the mask blank comprising:

the mask layer containing boron as the dopant, wherein

a dopant concentration of the mask layer is in a range of 1×10^{18} atm/cm³ to 1×10^{20} atm/cm³.

15

10. The mask blank according to claim 9, wherein

an etching rate of the mask layer in dry etching is 1.05 to 1.5 times an etching rate of a layer formed by using a non-doped target.

20 11. The mask blank according to claim 9 or claim 10, wherein
the mask layer contains nitrogen or oxygen.

12. The mask blank according to claim 11, wherein

25 a compositional ratio of nitrogen or oxygen in the mask layer is changed in a
film thickness direction.

13. The mask blank according to any one of claims 9 to 12, wherein the mask layer includes a phase-shift layer.
- 5 14. A method of manufacturing a photomask from the mask blank according to any one of claims 9 to 13, the method comprising:
- forming a resist pattern on a surface of the mask layer; and
- forming a mask pattern by patterning the mask layer using the resist pattern as a mask, wherein
- 10 the mask layer is dry-etched when the mask pattern is formed.
15. A photomask manufactured by the manufacturing method according to claim 14.