

## MASK BLANKS AND PHOTOMASK

## TECHNICAL FIELD

[0001]

5           The present invention relates to a mask blanks and a photomask.

## BACKGROUND ART

[0002]

10           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 blanks (mask blanks) are used. The mask blanks includes a mask layer stacked on one of main surfaces of a transparent substrate such as a glass substrate, or the like.

[0003]

15           In manufacture of the mask blanks, 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 may have a single layer structure or a structure in which a plurality of layers are stacked in layers. A resist pattern is formed on the mask layer, the resist pattern is used as a mask, a predetermined mask pattern is formed by selectively etching the mask layer, and therefore a photomask is  
20   manufactured.

[0004]

          As a mask layer formed in the mask blanks or the photomask, a layer or the like configured of a film containing silicon or a film containing silicon and molybdenum is known (Patent Document 1).

25   PRIOR ART DOCUMENTS

## PATENT DOCUMENTS

[0005]

[Patent Document 1] PCT International Publication No. WO2011/125337

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## SUMMARY OF THE INVENTION

## PROBLEMS TO BE SOLVED BY THE INVENTION

[0006]

However, when a patterned portion formed of a mask layer containing silicon (Si) and molybdenum (Mo) is irradiated with laser light as exposure light in an exposure step, a phenomenon referred to as Mo migration such that Mo excited by the laser light moves to outside of the patterned portion occurs. Furthermore, there is a problem in that silicon remaining in the patterned portion is oxidized and therefore silicon oxide is formed, the line width of the patterned portion increases because of the silicon oxide, and accuracy in shape of the patterned portion is degraded.

15 [0007]

The invention was conceived in view of the above-described circumstances and provides a mask blanks and a photomask which can suppress an increase in line width of a mask layer which is caused by Mo migration.

## MEANS FOR SOLVING THE PROBLEMS

20 [0008]

In order to solve the aforementioned problem, the invention provides the following configurations.

A mask blanks according to an aspect of the invention includes a blank mask layer. The blank mask layer includes a molybdenum compound layer that contains molybdenum, silicon, and nitrogen and that selectively contains oxygen. In the

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molybdenum compound layer, a ratio of a peak area of a Mo-Si bonding peak obtained by separation of peaks of a photoelectron spectrum of  $\text{Mo}_{3d3/2}$  and a photoelectron spectrum of  $\text{Mo}_{3d5/2}$  to peak areas of the photoelectron spectrums of  $\text{Mo}_{3d3/2}$  and  $\text{Mo}_{3d5/2}$  measured by X-ray photoelectron spectroscopy is greater than or equal to 73.0%.

5            In the mask blanks according to an aspect of the invention, the molybdenum compound layer may satisfy the following formula (1).

$$\{(\text{Si-O}/2) \times 4/3 + \text{Mo}/2 - \text{N}\} / \text{Si} \geq 0.25 \dots (1)$$

Here, Mo, Si, O, and N represented by the above-mentioned formula (1) mean mole fractions (mol%) of molybdenum, silicon, oxygen, and nitrogen, which are  
10    contained in the molybdenum compound layer, respectively. In a case in which the molybdenum compound layer does not contain oxygen, O represented by the above-mentioned formula (1) is 0.

In the mask blanks according to an aspect of the invention, the molybdenum compound layer may further satisfy the following formula (2).

15             $\text{Si}/\text{Mo} \geq 4.0 \dots (2)$

Here, Mo and Si represented by the above-mentioned formula (2) mean mole fractions (mol%) of molybdenum and silicon, which are contained in the molybdenum compound layer, respectively.

In the mask blanks according to an aspect of the invention, regarding  
20    compositions of molybdenum, silicon, nitrogen, and oxygen contained in the molybdenum compound layer, a content rate of silicon may be in a range of 35 to 50 mol%, a content rate of molybdenum may be in a range of 3 to 10 mol%, a content rate of oxygen may be in a range of 0 to 20 mol%, a content rate of nitrogen may be in a range of 35 to 60 mol%, and a content rate of carbon may be in a range of 0 to 1 mol%.

25            In the mask blanks according to an aspect of the invention, the molybdenum

compound layer may constitute any one or more of a phase-shifting layer, a light-shielding layer, an antireflection layer, an etching stopping layer, and a chemical resistance layer.

A photomask according to an aspect of the invention includes a mask layer.

- 5 The mask layer includes a molybdenum compound layer that contains molybdenum, silicon, and nitrogen and that selectively contains oxygen. In the molybdenum compound layer, a ratio of a peak area of a Mo-Si bonding peak obtained by separation of peaks of a photoelectron spectrum of  $\text{Mo}_{3d3/2}$  and a photoelectron spectrum of  $\text{Mo}_{3d5/2}$  to peak areas of the photoelectron spectrums of  $\text{Mo}_{3d3/2}$  and  $\text{Mo}_{3d5/2}$  measured by X-ray  
10 photoelectron spectroscopy is greater than or equal to 73.0%.

In the photomask according to an aspect of the invention, the molybdenum compound layer may satisfy the following formula (3).

$$\{(\text{Si-O}/2) \times 4/3 + \text{Mo}/2 - \text{N}\} / \text{Si} \geq 0.25 \dots (3)$$

- Here, Mo, Si, O, and N represented by the above-mentioned formula (3) mean  
15 mole fractions (mol%) of molybdenum, silicon, oxygen, and nitrogen, which are contained in the molybdenum compound layer, respectively. In a case in which the molybdenum compound layer does not contain oxygen, O represented by the above-mentioned formula (3) is 0.

- In the photomask according to an aspect of the invention, the molybdenum  
20 compound layer may further satisfy the following formula (4).

$$\text{Si}/\text{Mo} \geq 4.0 \dots (4)$$

Here, Mo and Si represented by the above-mentioned formula (4) mean mole fractions (mol%) of molybdenum and silicon, which are contained in the molybdenum compound layer, respectively.

- 25 In the photomask according to an aspect of the invention, regarding

compositions of molybdenum, silicon, nitrogen, and oxygen contained in the molybdenum compound layer, a content rate of silicon may be in a range of 35 to 50 mol%, a content rate of molybdenum may be in a range of 3 to 10 mol%, a content rate of oxygen may be in a range of 0 to 20 mol%, a content rate of nitrogen may be in a range of 35 to 60 mol%, and a content rate of carbon may be in a range of 0 to 1 mol%.

In the photomask according to an aspect of the invention, the molybdenum compound layer may constitute any one or more of a phase-shifting layer, a light-shielding layer, an antireflection layer, an etching stopping layer, and a chemical resistance layer.

Note that, in the following explanation, “ $\{(Si-O/2) \times 4/3 + Mo/2 - N\}/Si$ ” serving as the left member of the aforementioned formula (1) or of the aforementioned formula (3) may be referred to as a ratio of the deficient amount of nitrogen to the amount of silicon.

#### Effects of the Invention

[0009]

According to the invention, it is possible to provide a mask blanks and a photomask which can suppress an increase in line width of a mask layer which is caused by Mo migration.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0010]

FIG. 1 is a schematic cross-sectional view showing an example of a mask blanks according to an embodiment of the invention.

FIG. 2 is a schematic cross-sectional view showing another example of the mask blanks according to the embodiment of the invention.

FIG. 3 is a schematic cross-sectional view showing an example of a photomask

according to an embodiment of the invention.

FIG. 4 is a schematic cross-sectional view showing another example of the mask blanks according to the embodiment of the invention.

FIG. 5 is a schematic cross-sectional view showing another example of the mask  
5 blanks according to the embodiment of the invention.

FIG. 6 is a schematic cross-sectional view showing another example of the mask blanks according to the embodiment of the invention.

FIG. 7 is a schematic cross-sectional view showing another example of the mask blanks according to the embodiment of the invention.

10 FIG. 8 is a schematic cross-sectional view showing another example of the mask blanks according to the embodiment of the invention.

FIG. 9 is a schematic view showing a manufacturing apparatus of a mask blanks according to the embodiment of the invention.

FIG. 10 is a schematic view showing a manufacturing apparatus of a mask  
15 blanks according to the embodiment of the invention.

FIG. 11 is a view showing photoelectron spectrums of  $\text{Mo}_{3d3/2}$  and  $\text{Mo}_{3d5/2}$  after a processing of separating a peak measured by X-ray photoelectron spectroscopy.

## EMBODIMENTS FOR CARRYING OUT THE INVENTION

20 [0011]

A mask layer of the photomask has a single layer structure or a multilayered structure. Moreover, the mask layer may contain a molybdenum compound layer. In the specification, the molybdenum compound layer is a layer that contains silicon, molybdenum, and nitrogen and that selectively contains oxygen. The molybdenum  
25 compound layer is used as a phase-shifting layer, a light-shielding layer, an antireflection

layer, or the like in the mask layer. In an exposure step of a photoresist, when a patterned portion formed of a mask layer including the molybdenum compound layer is irradiated with laser light, a phenomenon referred to as Mo migration such that molybdenum moves to outside of the mask layer may occur. In the case in which the Mo migration occurs, oxygen or water which exist around the mask layer infiltrate into the portion from which molybdenum is removed. Silicon is oxidized due to the infiltrated oxygen or water, and therefore silicon oxide is formed. There is a concern that such formation of the silicon oxide causes the line width of the patterned portion formed of the mask layer to increase. In order to solve the problem, the inventors have done intensive research and have obtained the following knowledge.

[0012]

There is a case of causing the molybdenum compound layer to contain nitrogen or oxygen in order to adjust the optical characteristics of the molybdenum compound layer. In the mask layer, oxygen and nitrogen are likely to be bonded to silicon, and nitrogen is also likely to be bonded to molybdenum. When the amount of nitrogen and the amount of oxygen of the molybdenum compound layer are suitably adjusted in order to adjust the optical characteristics of the molybdenum compound layer, although an amount of bonding between silicon and nitrogen, an amount of bonding between silicon and oxygen, or an amount of bonding between molybdenum and nitrogen increases, an amount of bonding between molybdenum and silicon may decrease. The inventors discovered that the decrease of the amount of bonding between molybdenum and silicon contributes to Mo migration and completed the invention. Hereinbelow, an embodiment of the invention will be described.

[0013]

The mask blanks according to the embodiment includes a blank mask layer that

becomes a mask layer of a photomask. The blank mask layer includes a molybdenum compound layer that contains molybdenum, silicon, and nitrogen and that selectively contains oxygen. In the molybdenum compound layer, a ratio of a peak area of a Mo-Si bonding peak obtained by separation of peaks of a photoelectron spectrum of  $\text{Mo}_{3d3/2}$  and a photoelectron spectrum of  $\text{Mo}_{3d5/2}$  to peak areas of the photoelectron spectrums of  $\text{Mo}_{3d3/2}$  and  $\text{Mo}_{3d5/2}$  measured by X-ray photoelectron spectroscopy is greater than or equal to 73.0%.

Furthermore, the photomask according to the embodiment includes the mask layer. The mask layer includes a molybdenum compound layer that contains molybdenum, silicon, and nitrogen and that selectively contains oxygen. In the molybdenum compound layer, a ratio of a peak area of a Mo-Si bonding peak obtained by separation of peaks of a photoelectron spectrum of  $\text{Mo}_{3d3/2}$  and a photoelectron spectrum of  $\text{Mo}_{3d5/2}$  to peak areas of the photoelectron spectrums of  $\text{Mo}_{3d3/2}$  and  $\text{Mo}_{3d5/2}$  measured by X-ray photoelectron spectroscopy is greater than or equal to 73.0%.

[0014]

Additionally, the molybdenum compound layer of the mask blanks and of the photomask according to the embodiment may satisfy the following formula (A). Note that, in the following explanation, “ $\{(\text{Si}-\text{O}/2) \times 4/3 + \text{Mo}/2 - \text{N}\}/\text{Si}$ ” serving as the left member of the following formula (A) may be referred to as a ratio of the deficient amount of nitrogen to the amount of silicon.

[0015]

$$\{(\text{Si}-\text{O}/2) \times 4/3 + \text{Mo}/2 - \text{N}\}/\text{Si} \geq 0.25 \dots (\text{A})$$

[0016]

Here, in the aforementioned formula (A), Mo, Si, O, and N mean mole fractions (mol%) of molybdenum, silicon, oxygen, and nitrogen, which are contained in the

molybdenum compound layer, respectively. In the case in which the molybdenum compound layer does not contain oxygen, O represented by the formula (A) is 0.

[0017]

The photomask according to the embodiment is used in a photolithography  
5 process using exposure light, for example, exposure light having a wavelength of 200 nm or less, particularly, ArF excimer laser light (wavelength of 193 nm) used for photolithography via a phase-shifting mask.

Additionally, the mask blanks according to the embodiment is used as a material for manufacture of the photomask.

10 [0018]

FIG. 1 shows an example of a mask blanks according to the embodiment. The mask blanks according to the embodiment includes a glass substrate 11 (transparent substrate) and a blank mask layer 12 formed on the glass substrate 11. Furthermore, as shown in FIG. 2, the mask blanks according to the embodiment may be configured of the  
15 glass substrate 11, the blank mask layer 12 formed on the glass substrate 11, and a photoresist layer 13 formed on the blank mask layer 12.

[0019]

Moreover, FIG. 3 shows an example of a photomask according to the embodiment. The photomask according to the embodiment includes the glass substrate  
20 11 and a mask layer 12P formed on the glass substrate 11. The mask layer 12P is formed by patterning such that the blank mask layer of the mask blanks has a predetermined shape.

[0020]

As the glass substrate 11, a material having a high degree of transparency and  
25 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. The size of the glass substrate 11 is adequately selected depending on a substrate to be exposed by use of the mask layer 12P. Such a substrate is, for example, a substrate for an FPD, or the like such as a semiconductor, an LCD (liquid crystal display), a plasma display, an organic EL (electro luminescence) display, or the like.

[0021]

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 250 mm or more is applicable as the glass substrate 11. Furthermore, a substrate having a thickness of 1 mm or less, a substrate having a thickness of several mm, or a substrate having a thickness of 10 mm or more is also used as the glass substrate 11.

[0022]

Moreover, the flatness of the glass substrate 11 may be reduced by polishing a surface of the glass substrate 11. The flatness of the glass substrate 11 can be less than or equal to, for example, 5  $\mu\text{m}$ . 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, a value less than or equal to 0.5  $\mu\text{m}$ .

[0023]

The blank mask layer 12 and the mask layer 12P according to the embodiment may include the molybdenum compound layer containing molybdenum, silicon, and nitrogen. The blank mask layer 12 and the mask layer 12P according to the embodiment may include the molybdenum compound layer containing molybdenum, silicon, nitrogen, and oxygen. That is, in the case of an expression using constituent elements, the blank mask layer 12 and the mask layer 12P according to the embodiment

may include the molybdenum compound layer formed of MoSiN or MoSiON. The molybdenum compound layer according to the embodiment contains molybdenum, silicon, and nitrogen as basic components and further may contain oxygen or carbon. The contained amounts of nitrogen, oxygen, and carbon contained in the blank mask layer 12 and the mask layer 12P are adequately set in order to set the optical characteristics, the etching rate, or the like of the blank mask layer 12 and of the mask layer 12P to be in a desired range.

[0024]

The molybdenum compound layer according to the embodiment is a layer in which a ratio of a peak area of a Mo-Si bonding peak obtained by separation of peaks of the photoelectron spectrum of  $\text{Mo}_{3d3/2}$  and the photoelectron spectrum of  $\text{Mo}_{3d5/2}$  to peak areas of the photoelectron spectrums of  $\text{Mo}_{3d3/2}$  and  $\text{Mo}_{3d5/2}$  measured by X-ray photoelectron spectroscopy is greater than or equal to 73.0%. The photoelectron spectrum of  $\text{Mo}_{3d3/2}$  and the photoelectron spectrum of  $\text{Mo}_{3d5/2}$  are spectrums observed as two spectrums divided from a  $\text{Mo}_{3d}$  photoelectron spectrum. The ratio of the peak area of the Mo-Si bonding peak to the peak area of the photoelectron spectrum of  $\text{Mo}_{3d}$  means a ratio of the contained amount of molybdenum bonded to silicon to the contained amount of molybdenum contained in the molybdenum compound layer. By setting the ratio of the molybdenum having Mo-Si bonding to be greater than or equal to 73.0%, Mo migration is suppressed, and it is possible to prevent the line width of the mask layer from increasing. The ratio of silicon having Mo-Si bonding is preferably greater than or equal to 75.0%. Although it is not necessary to particularly limit the upper limit of the ratio of silicon having Mo-Si bonding, for example, the upper limit thereof may be less than or equal to 95.0%.

[0025]

The mechanism (effects) such that Mo migration is less easily generated as the amount of Mo-Si bonding increases is presumed as follows from the experimental results the inventors carried out. Si in the molybdenum compound layer easily forms oxide or nitride by being bonded to O or N. Furthermore, molybdenum easily forms nitride by being bonded to excess nitrogen that was not bonded to silicon. Additionally, since molybdenum contained in molybdenum nitride has a degree of chemical bonding lower than that of molybdenum bonded to silicon, migration easily occurs. It is presumed that, as the amount of molybdenum bonded to silicon increases, the amount of molybdenum bonded to nitrogen relatively decreases. Accordingly, it is conceivable that Mo migration is less easily generated as the amount of Mo-Si bonding increases. However, the mechanism described here is one of conjectures, and there is a possibility that an unknown other mechanism is related to suppression of Mo migration. Whether the above-described mechanism is clear or not, the fact that Mo migration is less easily generated as the amount of Mo-Si bonding increases was experimentally found by the inventors.

[0026]

Positions of the molybdenum compound layer to be measured by X-ray photoelectron spectroscopy may be on a surface of the molybdenum compound layer or may be at  $t/2$  position in the case in which the thickness of the molybdenum compound layer is  $t$  (i.e., the position is located at a halfway position of in the thickness direction). Additionally, the number of measurement points by X-ray photoelectron spectroscopy is not particularly limited. For example, measurement using X-ray photoelectron spectroscopy is carried out at ten measurement points, and an average value may be obtained by averaging the obtained plurality of measurement results.

[0027]

For measuring the peak areas of the photoelectron spectrum of  $\text{Mo}_{3d3/2}$  and the photoelectron spectrum of  $\text{Mo}_{3d5/2}$ , measurement is carried out by narrow scanning analysis using  $\text{AlK}\alpha$  as an X-ray source at binding energy in an approximate range of 220 to 240 eV. A photoelectron spectrum having a peak top that appears at approximately 227 eV is specified as the photoelectron spectrum of  $\text{Mo}_{3d5/2}$ . A photoelectron spectrum having a peak top that appears at approximately 230 eV is specified as the photoelectron spectrum of  $\text{Mo}_{3d3/2}$ . Next, a peak area of each of the two photoelectron spectrums is measured. Furthermore, the total area of the two peak areas is calculated. At this time, the background intensity is subtracted from the peak area.

10 [0028]

Furthermore, the Mo-Si bonding peak is specified by carrying out peak separation processing with respect to the photoelectron spectrums of  $\text{Mo}_{3d3/2}$  and  $\text{Mo}_{3d5/2}$ . A method of peak separation processing is not particularly limited. For example, software for peak separation provided in an X-ray photoelectron spectrometer may be utilized. A peak that appears in an approximate range of 226 to 227 eV by peak separation is specified as the Mo-Si bonding peak in the photoelectron spectrum of  $\text{Mo}_{3d5/2}$ . A peak that appears in an approximate range of 229 to 231 eV is specified as the Mo-Si bonding peak in the photoelectron spectrum of  $\text{Mo}_{3d3/2}$ . Next, the peak area of each of the Mo-Si bonding peaks is measured. Furthermore, the total area of the two peak areas is calculated. At this time, the background intensity is subtracted from the peak area. Next, the ratio (%) of the peak areas (the total area) of the Mo-Si bonding peaks to the peak areas (the total area) of the photoelectron spectrums of  $\text{Mo}_{3d3/2}$  and  $\text{Mo}_{3d5/2}$  is calculated.

[0029]

25 Particularly, it is preferable that the molybdenum compound layer according to

the embodiment satisfy the above-mentioned formula (A) in terms of further suppressing Mo migration. As a result of satisfying the formula (A), Mo migration is further less easily generated, and an increase in line width of the mask layer 12P of the photomask can be reliably prevented. The ratio of the deficient amount of nitrogen to the amount of silicon may be greater than or equal to 0.30 and may be greater than or equal to 0.35. Moreover, the upper limit of the left member (the ratio of the deficient amount of nitrogen to the amount of Si) of the aforementioned formula (A) is not particularly limited. For example, the ratio of the deficient amount of nitrogen to the amount of silicon may be less than or equal to 1.00, may be less than or equal to 0.70, and may be less than or equal to 0.60.

[0030]

Moreover, it is preferable that Si/Mo that means a molar ratio of molybdenum to silicon of the molybdenum compound layer be greater than or equal to 4.0. In the case of setting Si/Mo to be greater than or equal to 4.0, it is possible to preferably use the molybdenum compound layer in a photolithography process using exposure light, for example, exposure light having a wavelength of 200 nm or less, particularly, ArF excimer laser light (wavelength of 193 nm) used for photolithography via a phase-shifting mask.

[0031]

The reason that the above-mentioned formula (A) was derived is as follows. In the following explanation, Mo, Si, O, and N mean mole fractions (mol%) of molybdenum, silicon, oxygen, and nitrogen, which are contained in the molybdenum compound layer, respectively.

[0032]

In the case in which the mask layer includes the molybdenum compound layer

containing silicon, molybdenum, nitrogen, and oxygen, silicon of the molybdenum compound layer is bonded to oxygen of the molybdenum compound layer, and  $\text{SiO}_2$  is likely to be formed. Furthermore, excess silicon that was not bonded to oxygen of the molybdenum compound layer is bonded to nitrogen of the molybdenum compound layer, and therefore  $\text{Si}_3\text{N}_4$  is likely to be formed. Thus, the amount of nitrogen required for causing all of silicon of the molybdenum compound to be nitrided is represented as  $(\text{Si-O}/2) \times 4/3$ .

[0033]

Moreover, when molybdenum of the molybdenum compound layer is nitrided,  $\text{Mo}_2\text{N}$  is likely to be formed. Therefore, the amount of nitrogen required for causing all of molybdenum of the molybdenum compound layer to be nitrided is represented as  $\text{Mo}/2$ .

[0034]

Furthermore, in the case in which the amount of nitrogen required for causing all of silicon and molybdenum of the molybdenum compound layer to be nitrided is represented as  $N^*$ ,  $N^* = (\text{Si-O}/2) \times 4/3 + \text{Mo}/2$  is obtained.

[0035]

Here, the amount obtained by subtracting the amount of nitrogen  $N$  practically contained in the mask layer from the aforementioned  $N^*$ , that is,  $\{(\text{Si-O}/2) \times 4/3 + \text{Mo}/2 - N\}$  is the deficient amount with respect to the amount ( $N^*$ ) of nitrogen required for causing all of silicon and molybdenum to be nitrided. In the molybdenum compound layer, the larger the deficient amount, the smaller the amounts of silicon and molybdenum which are oxidized or nitrided, and this means that an amount of bonding between silicon and silicon and an amount of bonding between silicon and molybdenum increases.

Consequently, as the ratio of the deficient amount ( $=\{(\text{Si-O}/2) \times 4/3 + \text{Mo}/2 - N\}$ ) of

nitrogen to the amount of silicon of the molybdenum compound layer increases in addition to that the ratio of the peak area of the Mo-Si bonding peak increases, an increase in line width of the mask layer of the photomask can be effectively suppressed.

[0036]

5           Furthermore, in the molybdenum compound layer according to the embodiment, the constituent elements of the molybdenum compound layer may be set as described below in order to set predetermined optical characteristics, etching rate, or the like to be in a desired range. That is, in the case in which the total amount of molybdenum (Mo), silicon (Si), nitrogen (N), oxygen (O), and carbon (C) serving as constituent elements of  
10 the molybdenum compound layer is 100 mol%, the contained amounts of the constituent elements of the molybdenum compound layer may be set such that the content rate of Si is in a range of 35 to 50 mol%, the content rate of Mo is in a range of 3 to 10 mol%, the content rate of O is in a range of 0 to 20 mol%, the content rate of N is in a range of 35 to 60 mol%, and the content rate of C is in a range of 0 to 1 mol%.

15 [0037]

The compositions (mole fractions) of chemical elements contained in the molybdenum compound layer can be measured by wide scanning measurement of X-ray photoelectron spectroscopy (XPS). Subsequently, by substituting the mole fraction of each chemical element obtained by measurement using the X-ray photoelectron  
20 spectroscopy for the aforementioned formula (A), it is possible to determine whether or not the aforementioned formula (A) is satisfied. Additionally, it is possible to calculate the Si/Mo ratio from the mole fractions of molybdenum and silicon obtained by the measurement.

[0038]

25           The blank mask layer 12 and the mask layer 12P according to the embodiment

may be a mask layer including a single layer configured of the molybdenum compound layer or may be a mask layer configured of a multilayered body in which the molybdenum compound layer and the other layer are stacked in layers.

[0039]

5           In the case in which the blank mask layer 12 and the mask layer 12P are each the mask layer including the single layer configured of the molybdenum compound layer, it is preferable that the blank mask layer 12 and the mask layer 12P each function as a phase-shifting layer. In this case, it is preferable that a thickness of the mask layer be in a range of, for example, approximately 50 to 70 nm.

10   [0040]

          Moreover, in the case in which the blank mask layer 12 and the mask layer 12P are each configured of the multilayered body including the molybdenum compound layer, it is preferable that the molybdenum compound layer function as any one or more of a phase-shifting layer, a light-shielding layer, an antireflection layer, an etching stopping  
15   layer, a chemical resistance layer, or the like. In this case, it is preferable that a thickness of the molybdenum compound layer be in a range of, for example, approximately 60 to 80 nm.

[0041]

          That is, generally, in the case in which the blank mask layer 12 and the mask  
20   layer 12P are each configured of the multilayered body, for example, the function of each of layers constituting the blank mask layer 12 and the mask layer 12P is as follows.

- A phase-shifting function
- A light-shielding function of shielding exposure light
- An antireflection function of preventing reflection of exposure light
- 25   -       An adhesion function of increasing adherence with respect to photoresist when

forming a photomask

- An etching stopping function when forming a photomask
- A chemical resistance function of resisting etching solution or the like when forming a photomask

- 5     - A low reflectance function of reducing reflectance of exposure light.

In order to achieve the above function, the mask layer includes one or more layers selected from a phase-shifting layer, a light-shielding layer, an antireflection layer, an adhesion layer, an etching stopping layer, a chemical resistance layer, a low-reflectance layer, or the like. The molybdenum compound layer according to the embodiment may constitute any one of the phase-shifting layer, the light-shielding layer, the antireflection layer, the adhesion layer, the etching stopping layer, the chemical resistance layer, and the low-reflectance layer which are mentioned above.

[0042]

Hereinbelow, the configuration of the blank mask layer 12 and the mask layer 12P will be described with reference to, for example, the mask blanks.

In the case in which the blank mask layer 12 is configured of the multilayered body, as shown in FIG. 4, the blank mask layer 12 may have a structure in which a phase-shifting layer 12a and a Cr-based light-shielding layer 12b are stacked in layers on the glass substrate 11 in this order. In this case, the phase-shifting layer 12a serves as the molybdenum compound layer according to the embodiment.

[0043]

Furthermore, the Cr-based light-shielding layer 12b in the example shown in FIG. 4 contains, for example, Cr (chromium) and O (oxygen) as main components and further contains C (carbon) and N (nitrogen). More specifically, as a constituent material of the light-shielding layer 12b, one or more materials may be selected from a

group consisting of chromium oxide, chromium nitride, chromium carbide, chromium oxide nitride, chromium carbide nitride, and chromium oxide carbide nitride. In the case in which two or more materials are selected, the light-shielding layer 12b has a configuration in which the two or more materials are stacked in layers. Furthermore, the light-shielding layer 12b may have compositions different from each other in the thickness direction of the light-shielding layer 12b. For example, regarding the concentration of nitrogen, the concentration of oxygen, or the like, the light-shielding layer 12b may be configured so as to have gradient of concentration in the film thickness of the light-shielding layer 12b.

10 [0044]

Moreover, as shown in FIG. 5, the blank mask layer 12 may have a structure in which a phase-shifting layer 12c, an etching stopping layer 12d, and a Cr-based light-shielding layer 12e are stacked in layers on the glass substrate 11 in this order. In this case, one of or both of the phase-shifting layer 12c and the etching stopping layer 12d serve as the molybdenum compound layer according to the embodiment.

15 [0045]

The phase-shifting layer 12c in the example shown in FIG. 5 may be formed of not only the molybdenum compound layer but also a layer containing chromium as a main component. Specifically, the phase-shifting layer 12c may be configured of a layer formed of one selected from a group consisting of single chromium, chromium oxide, chromium nitride, chromium carbide, chromium oxide nitride, chromium carbide nitride, and chromium oxide carbide nitride. Also, the phase-shifting layer 12c may be configured by stacking two or more layers selected from the above-described material group.

20 [0046]

The etching stopping layer 12d in the example shown in FIG. 5 may be formed of not only the molybdenum compound layer but also a metal silicide compound layer containing nitrogen. The etching stopping layer 12d may be configured of, for example, a layer containing at least one metal selected from a group consisting of Ni, Co, Fe, Ti, Al, Nb, Mo, W, and Hf, a layer containing an alloy formed of the above metals and Si, a molybdenum silicide compound layer, and a  $\text{MoSi}_X$  ( $X \geq 2$ ) layer (for example, a  $\text{MoSi}_2$  film, a  $\text{MoSi}_3$  film, a  $\text{MoSi}_4$  film, or the like).

[0047]

Regarding the Cr-based light-shielding layer 12e in the example shown in FIG.

5, a layer containing, for example, Cr (chromium) and O (oxygen) as main components and further containing C (carbon) and N (nitrogen) may be adopted as the light-shielding layer 12e. More specifically, as the light-shielding layer 12e, one or more materials may be selected from a group consisting of chromium oxide, chromium nitride, chromium carbide, chromium oxide nitride, chromium carbide nitride, and chromium oxide carbide nitride. In the case in which two or more materials are selected, the light-shielding layer 12e has a configuration in which the two or more materials are stacked in layers. Furthermore, the light-shielding layer 12e may have compositions different from each other in the thickness direction of the light-shielding layer 12e. For example, regarding the concentration of nitrogen, the concentration of oxygen, or the like, the light-shielding layer 12e may be configured so as to have gradient of concentration in the film thickness of the light-shielding layer 12e.

[0048]

Additionally, as shown in FIG. 6, the blank mask layer 12 may have a structure in which a Cr-based phase-shifting layer 12f and an antireflection layer 12g are stacked in layers on the glass substrate 11 in this order. Moreover, as shown in FIG. 7, the

blank mask layer 12 may have a structure in which the Cr-based phase-shifting layer 12f, the antireflection layer 12g, and a Cr-based adhesion layer 12h are stacked in layers. In this case, the antireflection layer 12g serves as the molybdenum compound layer according to the embodiment.

5 [0049]

It is preferable that the Cr-based phase-shifting layer 12f in the example shown in FIGS. 6 and 7 be configured of a layer containing chromium as a main component and configured of a layer containing C (carbon), O (oxygen), and N (nitrogen). Specifically, the phase-shifting layer 12f may be configured of one selected from a group consisting of  
10 single chromium, chromium oxide, chromium nitride, chromium carbide, chromium oxide nitride, chromium carbide nitride, and chromium oxide carbide nitride. Also, the phase-shifting layer 12f may be configured by stacking two or more layers selected from the above-described material group.

[0050]

15 Furthermore, it is preferable that the Cr-based adhesion layer 12h in the example shown in FIG. 7 be configured of a layer containing Cr (chromium) and O (oxygen) as main components and configured of a layer containing C (carbon) and N (nitrogen). Specifically, the adhesion layer 12h may be configured by stacking one or more selected from a group consisting of single chromium, chromium oxide, chromium nitride,  
20 chromium carbide, chromium oxide nitride, chromium carbide nitride, and chromium oxide carbide nitride. Moreover, the adhesion layer 12h may have compositions different from each other in the thickness direction of the adhesion layer 12h.

[0051]

Additionally, as shown in FIG. 8, the blank mask layer 12 may have a structure  
25 in which a phase-shifting layer 12i, a low-reflectance layer 12j, and a chemical resistance

layer 12k are stacked in layers on the glass substrate 11 in this order. In this case, at least one of or two or more of the phase-shifting layer 12i, the low-reflectance layer 12j, and the chemical resistance layer 12k serve as the molybdenum compound layer according to the embodiment.

5 [0052]

The phase-shifting layer 12i and the chemical resistance layer 12k in the example shown in FIG. 8 may be formed of not only the molybdenum compound layer but also a silicide layer containing nitrogen. The phase-shifting layer 12i and the chemical resistance layer 12k may be configured of, for example, a layer containing a  
10 metal such as Ta, Ti, W, Mo, Zr, or the like, a layer containing an alloy formed of the above metals and silicon, and a  $\text{MoSi}_X$  ( $X \geq 2$ ) layer (for example, a  $\text{MoSi}_2$  film, a  $\text{MoSi}_3$  film, a  $\text{MoSi}_4$  film, or the like).

Furthermore, similar to the phase-shifting layer and the chemical resistance layer which are described above, not only the molybdenum compound layer but also a silicide  
15 layer containing nitrogen may be adopted as the low-reflectance layer 12j in the example shown in FIG. 8. Moreover, a layer containing oxygen may be adopted as the low-reflectance layer 12j.

[0053]

Although the examples of the mask blanks were described with reference to  
20 FIGS. 4 to 8, the configuration of the blank mask layer 12 shown in FIGS. 4 to 8 may be applied to the mask layer 12P of the photomask.

[0054]

Next, a method of manufacturing the mask blanks according to the embodiment will be described.

25 The method of manufacturing the mask blanks according to the embodiment is a

method of forming the blank mask layer 12 on the glass substrate 11. When forming the blank mask layer 12, the blank mask layer may be formed by stacking one or more layers selected from a phase-shifting layer, a light-shielding layer, an antireflection layer, an adhesion layer, an etching stopping layer, a chemical resistance layer, a

5 low-reflectance layer, or the like. At this time, one or more of the phase-shifting layer, the light-shielding layer, the antireflection layer, the adhesion layer, the etching stopping layer, the chemical resistance layer, and the low-reflectance layer may serve as the molybdenum compound layer according to the embodiment.

[0055]

10 FIG. 9 is a schematic view showing a manufacturing apparatus of a mask blanks according to the embodiment. FIG. 10 is a schematic view showing a manufacturing apparatus of a mask blanks according to the embodiment. The mask blanks according to the embodiment is manufactured by the manufacturing apparatus shown in FIG. 9 or FIG. 10.

15 [0056]

A manufacturing apparatus S10 shown in FIG. 9 is a single-wafer sputtering apparatus. The manufacturing apparatus S10 includes a load-unload chamber S11 and a film formation chamber (vacuum processing chamber) S12 connected to the load-unload chamber S11 via a hermetical sealing portion S13.

20 [0057]

The load-unload chamber S11 is provided with a transfer device S11a and a vacuum pumping device S11b. The transfer device S11a is configured to transfer the glass substrate 11 transferred from the outside to the inside of the manufacturing apparatus S10, to the film formation chamber S12. Furthermore, the transfer device

25 S11a is configured to transfer the glass substrate 11 to the outside of the film formation

chamber S12. The vacuum pumping device S11b is configured of a rotary pump or the like configured to carry out rough vacuuming of the inside of the load-unload chamber S11.

[0058]

5           The film formation chamber S12 is provided with: a substrate holding device S12a, a cathode electrode (backing plate) S12c that includes a target S12b and that serves as a device supplying a film forming material, a power supply S12d that is configured to apply a sputtering voltage of a negative electrical potential to the backing plate S12c, a gas introduction device S12e that is configured to introduce a gas into the inside of the film formation chamber S12, and a high-vacuum pumping device S12f such as a turbo-molecular pump or the like which is configured to carry out high vacuuming of the inside of the film formation chamber S12.

[0059]

          The substrate holding device S12a is configured to hold the glass substrate 11 such that the glass substrate 11 transferred by the transfer device S11a faces toward the target S12b during film formation. The substrate holding device S12a can transfer the glass substrate 11 from the load-unload chamber S11 to the film formation chamber S12 and can transfer the glass substrate 11 from the film formation chamber S12 to the load-unload chamber S11.

20   [0060]

          The target S12b is formed of materials having compositions necessary for forming a film on the glass substrate 11. For example, as a target in the case of forming the molybdenum compound layer, a target containing molybdenum and a target containing silicon may be used by combination, or a single target containing molybdenum and silicon may be used. Furthermore, a target containing chromium may

be used in order to form, for example, a Cr-based film. The above-mentioned targets may be replaced for each film forming process.

[0061]

In the manufacturing apparatus S10 shown in FIG. 9, the glass substrate 11 transferred from the load-unload chamber S11 is subjected to a sputtering film formation process in the film formation chamber S12. Thereafter, the post-film-formation glass substrate 11 is transferred from the load-unload chamber S11 to the outside of the manufacturing apparatus S10.

[0062]

In a film formation process, a sputtering gas and a reactive gas are supplied from the gas introduction device S12e to the film formation chamber S12, and a sputtering voltage is applied from an external power supply to the backing plate (cathode electrode) S12c. Furthermore, a predetermined magnetic field may be generated on the target S12b by a magnetron magnetic circuit. Ions of the sputtering gas excited by plasma in the film formation chamber S12 collide against the target S12b of the cathode electrode S12c, and particles of the film forming material are spattered from the target S12b. After the spattered particles and the reactive gas are bonded, the particles are attached to the glass substrate 11, and therefore a predetermined film is formed on the surface of the glass substrate 11.

[0063]

At this time, when forming the molybdenum compound layer according to the embodiment, that is, when forming the molybdenum compound layer that contains molybdenum, silicon, and nitrogen, selectively contains oxygen, and satisfies the aforementioned formula (A), the target containing molybdenum and the target containing silicon by combination are used as the target S12b, or the single target containing

molybdenum and silicon is used as the target S12b. The gas introduction device S12e controls partial pressures of the nitrogen gas and the oxygen-containing gas by changing each of the flow rate of a nitrogen gas and the flow rate of an oxygen-containing gas, and causes the compositions of gases to be in a set range. The gases having the set  
5 compositions described above are supplied from the gas introduction device S12e to the inside of the film formation chamber S12.

[0064]

Here, as the oxygen-containing gas, CO<sub>2</sub> (carbon dioxide), O<sub>2</sub> (oxygen), N<sub>2</sub>O (dinitrogen oxide), NO (nitrogen monoxide), or the like can be adopted.

10 [0065]

Next, a manufacturing apparatus S20 shown in FIG. 10 is a single-wafer sputtering apparatus. The manufacturing apparatus S20 includes a load chamber S21, a film formation chamber (vacuum processing chamber) S22 connected to the load chamber S21 via a hermetical sealing portion S23, and an unload chamber S25 connected  
15 to the film formation chamber S22 via a hermetical sealing portion S24.

[0066]

The load chamber S21 is provided with: a transfer device S21a that is configured to transfer the glass substrate 11 transferred from the outside to the inside of the manufacturing apparatus S20, to the film formation chamber S22; and a vacuum  
20 pumping device S21b that is configured of a rotary pump or the like configured to carry out rough vacuuming of the inside of the load chamber S21.

[0067]

The film formation chamber S22 is provided with: a substrate holding device S22a, a cathode electrode (backing plate) S22c that includes a target S22b and that serves  
25 as a device supplying a film forming material, a power supply S22d that is configured to

apply a sputtering voltage of a negative electrical potential to the backing plate S22c, a gas introduction device S22e that is configured to introduce a gas into the inside of the film formation chamber S22, and a high-vacuum pumping device S22f such as a turbo-molecular pump or the like which is configured to carry out high vacuuming of the inside of the film formation chamber S22.

[0068]

The substrate holding device S22a is configured to hold the glass substrate 11 such that the glass substrate 11 transferred by the transfer device S21a faces toward the target S22b during film formation. The substrate holding device S22a can transfer the glass substrate 11 from the load chamber S21 to the film formation chamber S22 and can transfer the glass substrate 11 from the film formation chamber S22 to the unload chamber S25.

[0069]

The target S22b is formed of materials having compositions necessary for forming a film on the glass substrate 11. Similar to the case of the apparatus shown in FIG. 9, as a target in the case of forming the molybdenum compound layer, a target containing molybdenum and a target containing silicon may be used by combination, or a single target containing molybdenum and silicon may be used. Furthermore, a target containing chromium may be used in order to form, for example, a Cr-based film. The above-mentioned targets may be replaced for each film forming process.

[0070]

The unload chamber S25 is provided with: a transfer device S25a that is configured to transfer the glass substrate 11 transferred from the film formation chamber S22, to the manufacturing apparatus S20; and a vacuum pumping device S25b that is configured of a rotary pump or the like configured to carry out rough vacuuming of the

inside of the unload chamber S25.

[0071]

In the manufacturing apparatus S20 shown in FIG. 10, the glass substrate 11 transferred from the load chamber S21 is subjected to a sputtering film formation process in the film formation chamber S22. Thereafter, the post-film-formation glass substrate 11 is transferred from the unload chamber S25 to the outside of the film formation chamber S22.

[0072]

In a film formation process, a sputtering gas and a reactive gas are supplied from the gas introduction device S22e to the film formation chamber S22, and a sputtering voltage is applied from an external power supply to the backing plate (cathode electrode) S22c. Furthermore, a predetermined magnetic field may be generated on the target S22b by a magnetron magnetic circuit. Ions of the sputtering gas excited by plasma in the film formation chamber S22 collide against the target S22b of the cathode electrode S22c, and particles of the film forming material are spattered from the target S22b. After the spattered particles and the reactive gas are bonded, the particles are attached to the glass substrate 11, and therefore a predetermined film is formed on the surface of the glass substrate 11.

[0073]

At this time, when forming the molybdenum compound layer according to the embodiment, that is, when forming the molybdenum compound layer that contains molybdenum, silicon, and nitrogen, selectively contains oxygen, and satisfies the aforementioned formula (A), the target containing molybdenum and the target containing silicon by combination are used as the target S22b, or the single target containing molybdenum and silicon is used as the target S22b. The gas introduction device S22e

controls partial pressures of the nitrogen gas and the oxygen-containing gas by changing each of the flow rate of a nitrogen gas and the flow rate of an oxygen-containing gas, and causes the compositions of gases to be in a set range. The gases having the set compositions described above are supplied from the gas introduction device S22e to the  
5 inside of the film formation chamber S22.

[0074]

Here, as the oxygen-containing gas, CO<sub>2</sub> (carbon dioxide), O<sub>2</sub> (oxygen), N<sub>2</sub>O (dinitrogen oxide), NO (nitrogen monoxide), or the like can be adopted.

[0075]

10 Next, a method of manufacturing the photomask according to the embodiment will be described.

In a resist pattern forming process, as shown in FIG. 2, the photoresist layer 13 is formed on the uppermost surface of the mask blanks. In another case, a mask blanks having the photoresist layer 13 formed in advance on the uppermost surface of the mask  
15 blanks may be prepared.

[0076]

Next, the photoresist layer 13 is subjected to an exposure process and a development process, and a resist pattern is formed. The resist pattern functions as a mask used for etching the blank mask layer 12.

20 [0077]

Next, the blank mask layer 12 is dry-etched via the resist pattern by use of a dry etching apparatus, and therefore the blank mask layer 12 is patterned so as to have a predetermined shape. As a gas used for etching with respect to the molybdenum compound layer of the blank mask layer 12 according to the embodiment, it is preferable  
25 to use a gas including at least one fluorocarbon gas selected from perfluorocarbon as

typified by carbon tetrafluoride and hydrofluorocarbon as typified by trifluoromethane.

[0078]

As described above, the photomask having the patterned mask layer 12P is obtained as shown in FIG. 3.

5 [0079]

The mask blanks and the photomask according to the embodiment of the invention each include the molybdenum compound layer in which the ratio of the peak area of the Mo-Si bonding peak to the peak areas of the photoelectron spectrums of  $\text{Mo}_{3d3/2}$  and  $\text{Mo}_{3d5/2}$  is greater than or equal to 73.0%. Accordingly, even where the photomask is irradiated with exposure light in the photolithography process, it is possible to suppress an increase of the line width of the patterned portion due to Mo migration. Particularly, the mask blanks and the photomask according to the embodiment can be applied to a photomask used in a photolithography process using exposure light, for example, exposure light having a wavelength of 200 nm or less, particularly, ArF excimer laser light (wavelength of 193 nm) used for photolithography via a phase-shifting mask.

15

#### Examples

[0080]

Hereinbelow, the invention will be particularly described with reference to Examples.

20

A large-scale glass substrate was prepared. The large-scale glass substrate is made of synthetic silica (QZ). The large-scale glass substrate has a thickness of 10 mm and a size of 850 mm × 1200 mm. A molybdenum compound layer (blank mask layer) was formed on the large-scale glass substrate by use of a large-scale in-line sputtering apparatus. Specifically, a  $\text{MoSi}_x$  target having X values of 5.4, 7.4, and 9.4 was

25

prepared. One or more of Ar gas, N<sub>2</sub> gas, CO<sub>2</sub> gas, and O<sub>2</sub> gas was used as a sputtering gas. A plurality of molybdenum compound layers having the respective film types a to g were formed. Table 1 shows conditions for film formation of the molybdenum compound layers having the film types a to g.

5 [0081]

The ratio of the peak area of the Mo-Si bonding peak of the molybdenum compound layer was calculated. Specifically, samples that have film types a to g and have a size of 10 mm × 20 mm were obtained by cutting substrates having the molybdenum compound layers having the respective film types A to G. Each of the  
10 samples was put into an X-ray photoelectron spectrometer (Quantera, manufactured by ULVAC-PHI, INCORPORATED), a narrow scanning analysis was carried out with respect to the surface of the molybdenum compound layer, and measurement was carried out at binding energy in an approximate range of 220 to 240 eV. A photoelectron spectrum having a peak top that appears at approximately 227 eV was specified as the  
15 photoelectron spectrum of Mo<sub>3d5/2</sub>. A photoelectron spectrum having a peak top that appears at approximately 230 eV was specified as the photoelectron spectrum of Mo<sub>3d3/2</sub>. Next, the total area the two photoelectron spectrums was calculated (measured) using data processing program provided in the X-ray photoelectron spectrometer. At this time, the background intensity was subtracted from the peak area.

20 [0082]

Next, peak separation processing was carried out with respect to the photoelectron spectrums of Mo<sub>3d3/2</sub> and Mo<sub>3d5/2</sub>. The peak separation processing was carried out using data processing program provided in the X-ray photoelectron spectrometer. A peak that appears in an approximate range of 226 to 227 eV by peak  
25 separation was specified as the Mo-Si bonding peak in the photoelectron spectrum of

Mo<sub>3d5/2</sub>. A peak that appears in an approximate range of 229 to 231 eV was specified as the Mo-Si bonding peak in the photoelectron spectrum of Mo<sub>3d3/2</sub>. Next, the peak area of each of the Mo-Si bonding peaks was measured. Furthermore, the total area of the two peak areas was calculated. At this time, the background intensity was subtracted from the peak area. Next, the ratio of the peak area of the Mo-Si bonding peak to the peak area of the photoelectron spectrums of Mo<sub>3d3/2</sub> and Mo<sub>3d5/2</sub> (%) was calculated. Table 1 shows the results. Furthermore, FIG. 11 shows examples of photoelectron spectrums of Mo<sub>3d3/2</sub> and Mo<sub>3d5/2</sub> after peak separation processing.

[0083]

Moreover, the compositions of the constituent elements of the molybdenum compound layers were measured by wide scanning analysis of X-ray photoelectron spectroscopy. The mole fraction of each chemical element obtained by measurement using the X-ray photoelectron spectroscopy is shown in Table 2. Table 2 also shows Si/Mo representing a ratio of the mole fractions of molybdenum and silicon and the calculated result of the left member of the aforementioned formula (A).

[0084]

Next, a patterned photoresist layer was formed on each of the molybdenum compound layers obtained by the conditions for film formation shown in Table 1. The molybdenum compound layer is patterned so as to have a line width of 100 nm by carrying out wet etching using the photoresist layer as a mask. The molybdenum compound layer patterned as mentioned above was used as a mask layer. Mo migration was generated by irradiating the post-patterned molybdenum compound layer with ArF excimer laser light (wavelength of 193 nm). Next, an amount of change of the line width of the molybdenum compound layer that has been irradiated with the ArF excimer laser light (wavelength of 193 nm) was measured. Table 1 shows the results.

[0085]

As shown in Table 1, it is apparent that, the larger the ratio of the peak area of the Mo-Si bonding peak, the smaller the increased amount of the line width of the molybdenum compound layer (mask layer). It was determined that, in order to cause the increased amount of the line width of the molybdenum compound layer (mask layer) to be less than or equal to 4 nm, it is preferable that the ratio of the peak area of the Mo-Si bonding peak be greater than or equal to 73.0% and more preferably greater than or equal to 75.0%.

[0086]

Additionally, as shown in Table 2, in the case in which the formula (A) is small even where the amount of molybdenum is small such as film type b, an increase in line width significantly occurs. In contrast, in the case in which the formula (A) is large even where the amount of molybdenum is large such as film type d, an increase in line width does not almost occur. Although the film type a is equal to the film type b in contained amount of Mo, the amount of nitrogen of the film type a is smaller than that of the film type b. Accordingly, it is presumed that, the amount of molybdenum nitride becomes small, as a result, the amount of molybdenum migration becomes small, and therefore the increased amount of the line width becomes small.

[0087]

(Table 1)

| FILM TYPE | TARGET                       | FLOW RATE OF SPUTTERING GAS (sccm) |                 |                | RATIO OF PEAK AREA OF Mo-Si BONDING IN PHOTOELECTRON SPECTRUM OF Mo <sub>3d</sub> [%] | RATIO OF PEAK AREA OTHER THAN Mo-Si BONDING IN Mo <sub>3d</sub> PEAK [%] | INCREASED AMOUNT OF LINE WIDTH |
|-----------|------------------------------|------------------------------------|-----------------|----------------|---------------------------------------------------------------------------------------|--------------------------------------------------------------------------|--------------------------------|
|           | X VALUE OF MoSi <sub>x</sub> | N <sub>2</sub>                     | CO <sub>2</sub> | O <sub>2</sub> |                                                                                       |                                                                          | [nm]                           |
| a         | 7.5                          | 13.5                               | 0               | 2              | 79                                                                                    | 23                                                                       | 2.0                            |
| b         | 9.5                          | 21                                 | 0               | 2              | <u>70.1</u>                                                                           | 29.9                                                                     | 4.8                            |
| c         | 7.5                          | 17                                 | 0               | 1              | 73.2                                                                                  | 26.8                                                                     | 3.2                            |
| d         | 5.5                          | 11                                 | 3               | 0              | 75                                                                                    | 25                                                                       | 2.3                            |
| e         | 9.5                          | 18                                 | 0               | 0              | <u>68.3</u>                                                                           | 31.7                                                                     | 5.1                            |
| f         | 5.5                          | 16                                 | 0               | 3              | <u>66</u>                                                                             | 34                                                                       | 5.5                            |
| g         | 9.5                          | 22                                 | 0               | 0              | <u>67.5</u>                                                                           | 32.5                                                                     | 4.8                            |

Underlined part means out of scope of the invention.

[0088]

5 (Table 2)

| FILM TYPE | COMPOSITION OF MOLYBDENUM COMPOUND LAYER (mol%) |     |     |      |     |       | Si/Mo RATIO | FORMULA (A) |
|-----------|-------------------------------------------------|-----|-----|------|-----|-------|-------------|-------------|
|           | Si                                              | Mo  | O   | N    | C   | total |             |             |
| a         | 46                                              | 6.2 | 3.2 | 44.6 | 0   | 100   | 7.4         | 0.38        |
| b         | 39.2                                            | 5.5 | 2.3 | 53   | 0   | 100   | 7.1         | 0.01        |
| c         | 44                                              | 6.7 | 1.3 | 48   | 0   | 100   | 6.6         | 0.30        |
| d         | 42.3                                            | 9.7 | 9.5 | 37.8 | 0.7 | 100   | 4.4         | 0.40        |
| e         | 40.1                                            | 4.9 | 0   | 55   | 0   | 100   | 8.2         | 0.02        |
| f         | 40.5                                            | 7.5 | 9   | 43   | 0   | 100   | 5.4         | 0.22        |
| g         | 39.6                                            | 5.4 | 0   | 55   | 0   | 100   | 7.3         | 0.01        |

FORMULA (A) =  $\{(Si - O/2) \times 4/3 + Mo/2 - N\} / Si$

## DESCRIPTION OF REFERENCE NUMERALS

[0089]

10 11 glass substrate

12 blank mask layer

12P mask layer

## CLAIMS

1. A mask blanks including a blank mask layer, wherein  
the blank mask layer includes a molybdenum compound layer that contains  
5 molybdenum, silicon, and nitrogen and that selectively contains oxygen, and  
in the molybdenum compound layer, a ratio of a peak area of a Mo-Si bonding  
peak obtained by separation of peaks of a photoelectron spectrum of  $\text{Mo}_{3d3/2}$  and a  
photoelectron spectrum of  $\text{Mo}_{3d5/2}$  to peak areas of the photoelectron spectrums of  
 $\text{Mo}_{3d3/2}$  and  $\text{Mo}_{3d5/2}$  measured by X-ray photoelectron spectroscopy is greater than or  
10 equal to 73.0%.
  
2. The mask blanks according to claim 1, wherein  
the molybdenum compound layer satisfies the following formula (1):  

$$\{(\text{Si-O}/2) \times 4/3 + \text{Mo}/2 - \text{N}\} / \text{Si} \geq 0.25 \dots (1),$$
15 here, Mo, Si, O, and N represented by the above-mentioned formula (1) mean  
mole fractions (mol%) of molybdenum, silicon, oxygen, and nitrogen, which are  
contained in the molybdenum compound layer, respectively, and  
in a case in which the molybdenum compound layer does not contain oxygen, O  
represented by the above-mentioned formula (1) is 0.  
20
  
3. The mask blanks according to claim 1 or claim 2, wherein  
the molybdenum compound layer further satisfies the following formula (2):  

$$\text{Si}/\text{Mo} \geq 4.0 \dots (2),$$
here, Mo and Si represented by the above-mentioned formula (2) mean mole  
25 fractions (mol%) of molybdenum and silicon, which are contained in the molybdenum

compound layer, respectively.

4. The mask blanks according to any one of claims 1 to 3, wherein  
 regarding compositions of molybdenum, silicon, nitrogen, and oxygen contained  
 5 in the molybdenum compound layer,  
     a content rate of silicon is in a range of 35 to 50 mol%,  
     a content rate of molybdenum is in a range of 3 to 10 mol%,  
     a content rate of oxygen is in a range of 0 to 20 mol%,  
     a content rate of nitrogen is in a range of 35 to 60 mol%, and  
 10     a content rate of carbon is in a range of 0 to 1 mol%.
  
5. The mask blanks according to any one of claims 1 to 4, wherein  
     the molybdenum compound layer constitutes any one or more of a  
 phase-shifting layer, a light-shielding layer, an antireflection layer, an etching stopping  
 15 layer, and a chemical resistance layer.
  
6. A photomask including a mask layer, wherein  
     the mask layer includes a molybdenum compound layer that contains  
 molybdenum, silicon, and nitrogen and that selectively contains oxygen, and  
 20     in the molybdenum compound layer, a ratio of a peak area of a Mo-Si bonding  
 peak obtained by separation of peaks of a photoelectron spectrum of  $\text{Mo}_{3d3/2}$  and a  
 photoelectron spectrum of  $\text{Mo}_{3d5/2}$  to peak areas of the photoelectron spectrums of  
 $\text{Mo}_{3d3/2}$  and  $\text{Mo}_{3d5/2}$  measured by X-ray photoelectron spectroscopy is greater than or  
 equal to 73.0%.

7. The photomask according to claim 6, wherein

the molybdenum compound layer satisfies the following formula (3):

$$\{(\text{Si-O}/2) \times 4/3 + \text{Mo}/2 - \text{N}\} / \text{Si} \geq 0.25 \dots (3),$$

here, Mo, Si, O, and N represented by the above-mentioned formula (3) mean

5 mole fractions (mol%) of molybdenum, silicon, oxygen, and nitrogen, which are

contained in the molybdenum compound layer, respectively, and

in a case in which the molybdenum compound layer does not contain oxygen, O represented by the above-mentioned formula (3) is 0.

10 8. The photomask according to claim 6 or claim 7, wherein

the molybdenum compound layer further satisfies the following formula (4):

$$\text{Si}/\text{Mo} \geq 4.0 \dots (4),$$

here, Mo and Si represented by the above-mentioned formula (4) mean mole fractions (mol%) of molybdenum and silicon, which are contained in the molybdenum

15 compound layer, respectively.

9. The photomask according to any one of claims 6 to 8, wherein

regarding compositions of molybdenum, silicon, nitrogen, and oxygen contained in the molybdenum compound layer,

20 a content rate of silicon is in a range of 35 to 50 mol%,

a content rate of molybdenum is in a range of 3 to 10 mol%,

a content rate of oxygen is in a range of 0 to 20 mol%,

a content rate of nitrogen is in a range of 35 to 60 mol%, and

a content rate of carbon is in a range of 0 to 1 mol%.

10. The photomask according to any one of claims 6 to 9, wherein  
the molybdenum compound layer constitutes any one or more of a  
phase-shifting layer, a light-shielding layer, an antireflection layer, an etching stopping  
layer, and a chemical resistance layer.