TITLE OF INVENTION: MASK BLANK AND METHOD OF MANUFACTURING MASK BLANK

TECHNICAL FIELD

[0001]

The present invention relates to a mask blank and a method of manufacturing a mask blank, and particularly relates to a preferred technique used for a mask blank including a chromium layer.

BACKGROUND ART

[0002]

In recent years, in a photolithography process of manufacturing an FPD (Flat Panel Display) such as a liquid crystal display, an organic EL display, a semiconductor device, or the like, high-definition of the panel or the device has significantly progressed. In accordance with this, there is a demand for a photomask having a fine pattern. Consequently, a binary mask using a light-shielding film, an edge enhanced phase-shift mask, a semitransparent halftone mask is conventionally used.

[0003]

In order to manufacture the above-described photomask, for example, a mask blank including a mask layer containing chromium is used.

[0004]

Recently, with an increase in the degree of definition of semiconductor devices, pattern formation using an excimer laser such as KrF, liquid immersion ArF, or the like is carried out.

Additionally, a step of processing a mask blank by use of a chemical solution

such as acid, alkali, ozone, or the like is necessary.

[CITATION LIST]

[PATENT LITERATURE]

[0005]

[Patent Literature 1] Japanese Unexamined Patent Application, First Publication No. 2019-066892

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0006]

However, although an improvement of accuracy of pattern formation is required in accordance with a demand for a high-definition pattern and a miniaturized pattern, a conventional technique has a problem in that the chemical resistance of a mask layer for obtaining the above-described high-definition pattern, miniaturized pattern, and accuracy is not sufficient. Particularly, in a case in which the chemical resistance is not sufficient, a defect occurs such that the film characteristics such as an optical density (OD value: Optical Density) or the like vary.

Moreover, there is a demand for improvement of adhesion between a mask layer and a resist layer and for improvement of adhesion between a mask layer and a lower layer located under the mask layer in a multi-layered structure. Furthermore, there is a requirement for both solving the above-mentioned problem and achieving the above-mentioned demand at the same time.

Additionally, it is desirable to achieve further improvement of a selection ratio during etching for increasing the thickness of a resist layer and for increasing the etching rate.

[0007]

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

1. To provide a sufficient chemical resistance to a mask layer containing chromium.

2. To improve an etching rate of a mask layer containing chromium.

3. To improve adhesion between a mask layer containing chromium and a resist layer serving as an upper layer located above the mask layer.

4. To improve adhesion between a mask layer containing chromium and a lower layer located under the mask layer.

MEANS FOR SOLVING THE PROBLEMS

[0008]

A mask blank according to one aspect of the invention includes: a transparent substrate having a surface; and a mask layer stacked on the surface of the transparent substrate. The mask layer contains nitrogen (N), carbon (C), oxygen (O), and chromium (Cr). The mask layer has an uppermost surface on the opposite side of the surface of the transparent substrate. An oxygen content rate of the uppermost surface of the mask layer is in a range of 65 to 72atm%.

In the mask blank according to one aspect of the invention, the mask layer may include a surface layer having an upper surface and a lower surface on the opposite side of the upper surface. The upper surface of the surface layer corresponds to the uppermost surface. An oxygen content rate of the upper surface of the surface layer may be in a range of 65 to 72atm%. An oxygen content rate of the lower surface of the surface layer may be in a range of 35 to 45atm%. The surface layer may have an oxygen concentration gradient such that an oxygen content rate gradually decreases in a

direction from the upper surface to the lower surface.

In the mask blank according to one aspect of the invention, in a case in which an oxygen content rate is represented as O (atm%) and a nitrogen content rate is represented as N (atm%), an oxygen-nitrogen compositional ratio is represented as O/(O+N), and the oxygen-nitrogen compositional ratio of the surface layer may be in a range of 0.9 to 0.98.

In the mask blank according to one aspect of the invention, the mask layer includes an upper-medium layer located closer to the transparent substrate than the surface layer, the upper-medium layer contains oxygen, and an oxygen content rate of the upper-medium layer may be lower than an oxygen content rate of the surface layer.

In the mask blank according to one aspect of the invention, the mask layer includes an intermediate layer located closer to the transparent substrate than the upper-medium layer, the intermediate layer contains oxygen, the intermediate layer has a surface, and an oxygen content rate of the upper-medium layer may be lower than an oxygen content rate of the surface of the intermediate layer.

In the mask blank according to one aspect of the invention, the mask layer includes: a light-shielding layer containing chromium; an intermediate layer stacked on the light-shielding layer, the intermediate layer containing chromium; an upper-medium layer stacked on the intermediate layer, the upper-medium layer containing chromium; and a surface layer stacked on the upper-medium layer, the surface layer containing chromium. The surface layer contains oxygen, nitrogen, and carbon. A chromium content rate of the surface layer may be in a range of 21 to 25atm%. An oxygen content rate of the surface layer may be in a range of 65 to 72atm%. A nitrogen content rate of the surface layer may be in a range of 1 to 5atm%. A carbon content rate of the surface layer may be in a range of 4 to 6atm%.

In the mask blank according to one aspect of the invention, in a dry etching

treatment using a mixed gas of chlorine and oxygen, in a case in which an etching rate of the light-shielding layer is defined as ER1, an etching rate of the intermediate layer is defined as ER2, an etching rate of the upper-medium layer is defined as ER3, and an etching rate of the surface layer is defined as ER4, ER3<ER2<ER4<ER1 may be satisfied.

In the mask blank according to one aspect of the invention, each of the intermediate layer and the upper-medium layer includes oxygen, and in a case in which a value of an oxygen content rate of the upper-medium layer is defined as VO1, a value of an oxygen content rate of the intermediate layer is defined as VO2, and a value of an oxygen content rate of the surface layer is defined as VO3, VO2<VO1<VO3 may be satisfied.

In the mask blank according to one aspect of the invention, each of the intermediate layer and the upper-medium layer includes nitrogen, and in a case in which a value of a nitrogen content rate of the upper-medium layer is defined as VN1, a value of a nitrogen content rate of the intermediate layer is defined as VN2, and a value of a nitrogen content rate of the surface layer is defined as VN3, VN2<VN1<VN3 may be satisfied.

In the mask blank according to one aspect of the invention, each of the intermediate layer and the upper-medium layer includes carbon, and in a case in which a value of a carbon content rate of the upper-medium layer is defined as VC1, a value of a carbon content rate of the intermediate layer is defined as VC2, and a value of a carbon content rate of the surface layer is defined as VC3, VC2<VC1<VC3 may be satisfied.

In the mask blank according to one aspect of the invention, the upper-medium layer contains oxygen, nitrogen, and carbon, a chromium content rate of the upper-medium layer may be in a range of 45 to 52atm%, an oxygen content rate of the upper-

medium layer may be in a range of 15 to 25atm%, a nitrogen content rate of the upper-medium layer may be in a range of 15 to 25atm%, and a carbon content rate of the upper-medium layer may be in a range of 5 to 15atm%.

In the mask blank according to one aspect of the invention, the intermediate layer contains oxygen, nitrogen, and carbon, a chromium content rate of the intermediate layer may be in a range of 45 to 52atm%, an oxygen content rate of the intermediate layer may be in a range of 10 to 20atm%, a nitrogen content rate of the intermediate layer may be in a range of 15 to 25atm%, and a carbon content rate of the intermediate layer may be in a range of 10 to 20atm%.

In the mask blank according to one aspect of the invention, the light-shielding layer contains oxygen, nitrogen, and carbon, a chromium content rate of the light-shielding layer may be in a range of 30 to 40atm%, an oxygen content rate of the light-shielding layer may be in a range of 25 to 35atm%, a nitrogen content rate of the light-shielding layer may be in a range of 14 to 24atm%, and a carbon content rate of the light-shielding layer may be in a range of 11 to 21atm%.

In the mask blank according to one aspect of the invention, a thickness ratio of the light-shielding layer, the intermediate layer, the upper-medium layer, and the surface layer may be in a range of 29:1:3:11 to 33:2:6:13.

A method of manufacturing a mask blank according to one aspect of the invention manufactures the mask blank according to the above-mentioned aspect. The manufacturing method includes a mask-layer formation step of forming the mask layer containing chromium on the transparent substrate by sputtering. In the mask-layer formation step, a target containing chromium is used, and the uppermost surface of the mask layer is formed by using a gas containing carbon dioxide (CO_2) serving as an oxygen-containing gas as a supply gas for the sputtering.

In the method of manufacturing a mask blank according to one aspect of the invention, in the mask-layer formation step, the uppermost surface of the mask layer may be formed by using a gas containing nitrogen monoxide (NO) serving as a nitrogen-containing gas as a supply gas for the sputtering.

In the method of manufacturing a mask blank according to one aspect of the invention, in the mask-layer formation step, the uppermost surface of the mask layer may be formed by using a gas containing methane (CH_4) serving as a carbon-containing gas as a supply gas for the sputtering.

A method of manufacturing a mask blank according to one aspect of the invention manufactures the mask blank according to the above-mentioned aspect. The manufacturing method includes a surface-layer formation step of forming the surface layer. In the surface-layer formation step, a target containing chromium is used, a gas containing argon (Ar) and oxygen is used as a supply gas for the sputtering, and the surface layer having an oxygen concentration gradient such that an oxygen content rate varies is formed by changing a supply amount of argon.

In the method of manufacturing a mask blank according to one aspect of the invention, in the surface-layer formation step, the surface layer may be formed by using a gas containing argon, methane, nitrogen monoxide, and carbon dioxide as a supply gas for the sputtering.

A method of manufacturing a mask blank according to one aspect of the invention manufactures the mask blank according to the above-mentioned aspect. The manufacturing method includes an upper-medium-layer formation step of forming the upper-medium layer. In the upper-medium-layer formation step, a target containing chromium is used, and the upper-medium layer is formed by using a gas containing argon, methane, and nitrogen monoxide as a supply gas for the sputtering.

A method of manufacturing a mask blank according to one aspect of the invention manufactures the mask blank according to the above-mentioned aspect. The manufacturing method includes an intermediate-layer formation step of forming the intermediate layer. In the intermediate-layer formation step, a target containing chromium is used, and the intermediate layer is formed by using a gas containing argon and nitrogen as a supply gas for the sputtering.

A method of manufacturing a mask blank according to one aspect of the invention manufactures the mask blank according to the above-mentioned aspect. The manufacturing method includes: a surface-layer formation step of forming the surface layer; an upper-medium-layer formation step of forming the upper-medium layer; an intermediate-layer formation step of forming the intermediate layer; and a light-shielding-layer formation step of forming the light-shielding layer. In the light-shielding-layer formation step, a target containing chromium is used, and the light-shielding layer is formed by using a gas containing argon, nitrogen, and carbon dioxide as a supply gas for the sputtering.

In the method of manufacturing a mask blank according to one aspect of the invention, the sputtering-supply power of the intermediate-layer formation step may be set to be higher than the sputtering-supply power of each of the light-shielding-layer formation step, the upper-medium-layer formation step, and the surface-layer formation step.

[0009]

A mask blank according to one aspect of the invention includes: a transparent substrate having a surface; and a mask layer stacked on the surface of the transparent substrate. The mask layer contains nitrogen (N), carbon (C), oxygen (O), and chromium (Cr). The mask layer has an uppermost surface on the opposite side of the

surface of the transparent substrate. An oxygen content rate of the uppermost surface of the mask layer is in a range of 65 to 72atm%.

Consequently, the chemical resistance of the uppermost surface of the mask layer is improved, and the optical characteristics such as optical density, reflectance, or the like, the wavelength-dependence with respect to the optical characteristics, and the film characteristics such as a resistance value, a film thickness, or the like can be prevented from being changed more than necessary before or after treatment using a chemical solution such as acid, alkali, ozone, or the like.

Additionally, since the oxygen content rate is in the aforementioned range on the uppermost surface of the mask layer, the uppermost surface of the mask layer functions as a chemical resistance layer when manufacturing a photomask from the mask blank. Therefore, it is possible to maintain the chemical resistance in a mask cleaning step by the chemical resistance layer. Accordingly, variation of the optical characteristics of the mask layer is suppressed in the cleaning step, and variation of the optical characteristics of the photomask manufactured from the mask blank can be suppressed.

At the same time, an optical-characteristic layer is formed so as to have an oxygen content rate lower than each of a chromium content rate and a nitrogen content rate. Because of this, due to the optical-characteristic layer, the mask layer can maintain the optical characteristics required for the photomask manufactured from the mask blank.

[0010]

In the mask blank according to one aspect of the invention, the mask layer may include a surface layer having an upper surface and a lower surface on the opposite side of the upper surface. The upper surface of the surface layer corresponds to the uppermost surface. An oxygen content rate of the upper surface of the surface layer may be in a range of 65 to 72atm%. An oxygen content rate of the lower surface of the

surface layer may be in a range of 35 to 45atm%. The surface layer may have an oxygen concentration gradient such that an oxygen content rate gradually decreases in a direction from the upper surface to the lower surface.

Consequently, it is possible to obtain the mask blank including the mask layer capable of simultaneously maintaining the chemical resistance with respect to the cleaning step or the like and suppressing the variation of the optical characteristics.

[0011]

In the mask blank according to one aspect of the invention, in a case in which an oxygen content rate is represented as O (atm%) and a nitrogen content rate is represented as N (atm%), an oxygen-nitrogen compositional ratio is represented as O/(O+N), and the oxygen-nitrogen compositional ratio of the surface layer may be in a range of 0.9 to 0.98.

Accordingly, it is possible to increase a degree of adhesion between the surface layer and the resist layer. At the same time, the adhesion of the surface layer with respect to the upper-medium layer is improved, and it is possible to reduce occurrence of a pattern defect. The chemical resistance of the surface layer is improved, and the etching rate of the mask layer increases. Therefore, it is possible to provide the mask blank including the mask layer having a required optical density.

In a step of using an alkaline fluid such as persulfuric acid water, NaOH, or the like, or ozone water, it is possible to maintain a state in which the variation of the optical characteristics is suppressed by the chemical resistance layer.

[0012]

In the mask blank according to one aspect of the invention, the mask layer includes an upper-medium layer located closer to the transparent substrate than the surface layer, the upper-medium layer contains oxygen, and an oxygen content rate of the upper-medium layer may be lower than an oxygen content rate of the surface layer.

Consequently, in the mask layer, the chemical resistance can be maintained, and it is possible to maintain characteristics in which the adhesion with respect to the resist layer and the adhesion with respect to the underlying layer are excellent. Particularly, it contributes to a high-definition pattern such that an aspect ratio, that is, a ratio of a film thickness and a pattern width is small, for example, approximately 0.6. Furthermore, an occurrence of a pattern defect, collapse of a resist, partial peeling of a resist, or the like can be sufficiently reduced.

[0013]

In the mask blank according to one aspect of the invention, the mask layer includes an intermediate layer located closer to the transparent substrate than the upper-medium layer, the intermediate layer contains oxygen, the intermediate layer has a surface, and an oxygen content rate of the upper-medium layer may be lower than an oxygen content rate of the surface of the intermediate layer.

Consequently, in the mask layer, the chemical resistance can be maintained, and it is possible to maintain characteristics in which the adhesion of the upper-medium layer with respect to the intermediate layer is excellent. Particularly, it contributes to a high-definition pattern such that an aspect ratio, that is, a ratio of a film thickness and a pattern width is small, for example, approximately 0.6. Furthermore, an occurrence of a pattern defect or the like can be sufficiently reduced.

[0014]

In the mask blank according to one aspect of the invention, the mask layer includes: a light-shielding layer containing chromium; an intermediate layer stacked on the light-shielding layer, the intermediate layer containing chromium; an upper-medium layer stacked on the intermediate layer, the upper-medium layer containing chromium; and a surface layer stacked on the upper-medium layer, the surface layer containing

chromium. The surface layer contains oxygen, nitrogen, and carbon. A chromium content rate of the surface layer may be in a range of 21 to 25atm%. An oxygen content rate of the surface layer may be in a range of 65 to 72atm%. A nitrogen content rate of the surface layer may be in a range of 1 to 5atm%. A carbon content rate of the surface layer may be in a range of 4 to 6atm%.

Consequently, the chemical resistance of the mask layer is improved, and the optical characteristics such as optical density, reflectance, or the like, the wavelength-dependence with respect to the optical characteristics, and the film characteristics such as a resistance value, a film thickness, or the like can be prevented from being changed more than necessary before or after treatment using a chemical solution such as acid, alkali, ozone, or the like. The mask layer functions as a chemical resistance layer when manufacturing a photomask from the mask blank. Therefore, it is possible to maintain the chemical resistance in a mask cleaning step by the chemical resistance layer. Accordingly, variation of the optical characteristics of the mask layer is suppressed in a step using a chemical solution, and variation of the optical characteristics of the photomask manufactured from the mask blank can be suppressed. Therefore, it is possible to obtain the mask blank including the mask layer capable of simultaneously maintaining the chemical resistance and suppressing the variation of the optical characteristics. Moreover, it is possible to maintain characteristics in which the chemical resistance, the adhesion with respect to the resist layer, and the adhesion with respect to the underlying layer are excellent. Particularly, it contributes to a high-definition pattern such that an aspect ratio, that is, a ratio of a film thickness and a pattern width is small, for example, approximately 0.6. Furthermore, an occurrence of a pattern defect, collapse of a resist, partial peeling of a resist, or the like can be sufficiently reduced.

[0015]

In the mask blank according to one aspect of the invention, in a dry etching treatment using a mixed gas of chlorine and oxygen, in a case in which an etching rate of the light-shielding layer is defined as ER1, an etching rate of the intermediate layer is defined as ER2, an etching rate of the upper-medium layer is defined as ER3, and an etching rate of the surface layer is defined as ER4, ER3<ER2<ER4<ER1 may be satisfied.

Consequently, a length of time required for etching treatment is reduced, a degree of workability increases, a film thickness of a required resist layer is reduced, and a reduction in thickness of the resist can be achieved. At the same time, since a length of etching time is shortened, a length of contact time of the mask layer and treatment liquid such as etching solution or the like is reduced, and it is possible to suppress variation of the optical characteristics.

[0016]

In the mask blank according to one aspect of the invention, each of the intermediate layer and the upper-medium layer includes oxygen, and in a case in which a value of an oxygen content rate of the upper-medium layer is defined as VO1, a value of an oxygen content rate of the intermediate layer is defined as VO2, and a value of an oxygen content rate of the surface layer is defined as VO3, VO2<VO1<VO3 may be satisfied.

Consequently, the adhesion between the intermediate layer and the upper-medium layer is improved, and it is possible to reduce an occurrence of a pattern defect.

[0017]

In the mask blank according to one aspect of the invention, each of the intermediate layer and the upper-medium layer includes nitrogen, and in a case in which

a value of a nitrogen content rate of the upper-medium layer is defined as VN1, a value of a nitrogen content rate of the intermediate layer is defined as VN2, and a value of a nitrogen content rate of the surface layer is defined as VN3, VN2<VN1<VN3 may be satisfied.

Accordingly, the chemical resistance of the surface layer is improved, the adhesion between the resist layer and the surface layer formed at an upper side of the upper-medium layer is improved, the adhesion between the intermediate layer and the upper-medium layer is improved, and furthermore the adhesion between the upper-medium layer and the surface layer is improved. Therefore, it is possible to reduce an occurrence of a pattern defect.

[0018]

In the mask blank according to one aspect of the invention, each of the intermediate layer and the upper-medium layer includes carbon, and in a case in which a value of a carbon content rate of the upper-medium layer is defined as VC1, a value of a carbon content rate of the intermediate layer is defined as VC2, and a value of a carbon content rate of the surface layer is defined as VC3, VC2<VC1<VC3 may be satisfied.

Accordingly, the chemical resistance of the surface layer is improved, the adhesion between the resist layer and the surface layer formed at an upper side of the upper-medium layer is improved, the adhesion between the intermediate layer and the upper-medium layer is improved, and furthermore the adhesion between the upper-medium layer and the surface layer is improved. Therefore, it is possible to reduce an occurrence of a pattern defect.

[0019]

In the mask blank according to one aspect of the invention, the upper-medium layer contains oxygen, nitrogen, and carbon, a chromium content rate of the upper-

medium layer may be in a range of 45 to 52atm%, an oxygen content rate of the upper-medium layer may be in a range of 15 to 25atm%, a nitrogen content rate of the upper-medium layer may be in a range of 15 to 25atm%, and a carbon content rate of the upper-medium layer may be in a range of 5 to 15atm%.

Accordingly, the chemical resistance of the surface layer is improved, the adhesion between the resist layer and the surface layer formed at an upper side of the upper-medium layer is improved, the adhesion between the intermediate layer and the upper-medium layer is improved, and furthermore the adhesion between the upper-medium layer and the surface layer is improved. Therefore, it is possible to reduce an occurrence of a pattern defect.

[0020]

In the mask blank according to one aspect of the invention, the intermediate layer contains oxygen, nitrogen, and carbon, a chromium content rate of the intermediate layer may be in a range of 45 to 52atm%, an oxygen content rate of the intermediate layer may be in a range of 10 to 20atm%, a nitrogen content rate of the intermediate layer may be in a range of 15 to 25atm%, and a carbon content rate of the intermediate layer may be in a range of 10 to 20atm%.

Consequently, the chemical resistance of the surface layer is improved, the adhesion between the surface layer and the resist layer is improved, the adhesion between the intermediate layer and the upper-medium layer is improved, and furthermore the adhesion between the upper-medium layer and the surface layer is improved. Therefore, it is possible to reduce an occurrence of a pattern defect.

[0021]

In the mask blank according to one aspect of the invention, the light-shielding layer contains oxygen, nitrogen, and carbon, a chromium content rate of the light-

shielding layer may be in a range of 30 to 40atm%, an oxygen content rate of the light-shielding layer may be in a range of 25 to 35atm%, a nitrogen content rate of the light-shielding layer may be in a range of 14 to 24atm%, and a carbon content rate of the light-shielding layer may be in a range of 11 to 21atm%.

Consequently, the chemical resistance of the surface layer is improved, the adhesion between the surface layer and the resist layer is improved, the adhesion between the intermediate layer and the upper-medium layer is improved, and furthermore the adhesion between the upper-medium layer and the surface layer is improved. An occurrence of a pattern defect is reduced, and it is possible to provide the mask blank including the mask layer having a necessary light-shielding property, that is, a required optical density.

[0022]

In the mask blank according to one aspect of the invention, a thickness ratio of the light-shielding layer, the intermediate layer, the upper-medium layer, and the surface layer may be in a range of 29:1:3:11 to 33:2:6:13.

Accordingly, it is possible to provide the mask blank including the light-shielding layer, the intermediate layer, the upper-medium layer, and the surface layer which constitute the mask layer having a required optical density.

[0023]

A method of manufacturing a mask blank according to one aspect of the invention manufactures the mask blank according to the above-mentioned aspect. The manufacturing method includes a mask-layer formation step of forming the mask layer containing chromium on the transparent substrate by sputtering. In the mask-layer formation step, a target containing chromium is used, and the uppermost surface of the mask layer is formed by using a gas containing carbon dioxide serving as an oxygen-

containing gas as a supply gas for the sputtering.

Consequently, when forming a high-definition pattern such that an aspect ratio thereof is small and a pattern width thereof is narrow, the chemical resistance of the surface layer is improved, the etching rate of the mask layer increases, and the adhesion between the surface layer and the resist layer is improved. Therefore, it is possible to manufacture the mask blank including the mask layer having a required optical density.

[0024]

In the method of manufacturing a mask blank according to one aspect of the invention, in the mask-layer formation step, the uppermost surface of the mask layer may be formed by using a gas containing nitrogen monoxide serving as a nitrogen-containing gas as a supply gas for the sputtering.

Consequently, the surface layer on which an occurrence of a pattern defect is reduced can be formed. At the same time, the chemical resistance of the surface layer is improved, the etching rate of the mask layer is improved, the adhesion between the surface layer and the resist layer is improved, and the adhesion of the surface layer with respect to the upper-medium layer is improved. Therefore, it is possible to manufacture the mask blank including the mask layer having a required optical density.

[0025]

In the method of manufacturing a mask blank according to one aspect of the invention, in the mask-layer formation step, the uppermost surface of the mask layer may be formed by using a gas containing methane serving as a carbon-containing gas as a supply gas for the sputtering.

Consequently, the surface layer on which an occurrence of a pattern defect is reduced can be formed. At the same time, the chemical resistance of the surface layer is improved, the etching rate of the mask layer increases, the adhesion between the surface

layer and the resist layer is improved, and the adhesion of the surface layer with respect to the upper-medium layer is improved. Therefore, it is possible to manufacture the mask blank including the mask layer having a required optical density.

[0026]

A method of manufacturing a mask blank according to one aspect of the invention manufactures the mask blank according to the above-mentioned aspect. The manufacturing method includes a surface-layer formation step of forming the surface layer. In the surface-layer formation step, a target containing chromium is used, a gas containing argon and oxygen is used as a supply gas for the sputtering, and the surface layer having an oxygen concentration gradient such that an oxygen content rate varies is formed by changing a supply amount of argon.

Accordingly, a surface layer that ensures optical characteristics that vary with respect to the upper-medium layer is formed, and the surface layer on which an occurrence of a pattern defect is reduced can be formed. At the same time, the chemical resistance of the surface layer is improved, the etching rate of the mask layer is improved, the adhesion between the surface layer and the resist layer is improved, and the adhesion of the surface layer with respect to the upper-medium layer is improved. Therefore, it is possible to manufacture the mask blank including the mask layer having a required optical density.

In a step of using an alkaline fluid such as persulfuric acid water, NaOH, or the like, or ozone water, it is possible to maintain a state in which the variation of the optical characteristics is suppressed by the chemical resistance layer.

[0027]

In the method of manufacturing a mask blank according to one aspect of the invention, in the surface-layer formation step, the surface layer may be formed by using a

gas containing argon, methane, nitrogen monoxide, and carbon dioxide as a supply gas for the sputtering.

Consequently, the surface layer on which an occurrence of a pattern defect is reduced can be formed. At the same time, the chemical resistance of the surface layer is improved, the etching rate of the mask layer is improved, the adhesion between the surface layer and the resist layer is improved, and the adhesion of the surface layer with respect to the upper-medium layer is improved. Therefore, it is possible to manufacture the mask blank including the mask layer having a required optical density.

In a step of using an alkaline fluid such as persulfuric acid water, NaOH, or the like, or ozone water, it is possible to maintain a state in which the variation of the optical characteristics is suppressed by the chemical resistance layer.

[0028]

A method of manufacturing a mask blank according to one aspect of the invention manufactures the mask blank according to the above-mentioned aspect. The manufacturing method includes an upper-medium-layer formation step of forming the upper-medium layer. In the upper-medium-layer formation step, a target containing chromium is used, and the upper-medium layer is formed by using a gas containing argon, methane, and nitrogen monoxide as a supply gas for the sputtering.

Consequently, the adhesion of the surface layer with respect to the upper-medium layer is improved, and defects of the surface layer are reduced. Even in a case in which an external force such that a scrub processing or the like is carried out after pattern formation is applied to the mask layer, it is possible to manufacture the mask layer such that an occurrence of a pattern defect does not increase. Furthermore, even in a narrow-width pattern serving as a high-definition pattern, it is possible to prevent an occurrence of a pattern defect from increasing. At the same time, the chemical

resistance of the surface layer is improved, and the etching rate of the mask layer increases. Therefore, it is possible to manufacture the mask blank including the mask layer having a required optical density.

[0029]

A method of manufacturing a mask blank according to one aspect of the invention manufactures the mask blank according to the above-mentioned aspect. The manufacturing method includes an intermediate-layer formation step of forming the intermediate layer. In the intermediate-layer formation step, a target containing chromium is used, and the intermediate layer is formed by using a gas containing argon and nitrogen as a supply gas for the sputtering.

Consequently, the adhesion of the intermediate layer with respect to the upper-medium layer is improved, and a pattern defect is reduced. Even in a case in which an external force such that a scrub processing or the like is carried out after pattern formation is applied to the mask layer, it is possible to manufacture the mask layer such that an occurrence of a pattern defect does not increase. Furthermore, even in a narrow-width pattern serving as a high-definition pattern, it is possible to prevent an occurrence of a pattern defect from increasing. At the same time, the etching rate of the mask layer increases. Therefore, it is possible to manufacture the mask blank including the mask layer having a required optical density.

[0030]

A method of manufacturing a mask blank according to one aspect of the invention manufactures the mask blank according to the above-mentioned aspect. The manufacturing method includes: a surface-layer formation step of forming the surface layer; an upper-medium-layer formation step of forming the upper-medium layer; an intermediate-layer formation step of forming the intermediate layer; and a light-

shielding-layer formation step of forming the light-shielding layer. In the light-shielding-layer formation step, a target containing chromium is used, and the light-shielding layer is formed by using a gas containing argon, nitrogen, and carbon dioxide as a supply gas for the sputtering.

Consequently, it is possible to manufacture the mask layer capable of reducing an occurrence of a pattern defect. Furthermore, even in a narrow-width pattern serving as a high-definition pattern, it is possible to prevent an occurrence of a pattern defect from increasing. At the same time, the chemical resistance of the surface layer is improved, and the etching rate of the mask layer increases. Therefore, it is possible to manufacture the mask blank including the mask layer having a required optical density.

[0031]

In the method of manufacturing a mask blank according to one aspect of the invention, the sputtering-supply power of the intermediate-layer formation step may be set to be higher than the sputtering-supply power of each of the light-shielding-layer formation step, the upper-medium-layer formation step, and the surface-layer formation step.

Consequently, the adhesion of the intermediate layer with respect to the upper-medium layer is improved, and a pattern defect is reduced. Even in a case in which an external force such that a scrub processing or the like is carried out after pattern formation is applied to the mask layer, it is possible to manufacture the mask layer such that an occurrence of a pattern defect does not increase. Furthermore, even in a narrow-width pattern serving as a high-definition pattern, it is possible to prevent an occurrence of a pattern defect from increasing. At the same time, the etching rate of the mask layer increases. Therefore, it is possible to manufacture the mask blank including the mask layer having a required optical density.

Effects of the Invention

[0032]

According to one aspect of the invention, an effect is achieved such that the mask blank can provide a sufficient chemical resistance to the mask layer containing chromium, the etching rate of the mask layer can be increased, and the adhesion between the mask layer and the resist layer can be improved, and the adhesion between the mask layer and the underlying layer can be improved.

BRIEF DESCRIPTION OF THE DRAWINGS

[0033]

FIG. 1A is a cross-sectional view showing a mask blank according to a first embodiment of the invention.

FIG. 1B is a cross-sectional view showing the mask blank according to the first embodiment of the invention and is a view showing a portion represented by reference letter P of FIG. 1A.

FIG. 2 is a cross-sectional view showing the mask blank according to the first embodiment of the invention.

FIG. 3 is a schematic view showing a film formation apparatus that carries out a method of manufacturing a mask blank according to the first embodiment of the invention.

FIG. 4 is a schematic view showing a film formation chamber of the film formation apparatus that carries out the method of manufacturing the mask blank according to the first embodiment of the invention.

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

FIG. 6 is a cross-sectional view explaining one step of the method of manufacturing the phase-shift mask according to the first embodiment of the invention.

FIG. 7 is a cross-sectional view explaining one step of the method of manufacturing the phase-shift mask according to the first embodiment of the invention.

FIG. 8 is a cross-sectional view explaining one step of the method of manufacturing the phase-shift mask according to the first embodiment of the invention.

FIG. 9 is a cross-sectional view explaining one step of the method of manufacturing the phase-shift mask according to the first embodiment of the invention.

FIG. 10 is a view showing Experimental Example according to the invention.

FIG. 11 is a view showing Experimental Example according to the invention.

FIG. 12 is a view showing Experimental Example according to the invention.

FIG. 13 is a view showing Experimental Example according to the invention.

FIG. 14 is a view showing Experimental Example according to the invention.

FIG. 15 is a view showing Experimental Example according to the invention.

FIG. 16 is a view showing Experimental Example according to the invention.

FIG. 17 is a view showing Experimental Example according to the invention.

FIG. 18 is a view showing Experimental Example according to the invention.

FIG. 19 is a view showing Experimental Example according to the invention.

FIG. 20 is a view showing Experimental Example according to the invention.

FIG. 21 is a view showing Experimental Example according to the invention.

FIG. 22 is a view showing Experimental Example according to the invention.

FIG. 23 is a view showing Experimental Example according to the invention.

FIG. 24 is a view showing Experimental Example according to the invention.

FIG. 25 is a view showing Experimental Example according to the invention.

FIG. 26 is a view showing Experimental Example according to the invention.

FIG. 27 is a view showing Experimental Example according to the invention.

FIG. 28 is a view showing Experimental Example according to the invention.

FIG. 29 is a view showing Experimental Example according to the invention.

FIG. 30 is a view showing Experimental Example according to the invention.

FIG. 31 is a view showing Experimental Example according to the invention.

FIG. 32 is a view showing Experimental Example according to the invention.

FIG. 33 is a view showing Experimental Example according to the invention.

FIG. 34 is a view showing Experimental Example according to the invention.

EMBODIMENTS FOR CARRYING OUT THE INVENTION

[0034]

Hereinafter, a mask blank and a method of manufacturing a mask blank according to the first embodiment of the invention will be described with reference to the drawings.

FIGS. 1A and 1B are cross-sectional view showing a mask blank according to an embodiment. FIG. 2 is a cross-sectional view showing the mask blank according to the embodiment. FIG. 1B is a view showing a portion represented by reference letter P of FIG. 1A. In FIG. 1A, reference numeral 10B is a mask blank.

[0035]

As the mask blank 10B according to the embodiment, for example, a mask blank used for manufacturing a phase-shift mask (photomask) is shown. The embodiment is not limited to the phase-shift mask. As long as a photomask including the mask layer containing chromium M can be formed, the embodiment is applicable to a halftone mask, a binary mask, or the like as well as the phase-shift mask.

[0036]

The mask blank 10B according to the embodiment is used for a phase-shift mask (photomask) used in a wavelength of exposure light in a range including an ultraviolet region (150 nm to 380 nm), for example, in a wavelength range of approximately 190 nm to 250 nm, particularly in a wavelength range of approximately 193 nm.

As shown in FIG. 1A, the mask blank 10B according to the embodiment is configured of a glass substrate 11 (transparent substrate), a phase-shift layer 12 (underlying layer) formed on the glass substrate 11, and a chromium-containing layer 13 formed on the phase-shift layer 12.

[0037]

That is, the chromium-containing layer 13 is provided at a position farther from the glass substrate 11 than the phase-shift layer 12. In other words, the phase-shift layer 12 is located between the chromium-containing layer 13 and the glass substrate 11.

The phase-shift layer 12 and the chromium-containing layer 13 mentioned above constitute the mask layer M serving as a multi-layered film having the optical characteristics necessary for a photomask. The chromium-containing layer 13 is exposed to the uppermost surface 13A of the mask layer M.

[0038]

Moreover, as shown in FIGS. 1A and 1B, the mask blank 10B according to the embodiment may have a configuration such that a photoresist layer 14 (resist layer) is previously formed on the mask layer M including the phase-shift layer 12 and the chromium-containing layer 13 stacked thereon as shown in FIG. 2.

[0039]

Note that, as well as the phase-shift layer 12 and the chromium-containing layer 13, the mask blank 10B according to the embodiment may have a configuration such that an etching stopping layer, an antireflection layer, a chemical resistance layer, a

passivation layer, an adhesion layer, or the like are stacked in layers. Furthermore, the resist layer 14 may be formed on the aforementioned multi-layered film as shown in FIG. 2.

[0040]

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 may 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 such as an LCD (liquid crystal display), a plasma display, an organic EL (electro luminescence) display, or the like, or a substrate such as a semiconductor).

[0041]

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 2000 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.

[0042]

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, 1 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.

[0043]

As the phase-shift layer 12, a metal such as a metal silicide film, for example, Ta

(tantalum), Ti (titanium), W (tungsten), Mo (molybdenum), Zr (zirconium), or the like, and a film including an alloy of the aforementioned metals and silicon may be used. Particularly, as the metal silicide, it is preferable to use molybdenum silicide. For example, a MoSiX (X≥2) film (for example, a $MoSi_2$ film, a $MoSi_6$ film, a $MoSi_8$ film, or the like) is adopted.

[0044]

As the phase-shift layer 12, it is preferable to use a molybdenum silicide film containing O (oxygen) and N (nitrogen).

In the phase-shift layer 12, an oxygen content rate (oxygen concentration) may be in a range of 1.0atm% to 50atm%.

Moreover, in the phase-shift layer 12, a nitrogen content rate (nitrogen concentration) may be in a range of 10atm% to 50atm%.

[0045]

Consequently, in a case in which the phase-shift layer 12 has a condition such that, with respect to a wavelength of approximately 193 nm, a transmissivity is in a range of 2. 0 to 8.0%, a refractive index is in a range of approximately 2.2 to 2.6, a reflectance is in a range of approximately 15 to 25%, an extinction coefficient is in a range of approximately 0.4 to 0.8, and a film thickness of the phase-shift layer 12 may be set in a range of approximately 60 to 80 nm.

Note that, a compositional ratio of chemical elements forming the phase-shift layer 12 and a film thickness of the phase-shift layer 12 are set depending on the optical characteristics required for a phase-shift mask 10 to be manufactured. The characteristics of the phase-shift layer 12 are not limited to each of the numerical values mentioned above.

[0046]

Note that, in the description, the underlying layer is, for example, the phase-shift layer 12. In a case of using a photomask different from the phase-shift mask 10, a layer different from the aforementioned layer can be formed.

[0047]

The chromium-containing layer 13 functions as a light-shielding layer. The chromium-containing layer 13 contains Cr (chromium) as a main component. Furthermore, the chromium-containing layer 13 contains C (carbon), O (oxygen), and N (nitrogen).

Moreover, the chromium-containing layer 13 may include a part configured such that compositions vary in a thickness direction. In this case, the chromium-containing layer 13 may be configured to contain a simple body of Cr. The chromium-containing layer 13 may have a multi-layered configuration in which each of the layers thereof contains one or more selected from an oxide, a nitride, a carbide, an oxynitride, a carbonitride, and an oxidized carbonitride of Cr.

[0048]

In the chromium-containing layer 13, as described below, a thickness of the chromium-containing layer 13, a content rate (atm%) of Cr, N, C, O, or the like, and a compositional ratio are set so as to obtain the film characteristics such as the predetermined optical characteristics or the like. Additionally, the aforementioned content rate (atm%) of Cr, N, C, O, or the like may vary in the film-thickness direction of the chromium-containing layer 13. Moreover, the chromium-containing layer 13 may be configured of a multi-layered film having the film characteristics such as the optical characteristics different from each other.

[0049]

As shown in FIG. 1B, the chromium-containing layer 13 is configured of a

plurality of layers. The chromium-containing layer 13 includes: a light-shielding layer 13a (first layer) located at the lowermost layer of the plurality of the layers; an intermediate layer 13b (second layer) stacked on the light-shielding layer 13a; an upper-medium layer 13c (third layer) stacked on the intermediate layer 13b; and a surface layer 13d (fourth layer) stacked on the upper-medium layer 13c. In other words, of the plurality of the layers constituting the chromium-containing layer 13, the light-shielding layer 13a is a layer located at the lower side of the intermediate layer 13b, the intermediate layer 13b is a layer located at the lower side of the upper-medium layer 13c, and the upper-medium layer 13c is a layer located at the lower side of the surface layer 13d.

[0050]

As shown in FIG. 1B, the light-shielding layer 13a is stacked on the phase-shift layer 12 serving as an underlying layer. Note that, another layer may be formed between the light-shielding layer 13a and the phase-shift layer 12.

The light-shielding layer 13a contains Cr (chromium) as a main component. Furthermore, the light-shielding layer 13a contains C (carbon), O (oxygen), and N (nitrogen).

In the light-shielding layer 13a, a thickness of the light-shielding layer 13a, the content rates (atm%) of Cr, N, C, O, or the like, or a compositional ratio are set so as to obtain the predetermined optical characteristics, adhesion, and etching rate. In the light-shielding layer 13a, the compositional ratio, the content rates, and the film thickness of the above-described materials can be set so that, for example, the optical density (OD) is in a range of approximately 1.0 to 1.4.

[0051]

Regarding the content rates of the chemical elements forming the light-shielding

layer 13a, the content rates of the light-shielding layer 13a can be set such that the chromium content rate (chromium concentration) is in a range of 30atm% to 40atm%, the oxygen content rate (oxygen concentration) is in a range of 25atm% to 35atm%, the nitrogen content rate (nitrogen concentration) is in a range of 14atm% to 24atm%, and the carbon content rate (carbon concentration) is in a range of 11atm% to 21atm%.

Particularly, in the light-shielding layer 13a, the chromium content rate is preferably 35atm%, the oxygen content rate is preferably 30atm%, the nitrogen content rate is preferably 19atm%, and the carbon content rate is preferably 19atm%.

The compositional ratio of the chemical elements forming the light-shielding layer 13a may vary such that the compositions thereof are different from each other in the thickness direction. For example, the compositional ratio can be set such that the etching rate of the light-shielding layer 13a varies in the thickness direction. Alternatively, regarding the compositional ratio of the light-shielding layer 13a, the light-shielding layer 13a may have a peak region in which the carbon concentration reaches the peak at a position adjacent to the intermediate layer 13b in the film-thickness direction.

[0052]

As shown in FIG. 1B, the intermediate layer 13b is stacked on the light-shielding layer 13a.

The intermediate layer 13b contains Cr (chromium) as a main component. Furthermore, the intermediate layer 13b contains C (carbon), O (oxygen), and N (nitrogen).

In the intermediate layer 13b, a thickness of the intermediate layer 13b, the content rates (atm%) of Cr, N, C, O, or the like, or a compositional ratio are set so as to obtain the predetermined optical characteristics, adhesion, and etching rate. In the

intermediate layer 13b, the compositional ratio, the content rates, and the film thickness of the above-described materials can be set so that, for example, the optical density (OD) is in a range of approximately 0.1 to 0.5.

[0053]

Regarding the content rates of the chemical elements forming the intermediate layer 13b, the content rates of the intermediate layer 13b can be set such that the chromium content rate (chromium concentration) is in a range of 45atm% to 52atm%, the oxygen content rate (oxygen concentration) is in a range of 10atm% to 20atm%, the nitrogen content rate (nitrogen concentration) is in a range of 15atm% to 25atm%, and the carbon content rate (carbon concentration) is in a range of 10atm% to 20atm%.

Particularly, in the intermediate layer 13b, the chromium content rate is preferably 50atm%, the oxygen content rate is preferably 15atm%, the nitrogen content rate is preferably 20atm%, and the carbon content rate is preferably 15atm%.

The compositional ratio of the chemical elements forming the intermediate layer 13b may vary such that the compositions thereof are different from each other in the thickness direction. For example, the compositional ratio can be set such that the etching rate of the intermediate layer 13b varies in the thickness direction. Alternatively, regarding the compositional ratio of the intermediate layer 13b, the intermediate layer 13b may have a peak region in which the nitrogen concentration reaches the peak at a position adjacent to the upper-medium layer 13c in the film-thickness direction.

[0054]

As shown in FIG. 1B, the upper-medium layer 13c is stacked on the intermediate layer 13b.

The upper-medium layer 13c contains Cr (chromium) as a main component.

Furthermore, the upper-medium layer 13c contains C (carbon), O (oxygen), and N (nitrogen).

In the upper-medium layer 13c, a thickness of the upper-medium layer 13c, the content rates (atm%) of Cr, N, C, O, or the like, or a compositional ratio are set so as to obtain the predetermined optical characteristics, adhesion, and etching rate. In the upper-medium layer 13c, the compositional ratio, the content rates, and the film thickness of the above-described materials can be set so that, for example, the optical density (OD) is in a range of approximately 0.05 to 0.15.

[0055]

Regarding the content rates of the chemical elements forming the upper-medium layer 13c, the content rates of the upper-medium layer 13c can be set such that the chromium content rate (chromium concentration) is in a range of 45atm% to 52atm%, the oxygen content rate (oxygen concentration) is in a range of 15atm% to 25atm%, the nitrogen content rate (nitrogen concentration) is in a range of 15atm% to 25atm%, and the carbon content rate (carbon concentration) is in a range of 5atm% to 15atm%.

Particularly, in the upper-medium layer 13c, the chromium content rate is preferably 50atm%, the oxygen content rate is preferably 20atm%, the nitrogen content rate is preferably 20atm%, and the carbon content rate is preferably 10atm%.

The compositional ratio of the chemical elements forming the upper-medium layer 13c may vary such that the compositions thereof are different from each other in the thickness direction. For example, the compositional ratio can be set such that the etching rate of the upper-medium layer 13c varies in the thickness direction. Alternatively, regarding the compositional ratio of the upper-medium layer 13c, the upper-medium layer 13c may have a peak region in which the carbon concentration reaches the peak at a position adjacent to the surface layer 13d in the film-thickness

direction.

[0056]

As shown in FIG. 1B, the surface layer 13d is stacked on the upper-medium layer 13c. The surface layer 13d has an upper surface 13T and a lower surface 13B on the opposite side of the upper surface 13T. The upper surface 13T of the surface layer 13d corresponds to the uppermost surface 13A of the mask layer M.

The surface layer 13d contains Cr (chromium) as a main component. Furthermore, the surface layer 13d contains C (carbon), O (oxygen), and N (nitrogen).

In the surface layer 13d, a thickness of the surface layer 13d, the content rates (atm%) of Cr, N, C, O, or the like, or a compositional ratio are set so as to obtain the predetermined optical characteristics, chemical resistance, an adhesion, and an etching rate. In the surface layer 13d, the compositional ratio, the content rates, and the film thickness of the above-described materials can be set so that, for example, the optical density (OD) is in a range of approximately 0.1 to 0.5.

[0057]

Regarding the content rates of the chemical elements forming the surface layer 13d, the content rates of the surface layer 13d can be set such that the chromium content rate (chromium concentration) is in a range of 21atm% to 25atm%, the oxygen content rate (oxygen concentration) is in a range of 65atm% to 72atm%, the nitrogen content rate (nitrogen concentration) is in a range of 1atm% to 5atm%, and the carbon content rate (carbon concentration) is in a range of 4atm% to 6atm%.

Particularly, in the surface layer 13d, the chromium content rate is preferably 23atm%, the oxygen content rate is preferably 70atm%, the nitrogen content rate is preferably 2atm%, and the carbon content rate is preferably 5atm%.

[0058]

Regarding the compositional ratio of the chemical elements forming the surface layer 13d, an oxygen content rate of the uppermost surface 13A is in a range of 65 to 72atm% in order to obtain a predetermined chemical resistance of the uppermost surface 13A. Particularly, the oxygen content rate is preferably 70atm%.

The compositional ratio of the chemical elements forming the surface layer 13d may vary such that the compositions thereof are different from each other in the thickness direction in order to obtain a predetermined chemical resistance, a predetermined etching rate, and a predetermined adhesion of the uppermost surface 13A. For example, the oxygen content rate of the upper surface 13T of the surface layer 13d is in a range of 65 to 72atm%. The oxygen content rate of the lower surface 13B of the surface layer 13d is in a range of 35 to 45atm%. In this case, the surface layer 13d has an oxygen concentration gradient such that the oxygen content rate thereof gradually decreases in a direction from the upper surface 13T to the lower surface 13B in a thickness direction of the glass substrate 11.

[0059]

In the chromium-containing layer 13, the oxygen content rate of the upper-medium layer 13c is lower than the oxygen content rate of the surface layer 13d. Additionally, in the chromium-containing layer 13, the oxygen content rate of the upper-medium layer 13c is lower than the oxygen content rate of the upper surface of the intermediate layer 13b.

[0060]

An etching rate in a case of using a mixed gas of chlorine and oxygen and carrying out dry etching treatment with respect to the chromium-containing layer 13 will be described. In a case in which the etching rate of the light-shielding layer 13a is defined as ER1, the etching rate of the intermediate layer 13b is defined as ER2, the

etching rate of the upper-medium layer 13c is defined as ER3, and the etching rate of the surface layer 13d is defined as ER4, ER3<ER2<ER4<ER1 is satisfied.

[0061]

In a case in which the value of the oxygen content rate of the upper-medium layer 13c is defined as VO1, the value of the oxygen content rate of the intermediate layer 13b is defined as VO2, and the value of the oxygen content rate of the surface layer 13d is defined as VO3 in the chromium-containing layer 13, VO2<VO1<VO3 is satisfied.

In a case in which the value of the nitrogen content rate of the upper-medium layer 13c is defined as VN1, the value of the nitrogen content rate of the intermediate layer 13b is defined as VN2, and the value of the nitrogen content rate of the surface layer 13d is defined as VN3 in the chromium-containing layer 13, VN2<VN1<VN3 is satisfied.

In a case in which the value of the carbon content rate of the upper-medium layer 13c is defined as VC1, the value of the carbon content rate of the intermediate layer 13b is defined as VC2, and the value of the carbon content rate of the surface layer 13d is defined as VC3 in the chromium-containing layer 13, VC2<VC1<VC3 is satisfied.

In the chromium-containing layer 13, the thickness ratio of the light-shielding layer 13a, the intermediate layer 13b, the upper-medium layer 13c, and the surface layer 13d is in a range of 29:1:3:11 to 33:2:6:1.

[0062]

Since the mask blank 10B according to the embodiment has the aforementioned configuration, the uppermost surface 13A of the chromium-containing layer 13, that is, the chemical resistance of the uppermost surface 13A of the surface layer 13d is improved. The optical characteristics such as optical density, reflectance, or the like,

the wavelength-dependence with respect to the optical characteristics, and the film characteristics such as a resistance value, a film thickness, or the like can be prevented from being changed more than necessary before or after treatment using a chemical solution such as acid, alkali, ozone, or the like.

Furthermore, the oxygen content rate is set in the aforementioned range on the uppermost surface 13A of the chromium-containing layer 13. Accordingly, the uppermost surface 13A of the chromium-containing layer 13 functions as a chemical resistance layer when manufacturing the phase-shift mask 10 from the mask blank 10B. Therefore, it is possible to maintain the chemical resistance in a mask cleaning step by the chemical resistance layer.

[0063]

Consequently, variation of the optical characteristics of the mask layer M is suppressed in the cleaning step, and variation of the optical characteristics of the phase-shift mask 10 manufactured from the mask blank 10B can be suppressed.

At the same time, the compositional ratio of nitrogen, carbon, oxygen, and chromium, that is, each of the content rates of nitrogen, carbon, oxygen, and chromium is set such that the mask layer M has the predetermined optical characteristics. Thus, the mask layer M is configured of the layers having the optical characteristics. Therefore, it is possible to maintain the mask layer M having the optical characteristics required for the phase-shift mask 10 manufactured from the mask blank 10B.

[0064]

According to the embodiment, the oxygen content rate of the surface layer 13d of the chromium-containing layer 13 has the concentration gradient as described above. Consequently, both sufficient chemical resistance with respect to treatment a chemical solution such as persulfuric acid water, NaOH water, concentrated sulfuric acid, ozone

water, or the like and suppressing the variation of the optical characteristics can be simultaneously maintained. Furthermore, since the chemical resistance is improved, the optical characteristics such as optical density, reflectance, or the like, the wavelength-dependence with respect to the optical characteristics, and the film characteristics such as a resistance value, a film thickness, or the like can be prevented from being changed more than necessary before or after treatment using a chemical solution such as acid, alkali, ozone, or the like.

[0065]

Concurrently, in the mask layer M, the chemical resistance can be maintained, and it is possible to maintain characteristics in which the adhesion with respect to the resist layer 14 and the phase-shift layer 12 is excellent. Particularly, it contributes to a high-definition pattern such that an aspect ratio, that is, a ratio of a film thickness and a pattern width is small, for example, approximately 0.6. Furthermore, an occurrence of a pattern defect, collapse of a resist, partial peeling of a resist, or the like can be sufficiently reduced.

Additionally, since the etching rate is set as described above, a length of time required for etching treatment is reduced, a degree of workability increases, a film thickness of a required resist layer 14 is reduced, and a reduction in thickness of the resist can be achieved.

[0066]

Therefore, the adhesion between the intermediate layer 13b and the upper-medium layer 13c is improved, the adhesion between the surface layer 13d and the resist layer 14 is improved, and furthermore the adhesion between the upper-medium layer 13c and the surface layer 13d is improved. An occurrence of a pattern defect is reduced, and it is possible to obtain the mask layer M having a necessary light-shielding property,

that is, a required optical density. Therefore, it is possible to provide the mask blank 10B having the chromium-containing layer 13 including the light-shielding layer 13a, the intermediate layer 13b, the upper-medium layer 13c, and the surface layer 13d.

[0067]

Hereinbelow, a method of manufacturing the mask blank according to the embodiment will be described.

[0068]

FIG. 3 is a schematic view showing the manufacturing apparatus that manufactures the mask blank according to the embodiment. FIG. 4 is a schematic view showing a film formation chamber of the manufacturing apparatus that manufactures the mask blank according to the embodiment.

The mask blank 10B according to the embodiment is manufactured by the manufacturing apparatus shown in FIGS. 3 and 4.

A method of manufacturing a mask blank according to the embodiment includes a mask-layer formation step. The mask-layer formation step includes an underlying-layer formation step and a chromium-containing-layer formation step.

In the underlying-layer formation step, the phase-shift layer 12 is formed on the glass substrate 11 by a manufacturing apparatus 100 shown in FIGS. 3 and 4. In the chromium-containing-layer formation step, the chromium-containing layer 13 is formed on the phase-shift layer 12 by the manufacturing apparatus 100 shown in FIGS. 3 and 4.

[0069]

The manufacturing apparatus 100 is a single wafer type sputtering apparatus. As shown in FIG. 3, the manufacturing apparatus 100 includes: a load chamber 101a to which the glass substrate 11 is to be loaded; an unload chamber 101b that transfers the glass substrate 11 to outside; film formation chambers 102 and 103 (vacuum processing

chamber) that forms a film on the glass substrate 11 by a sputtering method; and a transfer chamber 101c that is positioned among the film formation chambers 102 and 103, the load chamber 101a, and the unload chamber 101b.

[0070]

In the load chamber 101a, the glass substrate 11 transferred from the outside of the manufacturing apparatus 100 thereto is transferred to the film formation chamber 102. The load chamber 101a is provided with: a hermetical-sealing mechanism that causes the inside of the load chamber 101a to be hermetically-sealed or opened with respect to the outside thereof and allows the glass substrate 11 to transfer thereto; a hermetical-sealing mechanism that causes the inside of the load chamber 101a to be hermetically-sealed or opened with respect to the transfer chamber 101c; and a pumping mechanism such as a rotary pump or the like that roughly depressurizes the inside of the load chamber 101a.

[0071]

In the unload chamber 101b, the glass substrate 11 that has been film-formation completed in the film formation chamber 102 is transferred to the outside. The unload chamber 101b is provided with: a hermetical-sealing mechanism that causes the inside of the unload chamber 101b to be hermetically-sealed or opened with respect to the outside thereof and allows the glass substrate 11 to be transferred therefrom; a hermetical-sealing mechanism that causes the inside of the unload chamber 101b to be hermetically-sealed or opened with respect to the transfer chamber 101c; and a pumping mechanism such as a rotary pump or the like that roughly depressurizes the inside of the unload chamber 101b.

[0072]

The transfer chamber 101c is provided with a transfer mechanism 101d (transfer robot) that transfers the glass substrate 11 between the transfer chamber 101c and the

load chamber 101a, between the transfer chamber 101c and the unload chamber 101b, between the transfer chamber 101c and the film formation chamber 102, and between the transfer chamber 101c and the film formation chamber 103.

[0073]

In the film formation chamber 102, first film formation is carried out with respect to the glass substrate 11. In the film formation chamber 103, second film formation is carried out with respect to the glass substrate 11. The film formation chamber 103 is provided adjacent to the film formation chamber 102. The film formation chamber 102 and the film formation chamber 103 have substantially the same configuration.

Here, an explanation regarding the film formation chamber 102 is as follows. The explanation of the film formation chamber 102 may be applied to that of the film formation chamber 103. FIG. 4 shows a configuration of each of the film formation chamber 102 and the film formation chamber 103.

[0074]

As shown in FIG. 4, the film formation chamber 102 includes a vacuum chamber 53 having a depressurizable internal space. The vacuum chamber 53 is provided with three gas-introduction holes to which a gas-introduction mechanism (not shown in the drawings) is connected, that is, a reaction-gas-introduction hole 64a, an inert-gas-introduction hole 64b, and a mixed-gas-introduction hole 64c. Moreover, the vacuum chamber 53 is provided with two ports, that is, an exhaust port 64d and an exhaust port 64e. A pumping mechanism (not shown in the drawings, high-vacuum pumping mechanism) is connected to each port.

[0075]

In the internal space of the vacuum chamber 53, a target 54 and the glass

substrate 11 are disposed to face each other at a desired separation distance. The target 54 is mounted on a cathode electrode 55 (backing plate). The glass substrate 11 is mounted on a substrate holder 57 (substrate holding mechanism). A magnet plate 59 including a double magnet 60, for example, concentrically disposed thereon is provided on a back surface side of the cathode electrode 55. A power supply 62 is connected to the cathode electrode 55. A temperature control device 61 that controls a temperature of the substrate is provided on a back surface side of the substrate holder 57. The target 54, the cathode electrode 55, the substrate holder 57, the magnet plate 59, the power supply 62, and the temperature control device 61 constitute a film-formation mechanism.

[0076]

The film-formation mechanism of each of the film formation chambers 102 and 103 has a composition and a condition which are required for sequentially forming a film on the glass substrate 11.

In the embodiment, the film formation chamber 102 has a configuration corresponding to film formation of the phase-shift layer 12. The film formation chamber 103 has a configuration corresponding to film formation of the chromium-containing layer 13.

[0077]

Specifically, in the film formation chamber 102, as the composition required for forming the phase-shift layer 12 on the glass substrate 11, the target 54 is configured of a material containing molybdenum silicide.

[0078]

Furthermore, in the film formation chamber 102, as a gas to be suitably supplied from the gas-introduction mechanism via the gas-introduction holes 64a, 64b, and 64c to the vacuum chamber 53, a processing gas corresponding to film formation of the phase-

shift layer 12 is used. The processing gas contains carbon, nitrogen, oxygen, or the like. The processing gas contains a sputtering gas such as argon, nitrogen gas, or the like, and a condition of a predetermined partial pressure of the gases is set.

[0079]

Moreover, in accordance with the film formation conditions, vacuum pumping is carried out by the pumping mechanism via the exhaust ports 64d and 64e. Consequently, the internal space of the vacuum chamber 53 can be maintained in a high vacuum.

Additionally, in the film formation chamber 102, a sputtering voltage applied from the power supply 62 to the cathode electrode 55 is set corresponding to film formation of the phase-shift layer 12.

[0080]

Furthermore, in the film formation chamber 103, as the composition required for forming the chromium-containing layer 13 on the phase-shift layer 12, the target 54 is configured of a material containing chromium.

[0081]

Moreover, in the film formation chamber 103, as a gas to be suitably supplied from the gas-introduction mechanism via the gas-introduction holes 64a, 64b, and 64c to the vacuum chamber 53, a processing gas corresponding to film formation of the chromium-containing layer 13 is used. The processing gas contains carbon, nitrogen, oxygen, or the like. The processing gas contains a sputtering gas such as argon, an inert gas, or the like, and a condition of a predetermined partial pressure of the gases is set.

Additionally, as a gas to be appropriately supplied to the vacuum chamber 53 from the gas-introduction mechanism via the gas-introduction holes 64a, 64b, and 64c, the partial pressure of the gases of an oxygen-containing gas, a nitrogen-containing gas, a

carbon-containing gas, or the like can be adjusted to a predetermined amount of change in accordance with a film thickness of the formed chromium-containing layer 13.

[0082]

Furthermore, in accordance with the film formation conditions, vacuum pumping is carried out by the high-vacuum pumping mechanism via the exhaust ports 64d and 64e.

Additionally, in the film formation chamber 103, a sputtering voltage applied from the power supply 62 to the cathode electrode 55 is set corresponding to film formation of the chromium-containing layer 13.

[0083]

The method of manufacturing the mask blank 10B according to the embodiment includes a substrate-preparation step, the underlying-layer formation step, and a light-shielding-layer formation step.

In the explanation of the method of manufacturing the mask blank 10B according to the embodiment, processes using the manufacturing apparatus 100 shown in FIGS. 3 and 4 will be described.

[0084]

In the substrate-preparation step, the glass substrate 11 that was subjected to the aforementioned surface treatment or the like is prepared. Thereafter, the glass substrate 11 is loaded to the load chamber 101a shown in FIG. 3.

[0085]

After that, in the manufacturing apparatus 100 shown in FIG. 3, the glass substrate 11 is transferred from the load chamber 101a to the film formation chamber 102 via the transfer chamber 101c by the transfer mechanism 101d. In the film formation chamber 102, sputtering film formation of the underlying-layer formation step is carried

out with respect to the transferred glass substrate 11 while rotating the glass substrate by the substrate holder 57.

When film formation of the underlying layer is completed, the glass substrate 11 is transferred to the film formation chamber 103 via the transfer chamber 101c by the transfer mechanism 101d. In the film formation chamber 103, sputtering film formation of the chromium-containing-layer formation step is carried out while rotating the glass substrate 11 by the substrate holder 57.

Thereafter, the film-formation-completed glass substrate 11 is transferred from the unload chamber 101b to the outside via the transfer chamber 101c by the transfer mechanism 101d.

[0086]

Here, in the underlying-layer formation step, a sputtering gas and a reactive gas which serve as a supply gas are supplied from the gas-introduction mechanism of the film-formation mechanism to a region close to the cathode electrode 55 of the film formation chamber 102. In this state, a sputtering voltage is applied from the power supply 62 to the cathode electrode 55. Additionally, a predetermined magnetic field may be formed on the target 54 by a magnetron magnetic circuit.

[0087]

Ions of the sputtering gas excited by plasma near the target 54 in the film formation chamber 102 collide with the target 54 of the cathode electrode 55 and cause particles of the film-forming material to fly out. Subsequently, the flying particles and the reactive gas are bonded and thereafter are adhered to the glass substrate 11, and therefore the phase-shift layer 12 having a predetermined composition is formed on the surface of the glass substrate 11.

[0088]

Similarly, in the chromium-containing-layer formation step, a sputtering gas and a reactive gas which serve as a supply gas are supplied from the gas-introduction mechanism of the film-formation mechanism to a region close to the cathode electrode 55 of the film formation chamber 103. In this state, a sputtering voltage is applied from an external power supply to the cathode electrode 55. Additionally, a predetermined magnetic field may be formed on the target 54 by a magnetron magnetic circuit.

[0089]

Ions of the sputtering gas excited by plasma near the target 54 in the film formation chamber 103 collide with the target 54 of the cathode electrode 55 and cause particles of the film-forming material to fly out. Subsequently, the flying particles and the reactive gas are bonded and thereafter are adhered to the glass substrate 11, and therefore the chromium-containing layer 13 having a predetermined composition is formed on the surface of the glass substrate 11 having the phase-shift layer 12 formed thereon in a state of being stacked on the phase-shift layer 12.

[0090]

Here, in the film formation of the phase-shift layer 12 in the underlying-layer formation step, the sputtering gas, the oxygen-containing gas, and the like which have a predetermined partial pressure are supplied from the gas-introduction mechanism to the vacuum chamber 53, while controlling and switching the partial pressure of the gases, and the gas composition is in a set range. Simultaneously, in a case of forming the phase-shift layer 12 while varying the composition thereof in the film thickness direction, each partial pressure of the gases of the atmosphere gas can be changed depending on the formed film thickness.

[0091]

That is, in the film formation of the chromium-containing layer 13 in the

chromium-containing-layer formation step, the sputtering gas, the oxygen-containing gas, the carbon-containing gas, the nitrogen-containing gas, and the like which have a predetermined partial pressure are supplied from the gas-introduction mechanism to the vacuum chamber 53. The chromium-containing-layer formation step includes a light-shielding-layer formation step, an intermediate-layer formation step, an upper-medium-layer formation step, and a surface-layer formation step.

[0092]

In the chromium-containing-layer formation step, the above-described gases are controlled such that a concentration ratio, a flow ratio (supply amount) vary depending on an increase in the film formation thickness. Consequently, the chromium-containing layer 13 is formed such that the film characteristics, for example, the compositional ratio, the content rate, or the like of the chemical elements forming the chromium-containing layer 13 are distributed in the film-thickness direction corresponding to the light-shielding layer 13a, the intermediate layer 13b, the upper-medium layer 13c, and the surface layer 13d. Alternatively, the gas flow ratio or the concentration ratio of the supply gas is set such that the chemical elements forming each of the light-shielding layer 13a, the intermediate layer 13b, the upper-medium layer 13c, and the surface layer 13d have a concentration gradient in the film thickness direction.

At this time, in addition to the gas supply conditions, the sputtering conditions, for example, the sputtering voltage to be applied (sputtering-supply power), a length of processing time, a substrate temperature, or the like can also vary depending on the film characteristics such as the content rates or the like of the light-shielding layer 13a, the intermediate layer 13b, the upper-medium layer 13c, and the surface layer 13d.

[0093]

Specifically, in the film formation of the light-shielding layer 13a in the light-

shielding-layer formation step, the sputtering gas, the oxygen-containing gas, the carbon-containing gas, the nitrogen-containing gas, and the like are supplied to the vacuum chamber 53. At this time, the film thickness of and the film composition are set so as to obtain the optical characteristics such as the optical density (OD value), the reflectance, or the like required for the light-shielding layer 13a. The light-shielding layer 13a is formed until a predetermined film thickness is obtained.

[0094]

In the light-shielding-layer formation step, a concentration ratio and a flow ratio of gases mentioned above are controlled depending on an increase in the film formation thickness. Consequently, film formation is carried out such that the film characteristics such as the content rate or the like of the chemical elements forming the light-shielding layer 13a are equally distributed in the set film-thickness direction. Alternatively, the gas flow ratio or the concentration ratio of the supply gas is set such that the chemical elements forming the light-shielding layer 13a have a concentration gradient in the film thickness direction.

At this time, in addition to the gas supply conditions, the sputtering conditions, for example, the sputtering voltage to be applied, a length of processing time, a substrate temperature, or the like can also vary depending on the film characteristics such as the optical characteristics of the light-shielding layer 13a, the chemical resistance, the adhesion, the etching rate, or the like.

[0095]

Furthermore, after the film formation of the light-shielding layer 13a is completed, the intermediate layer 13b is formed by switching the supply gas type, the partial pressure of the gases or the gas flow ratio, and the supply power in the intermediate-layer formation step. At this time, the gases in a film formation

atmosphere may be prevented from being mixed together by use of a gas-atmosphere-changeover device, for example, a shutter or the like.

In the film formation of the intermediate layer 13b, the sputtering gas, the oxygen-containing gas, the carbon-containing gas, the nitrogen-containing gas, and the like are supplied to the vacuum chamber 53. In this situation, the film thickness, the OD value, and the film composition are set so as to obtain the film characteristics such as the optical characteristics, the chemical resistance, the adhesion, the etching rate, or the like required for the intermediate layer 13b. The intermediate layer 13b is formed on the light-shielding layer 13a until a predetermined film thickness is obtained.

[0096]

Furthermore, after the film formation of the intermediate layer 13b is completed, the upper-medium layer 13c is formed by switching the supply gas type, the partial pressure of the gases or the gas flow ratio, and the supply power in the upper-medium-layer formation step. At this time, the gases in a film formation atmosphere may be prevented from being mixed together by use of a gas-atmosphere-changeover device, for example, a shutter or the like.

In the film formation of the upper-medium layer 13c, the sputtering gas, the oxygen-containing gas, the carbon-containing gas, the nitrogen-containing gas, and the like are supplied to the vacuum chamber 53. In this situation, the film thickness, the OD value, and the film composition are set so as to obtain the film characteristics such as the optical characteristics, the chemical resistance, the adhesion, the etching rate, or the like required for the upper-medium layer 13c. The upper-medium layer 13c is formed on the intermediate layer 13b until a predetermined film thickness is obtained.

[0097]

Furthermore, after the film formation of the upper-medium layer 13c is

completed, the surface layer 13d near the surface of the chromium-containing layer 13 is formed by switching the supply gas type, the partial pressure of the gases or the gas flow ratio, and the supply power in the surface-layer formation step. At this time, the gases in a film formation atmosphere may be prevented from being mixed together by use of a gas-atmosphere-changeover device, for example, a shutter or the like.

In the film formation of the surface layer 13d, the sputtering gas, the oxygen-containing gas, the carbon-containing gas, the nitrogen-containing gas, and the like are supplied to the vacuum chamber 53. In this situation, the film thickness, the OD value, and the film composition are set so as to obtain the film characteristics such as the optical characteristics, the chemical resistance, the adhesion, the etching rate, or the like required for the surface layer 13d. The surface layer 13d is formed on the upper-medium layer 13c until a predetermined film thickness is obtained.

[0098]

Moreover, in a case of forming the resist layer 14 as the mask blank 10B in a resist-layer formation step, the resist layer 14 is formed on the surface layer 13d. In this case, a coater or the like applying a predetermined resist liquid can be used.

[0099]

Here, CO_2 (carbon dioxide), O_2 (oxygen), N_2O (dinitrogen oxide), NO (nitrogen monoxide), CO (carbon monoxide), or the like can be adopted as the oxygen-containing gas.

Additionally, CO_2 (carbon dioxide), CH_4 (methane), C_2H_6 (ethane), CO (carbon monoxide), or the like can be adopted as the carbon-containing gas.

Furthermore, N_2 (nitrogen gas), N_2O (dinitrogen oxide), NO (nitrogen monoxide), N_2O (dinitrogen oxide), NH_3 (ammonia), or the like can be adopted as the nitrogen-containing gas.

Moreover, Ar (argon), N_2 (nitrogen gas), or the like can be adopted as the sputtering gas.

Note that, in the film formation of the phase-shift layer 12 and the chromium-containing layer 13, the target 54 can be replaced if necessary.

[0100]

Additionally, in addition to such film formation of the phase-shift layer 12 and the chromium-containing layer 13, in a case of stacking another film thereon, film formation may be carried out by sputtering in accordance with sputtering conditions such as a target corresponding to another film, gases, or the like. Furthermore, the mask blank 10B according to the embodiment may be manufactured by stacking another film on the mask layer M by another film formation method.

[0101]

Hereinbelow, the film characteristics of the light-shielding layer 13a, the intermediate layer 13b, the upper-medium layer 13c, and the surface layer 13d according to the embodiment will be described.

[0102]

When the phase-shift mask 10 is manufactured from the mask blank 10B, the light-shielding layer 13a has a required light-shielding function with respect to predetermined exposure light. Accordingly, the light-shielding layer 13a has an OD value of 1.2, a film thickness of 25 to 35 nm, and the aforementioned content rates of Cr, O, C, and N in order to obtain a light-shielding function with respect to exposure light having a wavelength of, for example, approximately 193 nm.

Here, in the film formation of the light-shielding layer 13a, Ar, N_2, and CO_2 are selected as a supply gas and sputtering power of approximately 1.0 kW is used in order to obtain such film characteristics. At the same time, a flow ratio of Ar, N_2, and CO_2 can

be set so as to be Ar: N_2: CO_2=30:10:10.

[0103]

The intermediate layer 13b maintains a required adhesion between the light-shielding layer 13a and the upper-medium layer 13c, has a required chemical resistance, and provides the required optical characteristics for the chromium-containing layer 13 with respect to predetermined exposure light when the phase-shift mask 10 is manufactured from the mask blank 10B. In order to obtain such characteristics, the intermediate layer 13b has an OD value of 0.3, a film thickness of 2 to 4 nm, and the aforementioned content rates of Cr, O, C, and N.

Here, in the film formation of the intermediate layer 13b, Ar and N_2 are selected as a supply gas and sputtering power of approximately 1.5 kW is used in order to obtain such film characteristics. At the same time, a flow ratio of Ar and N_2 can be set so as to be Ar: N_2=15:10.

[0104]

The upper-medium layer 13c maintains a required adhesion between the intermediate layer 13b and the surface layer 13d, has a required chemical resistance, and provides the required optical characteristics for the chromium-containing layer 13 with respect to predetermined exposure light when the phase-shift mask 10 is manufactured from the mask blank 10B. In order to obtain such characteristics, the upper-medium layer 13c has an OD value of 0.1, a film thickness of 1 to 2 nm, and the aforementioned content rates of Cr, O, C, and N.

Here, in the film formation of the upper-medium layer 13c, Ar, CH_4, NO, and CO_2 are selected as a supply gas and sputtering power of approximately 1.0 kW is used in order to obtain such film characteristics. At the same time, a flow ratio of Ar, CH_4, and NO can be set so as to be Ar:CH_4:NO=10:2:2.

[0105]

The surface layer 13d maintains a required adhesion between the upper-medium layer 13c and the surface layer 13d, has a required chemical resistance with respect to a chemical solution such as acid, alkali, ozone, or the like used in a cleaning step or the like, and provides the required optical characteristics for the chromium-containing layer 13 with respect to predetermined exposure light when the phase-shift mask 10 is manufactured from the mask blank 10B. In order to obtain such characteristics, the surface layer 13d has an OD value of 0.3, a film thickness of 12 to 15 nm, the aforementioned content rates of Cr, O, C, and N, and has a concentration gradient of the content rate in the film thickness direction.

Here, in the film formation of the surface layer 13d, Ar, CH_4, NO, CO_2 are selected as a supply gas and sputtering power of approximately 1.0 kW is used in order to obtain such film characteristics. At the same time, a flow ratio of Ar, CH_4, and NO can be set so as to be Ar:CH_4:NO: CO_2=20:2:2:13.5. Furthermore, in order to obtain the concentration gradient of the content rates of Cr, O, C, and N, the flow rate of Ar can be increased such that a flow ratio of Ar, CH_4, NO, and CO_2 is changed to be Ar:CH_4:NO: CO_2=34.5:2:2:13 at the time of completion of the film formation.

Additionally, regarding a partial pressure ratio of NO and CO_2 of the supply gas, the value of CO_2/ (CO_2+NO) is set in a range of 0.75 to 0.87.

[0106]

As a result of forming the mask blank 10B having such a film configuration, it is possible to form the phase-shift mask 10 provided with the chromium-containing layer 13 that is formed of a chromium compound and includes the light-shielding layer 13a, the intermediate layer 13b, the upper-medium layer 13c, and the surface layer 13d.

[0107]

In the method of manufacturing the mask blank according to the embodiment, when forming a high-definition pattern such that an aspect ratio thereof is small and a pattern width thereof is narrow, the chemical resistance of the surface layer 13d is improved, the etching rate of the mask layer M increases, and the adhesion between the surface layer 13d and the resist layer 14 is improved. Therefore, it is possible to manufacture the mask blank 10B including the chromium-containing layer 13 having a required optical density.

Here, the chemical resistance of the surface layer 13d is improved with respect to the chemical solution, for example, acid such as persulfuric acid water and hot concentrated sulfuric acid, alkali such as NaOH and KOH, ozone water, or the like.

[0108]

Furthermore, the adhesion between the surface layer 13d and the upper-medium layer 13c is improved, an occurrence of a pattern defect can be reduced.

Consequently, the number of defects of the surface layer 13d is reduced. Even in a case in which an external force such that a scrub processing or the like is carried out after pattern formation is applied to the mask layer, it is possible to manufacture the mask layer such that an occurrence of a pattern defect does not increase. Furthermore, even in a narrow-width pattern serving as a high-definition pattern, it is possible to prevent an occurrence of a pattern defect from increasing. At the same time, the chemical resistance of the surface layer 13d is improved, and the etching rate of the mask layer M increases. Therefore, it is possible to manufacture the mask blank 10B including the mask layer M having a required optical density.

[0109]

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

described.

FIGS. 5 to 8 are cross-sectional views each showing a manufacturing process of the phase-shift mask according to the embodiment.

[0110]

The method of manufacturing the phase-shift mask according to the embodiment includes: a resist-layer formation step, a resist-pattern formation step, a chromium-containing-layer-pattern formation step, a peeling cleaning step, an underlying-layer-pattern formation step, and a peeling cleaning step.

[0111]

In the resist-layer formation step, as shown in FIG. 2, the resist layer 14 is formed on the chromium-containing layer 13 serving as the uppermost layer of the mask blank 10B. As the resist layer 14, a positive resist or a negative resist may be used. In the embodiment, a positive resist is used. As the resist layer 14, a liquid resist is used.

[0112]

In the resist-pattern formation step, the photoresist layer 14 is exposed and subjected to development, and therefore a photoresist pattern 14P1 having a predetermined pattern shape (opening pattern) is formed on the chromium-containing layer 13 (FIG. 5).

The photoresist pattern 14P1 functions as an etching mask for etching the chromium-containing layer 13. The shape of the photoresist pattern 14P1 is determined depending on the etching pattern of the chromium-containing layer 13.

[0113]

Next, in the chromium-containing-layer-pattern formation step, the chromium-containing layer 13 is subjected to dry etching via the photoresist pattern 14P1 by use of a predetermined dry-etching apparatus, and therefore a chromium-containing layer

pattern 13P1 is formed (FIG. 6).

At this time, in the dry etching of the chromium-containing layer 13 containing chromium, a chlorine-based gas contains oxygen or the like can be used.

[0114]

Next, in a first peeling cleaning step, the photoresist pattern 14P1 is removed by use of a predetermined peeling liquid (FIG. 7).

Persulfuric acid water or ozone water can be used as a cleaning liquid.

[0115]

Subsequently, in the underlying-layer-pattern formation step, the phase-shift layer 12 is subjected to dry etching via the chromium-containing layer pattern 13P1 by use of a predetermined dry-etching apparatus, and therefore an underlying layer pattern 12P1 is formed (FIG. 8).

The chromium-containing layer pattern 13P1 functions as an etching mask for etching the phase-shift layer 12.

Furthermore, in the etching of the phase-shift layer 12, an etching gas different from the case of etching the chromium-containing layer 13, for example, a fluorine compound gas, that is, at least one selected from tetrafluoro methane, sulfur hexafluoride, or the like can be used.

[0116]

After that, in the final peeling cleaning step, the chromium-containing layer pattern 13P1 and the underlying layer pattern 12P1 are rinsed by use of a predetermined peeling liquid.

Persulfuric acid water or ozone water can be used as a cleaning liquid.

Accordingly, the phase-shift mask 10 (phase-shift mask) is formed (FIG. 8).

[0117]

In the method of manufacturing the mask blank according to the embodiment, it is possible to manufacture the mask blank 10B that can manufacture the phase-shift mask 10. According to the phase-shift mask 10, when forming a high-definition pattern such that an aspect ratio thereof is small and a pattern width thereof is narrow, the chemical resistance of the surface layer 13d is improved, and it is possible to prevent the optical characteristics of the mask layer M from varying in a cleaning step using an alkaline fluid such as persulfuric acid water and NaOH, sulfuric acid, or ozone water.

[0118]

In the method of manufacturing the mask blank according to the embodiment, it is possible to manufacture the mask blank 10B that includes the chromium-containing layer 13 constituting the mask layer M having a required optical density and can reduce the thickness of the resist layer 14. In the mask layer M, the etching rate of the chromium-containing layer 13 constituting the mask layer M is improved, and it is possible to reduce the effect on the optical characteristics in the etching or the film characteristics such as the film thickness. Consequently, collapse of a resist can be prevented, and it is possible to manufacture the phase-shift mask 10 having the required film characteristics.

Here, “collapse of resist” means that the resist layer 14 is partially peeled off from the chromium-containing layer 13 after completion of pattern formation or during pattern formation, particularly, a portion occurs at which the photoresist pattern 14P1 is peeled off from the chromium-containing layer pattern 13P1 having a narrow width.

[0119]

In the method of manufacturing the mask blank according to the embodiment, the adhesion of the surface layer 13d with respect to the resist layer is improved, it is possible to prevent the collapse of the resist (resist peeling), and it is possible to

manufacture the mask blank 10B that can form a high-definition pattern. As a result, a required high-definition pattern is achieved, and it is possible to manufacture the phase-shift mask 10 with the pattern characteristics having a narrow width.

[0120]

In the method of manufacturing the mask blank according to the embodiment, the adhesion between the phase-shift layer 12 and the chromium-containing layer 13 is improved, it is possible to prevent the collapse of the pattern (pattern defect), and it is possible to manufacture the mask blank 10B that can form a high-definition pattern. For this reason, a required high-definition pattern is achieved, and it is possible to manufacture the phase-shift mask 10 with the pattern characteristics having a narrow width.

[0121]

In the method of manufacturing the mask blank according to the embodiment, the chemical resistance of the surface layer 13d is improved, the adhesion between the surface layer 13d and the resist layer 14 is improved, and the adhesion between the chromium-containing layer 13 and the phase-shift layer 12 is improved. A high-definition pattern can be achieved, a defect can be prevented from being generated in the formation of a pattern having a narrow width. Therefore, it is possible to provide the mask blank 10B that can manufacture the phase-shift mask 10 in which the optical characteristics of the mask layer can be prevented from varying in the cleaning step using persulfuric acid water, an alkaline fluid such as NaOH, sulfuric acid, or ozone water.

Examples

[0122]

Hereinbelow, Experimental Examples according to the embodiment will be described.

[0123]

Regarding specific examples of the mask blank 10B according to the invention, confirmation tests were carried out.

First of all, the etching characteristics regarding a chromium-containing layer serving as a light-shielding layer were evaluated.

<Experimental Examples 1 to 3>

In Experimental Examples 1 to 3, a chromium compound film used as the light-shielding layer was formed on a glass substrate by a sputtering method using a chromium target in a film formation apparatus.

The film formation conditions of each of Experimental Examples 1 to 3 are shown in FIG. 9.

Here, a film to be the formed chromium-containing layer has a predetermined optical density and contains chromium, oxygen, nitrogen, and carbon. The content rates of Cr, O, C, and N forming the chromium-containing layer are predetermined values with respect to the film thickness.

[0124]

Moreover, the chromium-containing layer 13 has a three-layered structure of a first layer to a third layer corresponding to the light-shielding layer 13a, the intermediate layer 13b, and the surface layer 13d, respectively. Regarding film formation conditions of each of the layers constituting the chromium-containing layer 13, the gas type and the flow rates of gases supplied to the film formation chamber during film formation and the sputtering power were changed corresponding to the thickness of the formed film. Here, the supply gas was suitably selected from Ar, N_2, CH_4, NO, and CO_2. A flow ratio (content rates) of the supply gas was set corresponding to the film thickness that increases during film formation.

In this situation, when changing the conditions corresponding to the three-layered structure including the first layer to the third layer, a target and a substrate are isolated from each other by using a shutter in all cases.

[0125]

Furthermore, the film formation conditions of each of Experimental Examples 1 to 3 were changed. Here, in Experimental Examples 1 to 3, the gas flow ratio was changed such that the content rates of the chemical elements forming the third layer serving as the uppermost layer have a concentration gradient. Note that, FIG. 9 shows the gas flow ratio at the time of completion of the film formation of the third layer.

[0126]

Furthermore, dry etching treatment using a MoSi layer as a metal mask was carried out with respect to each of the films formed by the above-described Experimental Examples 1 to 3, and therefore a pattern was formed. A length of time of dry etching in the dry etching treatment was measured. Here, the etching conditions were as follows.

- Chlorine: 150 sccm
- Oxygen: 60 sccm
- RF Power: 0.5 kW
- Bias Power: 50 W

[0127]

FIG. 10 shows each of the results of Experimental Examples 1 to 3. In FIG. 10, variation of plasma emission intensity with the etching time is shown. When a volatilization amount of the film decreases during the etching, since the emission intensity at the wavelength due to the volatilized material is sharply reduced, an end point representing completion of etching can be calculated.

Additionally, FIG. 11 shows a shortening rate of the etching time from start of

electric discharge to the end point in the condition of each of Experimental Examples 1 to 3. Here, regarding the time required for obtaining the same etching depth in the etching treatment of Experimental Examples 1 to 3, FIG. 11 shows that an etching-time shortening rate of each of the etching times of Experimental Examples 2 and 3 to the etching time of Experimental Example 1.

[0128]

From the results, in Experimental Example 3, it is apparent that a length of dry etching time can be reduced by approximately 20%. That is, it is apparent that in Experimental Example 3, the etching rate can be improved.

[0129]

Next, the chemical resistances regarding the chromium-containing layer serving as the light-shielding layer were evaluated.

<Experimental Examples 1 and 5 to 8>

Similarly, in Experimental Examples 3 to 6, the film formation conditions of the chromium-containing layer including the first layer to the third layer were changed, and film formation was carried out on a glass substrate.

[0130]

The characteristics of the film of each of Experimental Examples 3 to 6 were as follows.

- Experimental Example 3: the first layer is an N_2+CO_2 film, the second layer is an N_2 film, and the third layer is an NO-concentration gradient film (1:0).

- Experimental Example 4: the first layer is an N_2+CO_2 film, the second layer is an N_2 film, and the third layer is a CO_2-concentration gradient film (0:1).

- Experimental Example 5: the first layer is an N_2+CO_2 film, the second layer is an N_2 film, and the third layer is an NO+CO_2-mixture concentration gradient film (5:10).

- Experimental Example 6: the first layer is an N_2+CO_2 film, the second layer is an N_2 film, and the third layer is an NO+CO_2-mixture concentration gradient film (2:13).

Additionally, FIG. 12 shows the film formation conditions of each of Experimental Examples 3 to 6 and an oxygen-nitrogen compositional ratio "O/(O+N)" of oxygen and nitrogen serving as the chemical elements forming the uppermost layer evaluated by Auger electron spectroscopy. Here, in a case in which the oxygen content rate is represented as O (atm%) and the nitrogen content rate is represented as N (atm%), an oxygen-nitrogen compositional ratio is represented by O/(O+N).

[0131]

Thereafter, regarding the resistance to acid, alkali, and ozone water of the film obtained by each of Experimental Examples 3 to 6, the optical characteristics of each film before and after exposure to a chemical solution were measured. Here, variation of the OD value of the optical density and variation of reflectance were measured as the optical characteristics.

[0132]

Here, regarding evaluation of acid resistance of the film with respect to a chemical solution, the variation with respect to a sulfuric-acid concentration of 96% at a temperature of 100°C was measured. Additionally, an immersion time was changed such as 5 minutes, 15 minutes, 30 minutes, 60 minutes, and 120 minutes.

Additionally, regarding evaluation of alkaline resistance of the film with respect to a chemical solution, the variation with respect to a NaOH-liquid concentration of 30% at a temperature of 20°C was measured. Similarly, an immersion time was changed such as 5 minutes, 15 minutes, 30 minutes, 60 minutes, and 120 minutes.

Furthermore, regarding evaluation of ozone resistance of the film with respect to a chemical solution, the variation with respect to an ozone-water concentration of 20 ppm

at a temperature of 20°C was measured. Similarly, an immersion time was changed such as 5 minutes, 15 minutes, 30 minutes, and 60 minutes.

[0133]

First of all, after film formation, the OD value with respect to a wavelength of 193 nm as the optical characteristics was measured, and a relative reflectance of a film surface with respect to an Al film as reference was measured.

The reflectance was measured by spectrophotometer UH4150 produced by Hitachi High-Tech Corporation.

Moreover, after the film was immersed in the chemical solution, the film was rinsed by a rinsing apparatus, and the optical characteristics were measured again in the same manner.

[0134]

The results of spectrum measurement after sulfuric-acid immersion are shown in FIGS. 13 to 16.

From the results shown in FIGS. 13 to 16, it is apparent that a degree of overall spectrum shift (peroxidation due to sulfuric acid) is small in Experimental Example 4. It is apparent that a degree of overall spectrum shift (peroxidation due to sulfuric acid) is small in Experimental Example 6.

[0135]

A change rate of the optical characteristics (the OD value and the reflectance) between before and after a chemical solution immersion was calculated, and a relationship of the maximum change rate of the optical characteristics (the OD value and the reflectance) under each of the conditions and the oxygen-nitrogen compositional ratio of the uppermost layer was evaluated. The results were shown in FIG. 17. In FIG. 17, the measurement results regarding sulfuric acid, alkali, and ozone are plotted.

[0136]

From the results shown in FIG. 17, it is apparent that the measurement results regarding sulfuric acid, alkali, and ozone corresponding to the order of Experimental Example 3, Experimental Example 5, Experimental Example 6, and Experimental Example 4 are arranged from the left side to the right side of the graph. That is, in a case in which the chemical solution is sulfuric acid, alkali, and ozone, as shown in Experimental Example 4, Experimental Example 5, and Experimental Example 6, it was found that an excellent result is obtained when the oxygen-nitrogen compositional ratio O/(O+N) of the uppermost layer is greater than or equal to 0.9.

[0137]

Next, the adhesion of the chromium-containing layer serving as the light-shielding layer with respect to the resist layer was evaluated.

In Experimental Examples 3 to 6, a resist layer was formed on the formed chromium-containing layer, a pattern was formed by carrying out exposure and development, the presence or absence of collapse of a resist was determined, a peeling test was carried out, and furthermore surface observation was carried out.

Note that, in this situation, the conditions were as follows.

- Method of forming resist: formation by coating
- Resist material: chemical amplification type positive resist (produced by Fuji Film Arch co., FEP171)
- Thickness of resist: 300 nm
- Method of forming pattern: EB drawing (produced by ELIONIX INC.: ELS-S50), PEB AHC-150UL
- Developing solution: tetramethylammonium hydroxide (TMAH) 2.38%
- SEM observation used for evaluation of collapse of resist: ELS-S50

- Peeling test: test using a tape produced by SCOTCH Corporation

- Microscope observation: L300ND (produced by Nikon Corporation)

[0138]

Here, a pattern size of the pattern to be formed, that is, a pattern width was changed. Specifically, since the thickness of the resist film was 300 nm, an aspect ratio, that is, the values (resist film thickness / pattern size) were as follows.

Pattern width: 100 nm: aspect ratio 3.0

Pattern width: 200 nm: aspect ratio 1.5

Pattern width: 300 nm: aspect ratio 1.0

Pattern width: 500 nm: aspect ratio 0.6

Pattern width: 1000 nm: aspect ratio 0.3

[0139]

Furthermore, as shown in FIG. 18, a region on which a pattern is to be formed was sectioned into four areas of A to D. Subsequently, as shown in FIG. 19, a pattern density of each of areas was changed. Note that, the pattern density means the area ratio (β^2/α^2) obtained by a pattern width α and a pattern pitch β shown in FIG. 20.

FIGS. 21 and 22 show the results of the tape peeling test at an aspect ratio of 0.6 after exposure and development. FIG. 21 shows the result under the condition in which an oxygen composition of the uppermost layer of Experimental Example 4 is high, and it is apparent that a black region representing a pattern peeling is large. FIG. 22 shows the result under the condition in which an oxygen content rate of the uppermost layer of Experimental 5 is low, there is a tendency that a pattern peeling is small, and it is apparent that a significant difference was observed by controlling the composition of the uppermost layer by change of the gas flow ratio.

[0140]

FIGS. 23 and 24 shows pattern residual rates after a peeling test with respect to the oxygen content rate of the uppermost layer having the density of 1.1% (upper right) of the 500 nm pattern on the area B.

[0141]

As shown in FIG. 24, it is understood that there is a tendency that the adhesion between the chromium-containing layer and the resist layer can be maintained in the range in which the oxygen-nitrogen compositional ratio O/(O+N) of the uppermost layer is less than or equal to 0.98.

From the aforementioned results, it is was found that the range of the oxygen-nitrogen compositional ratio O/ (N+O) of the uppermost layer which satisfies both of the chemical resistance and the adhesion with respect to the resist is in a range of 0.9 to 0.98.

[0142]

Next, the adhesion regarding the chromium-containing layer serving as the light-shielding layer was evaluated.

<Experimental Examples 3, 4, 6, and 7>

In addition to Experimental Examples 3, 4, and 6, similarly, Experimental Example 7 was carried out in which a third layer corresponding to the upper-medium layer 13c was newly formed between the second layer and the third layer of Experimental Example 6. That is, in Experimental Example 7, the chromium-containing layer has a four-layer configuration. In this case, the surface layer 13d is a fourth layer.

Here, regarding the film-forming gas for forming the third layer serving as the upper-medium layer 13c, a CH_4 gas was supplied instead of a CO_2 gas used for the film-forming gas for forming the intermediate layer 13b and the surface layer 13d.

Hereinbelow, the film characteristics of Experimental Example 7 are shown.

- Experimental Example 7: the first layer is an N_2+CO_2 film, the second layer is an N_2 film, the third layer is an N_2+CH_4 film, and the fourth layer is an NO+CO_2-mixture concentration gradient film (2:13).

Additionally, the film formation conditions of each of Experimental Examples 3, 4, 6, and 7 are collectively shown in FIG. 25.

[0143]

First of all, each of the mask blank of Experimental Examples 3, 4, 6, and 7 was patterned so as to have a dotted pattern with a width dimension α of 1 μm shown in FIG. 20. Thereafter, a formed state obtained by the patterning was a primal initial (initial state). Of each of Experimental Examples 3, 4, 6, and 7, the number of patterns, particularly, the number of defects were counted using an optical microscope.

Note that, the conditions for forming the pattern were as follows.

- Resist material: alkali-soluble resin, diazonaphthoquinone-containing positive photoresist THMR-iP3500 (produced by TOKYO OHKA KOGYO CO., LTD)

- Exposure time: 6.5 sec

- Developing solution: TMAH (tetramethylammonium hydroxide)

- Development time: 30 sec

- Etching time: 16 sec

[0144]

Subsequently, the mask blank of each of Experimental Examples 3, 4, 6, and 7 was immersed in sulfuric acid liquid at a concentration of 96% for 5 min.

Furthermore, after rinsing using deionized water was carried out, scrub processing using a nylon brush was carried out for 3 min in a cleaning liquid containing potassium phosphate and a surface-active agent as main components at a concentration of 3%, and thereafter such sulfuric-acid immersion processing and scrub processing were

repeatedly carried out three times.

For each pattern formation, the number of patterns, particularly, the number of defects were counted using an optical microscope, and the increased number of defects from the initial state was measured.

[0145]

FIG. 26 shows each of defect data of the initial state of Experimental Example 7 and the number of defects after the scrub processing (after friction).

Note that, regarding the counting of pattern defects, FIG. 27 shows a typical pattern image.

As shown in FIG. 27, the counting of pattern defects was carried out such that the image at which the pattern was completely defected and the image at which only the surface layer of the Cr film was defected are distinguished from each other.

[0146]

The results of the number of pattern defects for each type with respect to the oxygen-nitrogen compositional ratio of the surface layer are collectively shown in FIG. 28.

From the results shown in FIG. 28, in a case in which the oxygen-nitrogen compositional ratio O/(O+N) of the surface layer is high, it is apparent that the number of pattern defects of the surface layer increases. Furthermore, even in the case in which the oxygen-nitrogen compositional ratio of the surface layer is high, it is apparent that the pattern defect is improved by providing the upper-medium layer serving as an NO-based thin film between the intermediate layer and the surface layer.

Furthermore, in Experimental Example 7, it is apparent that the characteristics of chemical resistance, the adhesion with respect to the resist layer, and the adhesion of the Cr film are all excellent.

[0147]

Next, content rates of chemical elements forming the chromium-containing layer serving as the light-shielding layer were measured.

<Experimental Examples 3, 4, 6, and 7>

Regarding the chromium-containing layer of each of Experimental Examples 3, 4, 6, and 7, the content rates and the composition of Cr, C, N, and O of the light-shielding layer serving as the first layer, the intermediate layer serving as the second layer, the upper-medium layer serving as the third layer, and the surface layer serving as the fourth layer were evaluated by use of Auger electron spectroscopy.

The results are collectively shown in FIG. 29.

Note that, in FIG. 29, the content rates of the surface layer represent the content rates of the fourth layer.

Furthermore, FIG. 30 shows the evaluation results of the composition of the chromium-containing layer of Experimental Example 7. In FIG. 30, the horizontal axis represents a length of sputtering etching time by Ar ions. In other words, the sputtering etching is a processing of etching the surface of the chromium-containing layer. The composition was measured for each second in the sputtering etching. In the measurement of composition, Auger electron spectroscopy was used. From the results shown in FIG. 30, it was confirmed that an intermediate composition film can be formed by adding the upper-medium layer into the chromium-containing layer.

[0148]

Subsequently, an etching rate regarding the chromium-containing layer serving as the light-shielding layer was measured.

<Experimental Example 7>

An etching treatment was carried out with respect to the light-shielding layer

serving as the first layer, the intermediate layer serving as the second layer, the upper-medium layer serving as the third layer, and the surface layer serving as the fourth layer of the chromium-containing layer. When the etching treatment was carried out, the etching rates of the first layer to the fourth layer were compared to each other.

In this situation, the etching conditions were as follows.

- Chlorine: 150 sccm
- Oxygen: 60 sccm
- RF Power: 0.5 kW
- Bias Power: 50 W

[0149]

In a case in which an etching rate of the light-shielding layer is defined as ER1, an etching rate of the intermediate layer is defined as ER2, an etching rate of the upper-medium layer is defined as ER3, and an etching rate of the surface layer is defined as ER4, the relationship of ER3<ER2<ER4<ER1 is obtained.

[0150]

Furthermore, dry etching treatment using a MoSi film as a metal mask was carried out with respect to each of the films formed by the above-described Experimental Examples 3 and 7, and therefore a pattern was formed. In the obtained pattern, cross-sectional SEM images were obtained.

The results are shown in FIGS. 31 and 32.

Regarding the inclination of the cross-sectional surface of the Cr layer, the inclination of the cross-sectional surface of Experimental Example 7 is close to a vertical shape as compared with Experimental Example 3, it is apparent that an excellent cross-sectional shape is obtained.

[0151]

Next, the optical characteristics regarding the chromium-containing layer serving as the light-shielding layer were measured.

<Experimental Examples 1 and 7>

First of all, in Experimental Examples 1 and 7, reflectance was measured with respect to a measurement light wavelength of 193 nm corresponding to an exposure light. At this time, spectrophotometer UH4150 produced by Hitachi High-Tech Corporation was used.

The results are shown in FIG. 33.

[0152]

Furthermore, an optical density of the film surface of each of Experimental Examples 1 and 7 was measured with respect to a measurement light wavelength of 193 nm corresponding to an exposure light. Similarly, spectrophotometer UH4150 produced by Hitachi High-Tech Corporation was used.

The results are shown in FIG. 34.

[0153]

From the results shown in FIG. 33, the bottom of the reflectance can be shifted to the short-wavelength side such that the reflectance becomes 23%.

By lowering the reflectance, it is possible to suppress generation of a steady wave during exposure. Additionally, an effect is achieved such that multiple reflection between a mask and a lens can be suppressed when wafer transfer is carried out.

[0154]

From the results shown in FIG. 34, the OD value at 193 nm can be controlled to be approximately 1.9.

Accordingly, an effect is achieved such that a sufficient light-shielding property can be obtained when wafer transfer is carried out.

[0155]

From the above-described results, according to the invention, at the same time the chemical resistance of the chromium-containing layer 13 can be improved, the adhesion of the chromium-containing layer 13 with respect to the resist layer can be improved, the adhesion between the chromium-containing layer 13 and the phase-shift layer 12 serving as an underlying layer can be improved, and the etching rate can be improved.

DESCRIPTION OF REFERENCE NUMERALS

[0156]

10...phase-shift mask (photomask)

10B...mask blank

11...glass substrate (transparent substrate)

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

12P1... underlying layer pattern

13...chromium-containing layer

13a...light-shielding layer (first layer)

13b...intermediate layer (second layer)

13c...upper-medium layer (third layer)

13d...surface layer (fourth layer)

13P1...chromium-containing layer pattern (light-shielding pattern)

14...resist layer (photoresist layer)

14P1...photoresist pattern (resist pattern)

M...mask layer

CLAIMS

1. A mask blank comprising:

a transparent substrate having a surface; and

a mask layer stacked on the surface of the transparent substrate, the mask layer containing nitrogen, carbon, oxygen, and chromium, the mask layer having an uppermost surface on an opposite side of the surface of the transparent substrate, wherein

an oxygen content rate of the uppermost surface of the mask layer is in a range of 65 to 72atm%.

2. The mask blank according to claim 1, wherein

the mask layer includes a surface layer,

the surface layer has an upper surface and a lower surface on an opposite side of the upper surface,

the upper surface of the surface layer corresponds to the uppermost surface,

an oxygen content rate of the upper surface of the surface layer is in a range of 65 to 72atm%,

an oxygen content rate of the lower surface of the surface layer is in a range of 35 to 45atm%, and

the surface layer has an oxygen concentration gradient such that an oxygen content rate gradually decreases in a direction from the upper surface to the lower surface.

3. The mask blank according to claim 2, wherein

in a case in which an oxygen content rate is represented as O (atm%) and a

nitrogen content rate is represented as N (atm%), an oxygen-nitrogen compositional ratio is represented as O/(O+N), and

the oxygen-nitrogen compositional ratio of the surface layer is in a range of 0.9 to 0.98.

4. The mask blank according to claim 2 or claim 3, wherein

the mask layer includes an upper-medium layer located closer to the transparent substrate than the surface layer,

the upper-medium layer contains oxygen, and

an oxygen content rate of the upper-medium layer is lower than an oxygen content rate of the surface layer.

5. The mask blank according to claim 4, wherein

the mask layer includes an intermediate layer located closer to the transparent substrate than the upper-medium layer,

the intermediate layer contains oxygen,

the intermediate layer has a surface, and

an oxygen content rate of the upper-medium layer is lower than an oxygen content rate of the surface of the intermediate layer.

6. The mask blank according to any one of claims 1 to 5, wherein

the mask layer includes:

a light-shielding layer containing chromium;

an intermediate layer stacked on the light-shielding layer, the intermediate layer containing chromium;

an upper-medium layer stacked on the intermediate layer, the upper-medium layer containing chromium; and

a surface layer stacked on the upper-medium layer, the surface layer containing chromium, and wherein

the surface layer contains oxygen, nitrogen, and carbon,

a chromium content rate of the surface layer is in a range of 21 to 25atm%,

an oxygen content rate of the surface layer is in a range of 65 to 72atm%,

a nitrogen content rate of the surface layer is in a range of 1 to 5atm%, and

a carbon content rate of the surface layer is in a range of 4 to 6atm%.

7. The mask blank according to claim 6, wherein

in a dry etching treatment using a mixed gas of chlorine and oxygen, in a case in which an etching rate of the light-shielding layer is defined as ER1, an etching rate of the intermediate layer is defined as ER2, an etching rate of the upper-medium layer is defined as ER3, and an etching rate of the surface layer is defined as ER4,

ER3<ER2<ER4<ER1 is satisfied.

8. The mask blank according to claim 6 or claim 7, wherein

each of the intermediate layer and the upper-medium layer includes oxygen, and

in a case in which a value of an oxygen content rate of the upper-medium layer is defined as VO1, a value of an oxygen content rate of the intermediate layer is defined as VO2, and a value of an oxygen content rate of the surface layer is defined as VO3,

VO2<VO1<VO3 is satisfied.

9. The mask blank according to claim 7 or claim 8, wherein

each of the intermediate layer and the upper-medium layer includes nitrogen, and

in a case in which a value of a nitrogen content rate of the upper-medium layer is defined as VN1, a value of a nitrogen content rate of the intermediate layer is defined as VN2, and a value of a nitrogen content rate of the surface layer is defined as VN3,

VN2<VN1<VN3 is satisfied.

10. The mask blank according to any one of claims 7 to 9, wherein

each of the intermediate layer and the upper-medium layer includes carbon, and

in a case in which a value of a carbon content rate of the upper-medium layer is defined as VC1, a value of a carbon content rate of the intermediate layer is defined as VC2, and a value of a carbon content rate of the surface layer is defined as VC3,

VC2<VC1<VC3 is satisfied.

11. The mask blank according to any one of claims 7 to 10, wherein

the upper-medium layer contains oxygen, nitrogen, and carbon,

a chromium content rate of the upper-medium layer is in a range of 45 to 52atm%,

an oxygen content rate of the upper-medium layer is in a range of 15 to 25atm%,

a nitrogen content rate of the upper-medium layer is in a range of 15 to 25atm%, and

a carbon content rate of the upper-medium layer is in a range of 5 to 15atm%.

12. The mask blank according to any one of claims 7 to 11, wherein

the intermediate layer contains oxygen, nitrogen, and carbon,

a chromium content rate of the intermediate layer is in a range of 45 to 52atm%,

an oxygen content rate of the intermediate layer is in a range of 10 to 20atm%,

a nitrogen content rate of the intermediate layer is in a range of 15 to 25atm%, and

a carbon content rate of the intermediate layer is in a range of 10 to 20atm%.

13. The mask blank according to any one of claims 7 to 12, wherein

the light-shielding layer contains oxygen, nitrogen, and carbon,

a chromium content rate of the light-shielding layer is in a range of 30 to 40atm%,

an oxygen content rate of the light-shielding layer is in a range of 25 to 35atm%,

a nitrogen content rate of the light-shielding layer is in a range of 14 to 24atm%, and

a carbon content rate of the light-shielding layer is in a range of 11 to 21atm%.

14. The mask blank according to claim 7, wherein

a thickness ratio of the light-shielding layer, the intermediate layer, the upper-medium layer, and the surface layer is in a range of 29:1:3:11 to 33:2:6:13.

15. A method of manufacturing a mask blank according to claim 1, comprising:

a mask-layer formation step of forming the mask layer containing chromium on the transparent substrate by sputtering, wherein

in the mask-layer formation step, a target containing chromium is used, and

the uppermost surface of the mask layer is formed by using a gas containing carbon dioxide serving as an oxygen-containing gas as a supply gas for the sputtering.

16. The method of manufacturing a mask blank according to claim 15, wherein

in the mask-layer formation step, the uppermost surface of the mask layer is formed by using a gas containing nitrogen monoxide serving as a nitrogen-containing gas as a supply gas for the sputtering.

17. The method of manufacturing a mask blank according to claim 15, wherein

in the mask-layer formation step, the uppermost surface of the mask layer is formed by using a gas containing methane serving as a carbon-containing gas as a supply gas for the sputtering.

18. A method of manufacturing a mask blank according to claim 2, comprising:

a surface-layer formation step of forming the surface layer, wherein

in the surface-layer formation step, a target containing chromium is used,

a gas containing argon and oxygen is used as a supply gas for the sputtering, and

the surface layer having an oxygen concentration gradient such that an oxygen content rate varies is formed by changing a supply amount of argon.

19. The method of manufacturing a mask blank according to claim 18, wherein

in the surface-layer formation step, the surface layer is formed by using a gas containing argon, methane, nitrogen monoxide, and carbon dioxide as a supply gas for the sputtering.

20. A method of manufacturing a mask blank according to claim 4, comprising:

an upper-medium-layer formation step of forming the upper-medium layer,

wherein

in the upper-medium-layer formation step, a target containing chromium is used, and

the upper-medium layer is formed by using a gas containing argon, methane, and nitrogen monoxide as a supply gas for the sputtering.

21. A method of manufacturing a mask blank according to claim 5, comprising:

an intermediate-layer formation step of forming the intermediate layer, wherein

in the intermediate-layer formation step, a target containing chromium is used, and

the intermediate layer is formed by using a gas containing argon and nitrogen as a supply gas for the sputtering.

22. A method of manufacturing a mask blank according to claim 6, comprising:

a surface-layer formation step of forming the surface layer;

an upper-medium-layer formation step of forming the upper-medium layer;

an intermediate-layer formation step of forming the intermediate layer; and

a light-shielding-layer formation step of forming the light-shielding layer, wherein

in the light-shielding-layer formation step, a target containing chromium is used, and

the light-shielding layer is formed by using a gas containing argon, nitrogen, and carbon dioxide as a supply gas for the sputtering.

23. The method of manufacturing a mask blank according to claim 22, wherein

a sputtering-supply power of the intermediate-layer formation step is set to be higher than a sputtering-supply power of each of the light-shielding-layer formation step, the upper-medium-layer formation step, and the surface-layer formation step.