

[DOCUMENT] SPECIFICATION

[TITLE OF THE INVENTION] MASK BLANK, PHASE SHIFT MASK, AND METHOD
OF MANUFACTURING SEMICONDUCTOR DEVICE

[Technical Field]

[0001]

This invention relates to a mask blank and a phase shift mask manufactured using the mask blank. This invention further relates to a method of manufacturing a semiconductor device using the phase shift mask.

[Background Art]

[0002]

In a manufacturing process of a semiconductor device, a fine pattern is formed using a photolithography method. A number of transfer masks are usually used to form the fine pattern. In order to miniaturize a pattern of a semiconductor device, in addition to miniaturization of a mask pattern formed in a transfer mask, it is necessary to shorten a wavelength of an exposure light source used in photolithography. In recent years, application of an ArF excimer laser (wavelength 193nm) is increasing as an exposure light source in the manufacture of semiconductor devices.

[0003]

A type of a transfer mask is a half tone phase shift mask. A phase shift film of a half tone phase shift mask formed of a material containing nitrogen and silicon is known. For example, Patent Document 1 discloses a method of manufacturing a mask blank having such a phase shift film, including a phase shift film forming step of using a silicon target or a target consisting of a material containing silicon and one or more elements selected from a metalloid element and a non-metallic element and forming a

high transmitting layer and a low transmitting layer containing relatively less nitrogen content than the high transmitting layer by reactive sputtering in sputtering gas containing nitrogen-based gas, krypton gas, and helium gas to form a phase shift film, and a heat treatment step of heating treatment at a temperature of 300°C or higher.

[0004]

Further, Patent Document 2 discloses a method of manufacturing a mask blank having such a phase shift film, including a phase shift film forming step of using a silicon target or a target consisting of a material containing silicon and one or more elements selected from a metalloid element and a non-metallic element and forming a high transmitting layer and a low transmitting layer containing relatively less nitrogen content than the high transmitting layer by reactive sputtering in sputtering gas containing nitrogen-based gas, xenon and helium gas to form a phase shift film, and a heat treatment step of heating treatment at a temperature of 180°C or higher.

[0005]

Further, Patent Document 3 discloses a method of forming a silicon nitride film effective as a mask material for X-ray lithography. Specifically, disclosed is a method of manufacturing a silicon nitride thin film by reactive sputtering at least including the step of introducing a predetermined amount of krypton gas into nitrogen gas plasma and depositing a silicon nitride thin film under a sputtering condition where internal stress of the thin film to be formed is a tensile stress.

[0006]

Further, Patent Document 4 discloses a mask blank provided with a phase shift film, the phase shift film having a structure

where a low transmitting layer and a high transmitting layer are stacked, where the low transmitting layer and the high transmitting layer are formed of a material consisting of silicon and nitrogen or a material containing such material and one or more elements selected from a metalloid element, a non-metallic element, and noble gas, and the low transmitting layer has a nitrogen content that is relatively less than the high transmitting layer.

[Prior Art Publications]

[Patent Documents]

[0007]

[Patent Document 1]

Japanese Patent Application Publication 2016-20949

[Patent Document 2]

Japanese Patent Application Publication 2016-20950

[Patent Document 3]

Japanese Patent Application Publication H08-115912

[Patent Document 4]

Japanese Patent Application Publication 2014-137388

[Summary of the Invention]

[Problems to be Solved by the Invention]

[0008]

As mentioned above, a phase shift film is conventionally known which is provided with a phase shift film having a stacked structure of a high nitrided layer with a relatively high nitrogen content and a low nitrided layer with a relatively low nitrogen content. In recent years, however, there is an increasing demand for miniaturization and complication of a mask pattern formed in a transfer mask. To cope with this demand, it is desired to further improve an in-plane uniformity of a transmittance and a phase difference required in a phase shift film. On the other hand, it

was found that improving an in-plane uniformity of a transmittance and a phase difference causes excess film stress, causing difficulty in satisfying required quality.

[0009]

This invention has been made to solve the conventional problem, and the object is to provide a mask blank including a phase shift film with a stacked structure of a high nitrided layer with a relatively high nitrogen content and a low nitrided layer with a relatively low nitrogen content, having a good in-plane uniformity of a transmittance and a phase difference, with a film stress within a tolerable range. A further object of this invention is to provide a phase shift mask manufactured using the mask blank. Yet another object of this invention is to provide a method of manufacturing a semiconductor device using such a phase shift mask.

[Means for Solving the Problem]

[0010]

For solving the above problem, this invention includes the following configurations.

(Configuration 1)

A mask blank including a phase shift film on a transparent substrate,

in which the phase shift film has a high nitrided layer and a low nitrided layer, and

in which the high nitrided layer and the low nitrided layer contain silicon, nitrogen, krypton, and xenon.

[0011]

(Configuration 2)

The mask blank according to Configuration 1, in which the high nitrided layer has a nitrogen content of 50atom% or more.

(Configuration 3)

The mask blank according to Configuration 1 or 2, in which the low nitrided layer has a nitrogen content of less than 50atom%.
[0012]

(Configuration 4)

The mask blank according to Configuration 1, in which the high nitrided layer and the low nitrided layer have a total content of silicon, nitrogen, krypton, and xenon of 90atom% or more.

(Configuration 5)

The mask blank according to any of Configurations 1 to 4, in which a total thickness of a thickness of the high nitrided layer and a thickness of the low nitrided layer is 70% or more of a thickness of the phase shift film.

(Configuration 6)

The mask blank according to any of Configurations 1 to 5, in which the phase shift film has a structure where two or more of the high nitrided layers and two or more of the low nitrided layers are stacked alternately.

[0013]

(Configuration 7)

The mask blank according to any of Configurations 1 to 6, in which the phase shift film has a function to transmit an exposure light of an ArF excimer laser at a transmittance of 2% or more, and a function to generate a phase difference of 150 degrees or more and 210 degrees or less between the exposure light transmitted through the phase shift film and the exposure light transmitted through the air for a same distance as a thickness of the phase shift film.

(Configuration 8)

The mask blank according to any of Configurations 1 to 7 including a light shielding film on the phase shift film.

[0014]

(Configuration 9)

A phase shift mask including a phase shift film having a transfer pattern formed on a transparent substrate,

in which the phase shift film has a high nitrided layer and a low nitrided layer, and

in which the high nitrided layer and the low nitrided layer contain silicon, nitrogen, krypton, and xenon.

(Configuration 10)

The phase shift mask according to Configuration 9, in which the high nitrided layer has a nitrogen content of 50atom% or more.

[0015]

(Configuration 11)

The phase shift mask according to Configuration 9 or 10, in which the low nitrided layer has a nitrogen content of less than 50atom%.

(Configuration 12)

The phase shift mask according to any of Configurations 9 to 11, in which the high nitrided layer and the low nitrided layer have a total content of silicon, nitrogen, krypton, and xenon of 90atom% or more.

[0016]

(Configuration 13)

The phase shift mask according to any of Configurations 9 to 12, in which a total thickness of a thickness of the high nitride layer and a thickness of the low nitrided layer is 70% or more of a thickness of the phase shift film.

(Configuration 14)

The phase shift mask according to any of Configurations 9 to 13, in which the phase shift film has a structure where two or

more of the high nitrided layers and two or more of the low nitrided layers are stacked alternately.

[0017]

(Configuration 15)

The phase shift mask according to any of Configurations 9 to 14, in which the phase shift film has a function to transmit an exposure light of an ArF excimer laser at a transmittance of 2% or more, and a function to generate a phase difference of 150 degrees or more and 210 degrees or less between the exposure light transmitted through the phase shift film and the exposure light transmitted through the air for a same distance as a thickness of the phase shift film.

[0018]

(Configuration 16)

The phase shift mask according to any of Configurations 9 to 15 including a light shielding film having a light shielding pattern formed on the phase shift film.

(Configuration 17)

A method of manufacturing a semiconductor device including the step of using the phase shift mask according to any of Configurations 9 to 16 and exposure-transferring a transfer pattern in a resist film on a semiconductor substrate.

[Effect of the Invention]

[0019]

The mask blank of this invention is a mask blank featured in including a phase shift film on a transparent substrate, in which the phase shift film has a high nitrided layer and a low nitrided layer, and the high nitrided layer and the low nitrided layer contain silicon, nitrogen, krypton, and xenon. Creating a mask blank of the above structure can achieve a phase shift film having

a stacked structure of a high nitrided layer with a high nitrogen content and a low nitrided layer with a low nitrogen content, having a good in-plane uniformity of a transmittance and a phase difference, with a film stress within a tolerable range.

[0020]

Further, the phase shift mask of this invention is featured in that a phase shift film having a transfer pattern has a configuration that is similar to the phase shift film of the mask blank of this invention. Creating such a phase shift mask can achieve a phase shift film having a stacked structure of a high nitrided layer with a high nitrogen content and a low nitrided layer with a low nitrogen content, having a good in-plane uniformity of a transmittance and a phase difference, with a film stress within a tolerable range. Therefore, high transfer precision can be provided with the phase shift mask of this invention.

[Brief Description of the Drawings]

[0021]

[FIG. 1] FIG. 1 is a cross-sectional view showing a configuration of the mask blank of the embodiment of this invention.

[FIG. 2] FIG. 2 is a cross-sectional view showing a manufacturing process of the phase shift mask of the embodiment of this invention.

[FIG. 3] FIG. 3 is a graph showing the relationship of an in-plane distribution of a phase shift amount and a flatness of the mask blank in Examples 1 and 2 and Comparative Examples 1 and 2 of this invention.

[FIG. 4] FIG. 4 is a graph showing the relationship of an in-plane distribution of a transmittance and a flatness of the mask blank in Examples 1 and 2 and Comparative Examples 1 and 2 of this invention.

[FIG. 5] FIG. 5 is a graph showing an observation result of HR-RBS of Example 2 of this invention.

[FIG. 6] FIG. 6 is a graph showing an observation result of HR-RBS of Comparative Example 2 of this invention.

[Embodiments for Carrying Out the Invention]

[0022]

First, the proceeding that has resulted in the completion of this invention is described. The inventors studied diligently on a mask blank including a phase shift film having a stacked structure of a high nitrided layer with a relatively high nitrogen content and a low nitrided layer with a relatively low nitrogen content, having a good in-plane uniformity of a transmittance and a phase difference, with a film stress within a tolerable range.

[0023]

Generally, there are two major methods given below in forming a thin film of a metal compound through sputtering.

One method is to form in advance a sputtering target from a metal compound having the same composition as the thin film. In this case, sputtering particles are stacked on a substrate by sputtering using only noble gas as sputtering gas to form a thin film of a metal compound on the substrate.

A second method is to form a sputtering target from a metal having the same metal component as the thin film. In this case, sputtering particles and non-metallic element compound are stacked on a substrate by reactive sputtering using mixed gas of gas containing the non-metallic element of the thin film (e.g., N₂ gas) and noble gas as sputtering gas to form a thin film of a metal compound on the substrate.

[0024]

In a phase shift film including a stacked structure of a

high nitrided layer having a relatively high nitrogen content and a low nitrided layer having a relatively low nitrogen content, in forming the film by the second method described above, the degree of nitridation of each layer formed on the substrate is adjusted by increasing or decreasing the flow rate ratio of nitrogen gas in sputtering gas, using a Si target and reactive sputtering using mixed gas of N₂ gas (reactive gas) and Kr gas and He gas (noble gas) as the sputtering gas. While the inventors initially examined the adjustment of film forming conditions such as flow rate ratio of each gas in the sputtering gas, gas pressure in the sputtering chamber, sputtering power, etc., sufficient improvement could not be made.

[0025]

Next, the inventors attempted to form a film by removing He gas from noble gas of sputtering gas (i.e., the sputtering gas includes only N₂ gas and Kr gas). As a result, an in-plane uniformity of a phase difference and in-plane uniformity of a transmittance of the phase shift film could be increased to a desired range. However, since a film stress of this phase shift film was further increased (stress to cause large deformation of substrate in convex direction; absolute value of the stress is larger than before the change), it was necessary to find a film forming method for simultaneously reducing the film stress.

As a result of further study, the inventors found forming a phase shift film by reactive sputtering using mixed gas containing Kr gas and Xe gas as noble gas of the sputtering gas. It was found that the phase shift film formed by the film forming method has a height in which a uniformity of an in-plane phase difference and a uniformity of an in-plane transmittance with respect to an ArF exposure light satisfy a predetermined standard, and the film

stress after annealing treatment is also within a range without issue. In addition, it was found that even when a film is formed by a method where a sputtering target is formed in advance with a metal compound having the same composition as the phase shift film, using mixed gas containing Kr gas and Xe gas as noble gas of the sputtering gas can achieve a height in which a uniformity of an in-plane phase difference and a uniformity of an in-plane transmittance with respect to an ArF exposure light satisfy a predetermined standard, and a film stress after annealing treatment is also within a range without issue.

The inventors estimate that by using mixed gas containing Kr gas and Xe gas as the noble gas of the sputtering gas, the spread of plasma distribution of the mixed gas in a film forming chamber upon film formation is improved, thereby obtaining the above-mentioned effect. However, this estimation is based on the inference by the inventors as of the filing of this application, which by no means limits the scope of this invention.

[0026]

Thus, the mask blank of this invention is a mask blank featured in including a phase shift film on a transparent substrate, in which the phase shift film has a high nitrided layer and a low nitrided layer, and the high nitrided layer and the low nitrided layer contain silicon, nitrogen, krypton, and xenon.

[0027]

Next, each embodiment for carrying out this invention is explained. FIG. 1 is a cross-sectional view showing a configuration of a mask blank 100 of an embodiment of this invention. The mask blank 100 shown in FIG. 1 has a structure where a transparent substrate 1 has a phase shift film 2, a light shielding film 3, and a hard mask film 4 stacked thereon in this order.

[0028]

The transparent substrate 1 can be formed of quartz glass, aluminosilicate glass, soda-lime glass, low thermal expansion glass ($\text{SiO}_2\text{-TiO}_2$ glass, etc.), etc., in addition to synthetic quartz glass. Among these materials, synthetic quartz glass has a high transmittance to an ArF excimer laser light (wavelength: 193nm), which is particularly preferable as a material for forming a transparent substrate of a mask blank.

[0029]

To exhibit effective phase shifting effect, the phase shift film 2 has a transmittance to an ArF excimer laser exposure light (hereafter referred to as ArF exposure light) of preferably 1% or more, and more preferably 2% or more. Further, the phase shift film 2 is preferably adjusted so that a transmittance to an ArF exposure light is 30% or less, more preferably 20% or less, and even more preferably 18% or less.

Further, the phase shift film 2 preferably has an in-plane distribution (in-plane uniformity) of a transmittance to an ArF exposure light of within 0.2% or less ($\pm 0.2\%$) at an absolute value to a target value, and more preferably 0.18% or less (within $\pm 0.18\%$) at an absolute value.

[0030]

To obtain a proper phase shifting effect, it is necessary for the phase shift film 2 to have a function to generate a predetermined phase difference between the transmitting an ArF exposure light and the light transmitted through the air for the same distance as the thickness of the phase shift film 2. The phase difference is preferably adjusted within the range of 150 degrees or more and 210 degrees or less. The lower limit of the phase difference in the phase shift film 2 is preferably 160 degrees or

more, and more preferably 170 degrees or more. On the other hand, the upper limit of the phase difference of the phase shift film 2 is preferably 200 degrees or less, and more preferably 190 degrees or less.

Further, the phase shift film 2 preferably has an in-plane distribution (in-plane uniformity) of a phase difference to an ArF exposure light of 1.0 degree or less (± 1.0 degree) at an absolute value to a target value.

[0031]

The phase shift film 2 of this invention at least includes a structure having one set of stacked structure of a high nitrided layer 22 and a low nitrided layer 21 (two-layer structure). The phase shift film 2 of this invention preferably includes a structure in which two or more high nitrided layers 22 and two or more low nitrided layers 21 are stacked alternately, from the viewpoint of controllability of pattern sidewalls when the phase shift film 2 is patterned by etching. The phase shift film 2 of FIG. 1 includes five sets of a stacked structure set consisting of the high nitrided layer 22 and the low nitrided layer 21. This phase shift film 2 has a structure including five sets of a stacked structure set including the high nitrided layer 22 and the low nitrided layer 21 stacked in this order from the side of the transparent substrate 1, and an uppermost layer 23 further stacked on the topmost low nitrided layer 21.

[0032]

The high nitrided layer 22 and the low nitrided layer 21 are formed of a material containing silicon, nitrogen, krypton, and xenon. Noble gas including krypton and xenon is an element which, when present in a film forming chamber in forming a thin film by reactive sputtering, can increase deposition rate to enhance

productivity. The noble gas is plasmarized and collided on the target so that target constituent elements eject out from the target, and while incorporating reactive gas on the way, are stacked on the transparent substrate 1 to form a thin film. While the target constituent elements eject out from the target until adhered on the transparent substrate, a small amount of noble gas in the film forming chamber is incorporated. As mentioned above, the phase shift film 2 can be formed to have a good in-plane uniformity of a transmittance and a phase difference and with a film stress of a tolerable range by using krypton and xenon as noble gas needed in the reactive sputtering.

[0033]

From the viewpoint of light fastness to an ArF exposure light, it is preferable that the low nitrided layer 21 and the high nitrided layer 22 have a transition metal content of less than 1atom%, more preferably, free of a transition metal. It is preferable that the high nitrided layer 22 and the low nitrided layer 21 are also free of metal elements excluding a transition metal, in view of light fastness to an ArF exposure light. The high nitrided layer 22 and the low nitrided layer 21 are preferably formed of a material consisting of silicon, nitrogen, krypton, and xenon, or a material consisting of silicon, nitrogen, krypton, xenon, and one or more elements selected from a metalloid element and a non-metallic element. The high nitrided layer 22 and the low nitrided layer 21 can contain any metalloid elements in addition to silicon. Among these metalloid elements, it is preferable to include one or more elements selected from boron, germanium, antimony, and tellurium, since enhancement in conductivity of silicon to be used as a sputtering target can be expected.

[0034]

The high nitrided layer 22 and the low nitrided layer 21 can contain any non-metallic elements in addition to silicon, nitrogen, krypton, and xenon. The non-metallic elements in this invention refer to those including non-metallic elements in a narrow sense (nitrogen, carbon, oxygen, phosphorus, sulfur, selenium), halogen, and noble gas other than krypton and xenon. Among these non-metallic elements, it is preferable to include one or more elements selected from carbon, fluorine, and hydrogen. In the high nitrided layer 22 and the low nitrided layer 21, it is preferable that an oxygen content is reduced to 10atom% or less, more preferably 5atom% or less, and further preferable not to positively include oxygen (lower detection limit or less when composition analysis was conducted by X-ray photoelectron spectroscopy, etc.). An extinction coefficient k tends to significantly decrease when a silicon nitride-based material film contains oxygen, causing increase in overall thickness of the phase shift film 2.

Total content of silicon, nitrogen, krypton, and xenon of the high nitrided layer 22 and the low nitrided layer 21 is preferably 90atom% or more, more preferably 95atom% or more, even more preferably 98atom% or more, and further preferably 99atom% or more.

[0035]

A transparent substrate is generally formed of a material containing SiO_2 such as synthetic quartz glass as a main component. In the case where any one of the high nitrided layer 22 and the low nitrided layer 21 is formed in contact with a surface of the transparent substrate 1 and if the layer contains oxygen, difference between the composition of the silicon nitride-based material film containing oxygen and the glass composition becomes small, which may cause a problem where, in dry etching using

fluorine-based gas conducted in forming a pattern in the phase shift film 2, it will be difficult to obtain an etching selectivity between the layer in contact with the transparent substrate 1 (high nitrided layer 22 or low nitrided layer 21) and the transparent substrate 1.

[0036]

The high nitrided layer 22 and the low nitrided layer 21 can contain any noble gas other than krypton and xenon. However, from the viewpoint of mitigating film stress and in-plane uniformity, it is preferable not to positively include noble gas other than krypton and xenon. Namely, noble gas is preferably only krypton and xenon.

[0037]

The high nitrided layer 22 preferably has 50atom% or more nitrogen content. A silicon-based film has an extremely small refractive index n to an ArF exposure light, and has a large extinction coefficient k to an ArF exposure light (hereafter, simple refractive index n refers to a refractive index n to an ArF exposure light; simple extinction coefficient k refers to an extinction coefficient k to an ArF exposure light). As a nitrogen content in the silicon-based film increases, a refractive index n tends to increase and an extinction coefficient k tends to decrease. To secure a transmittance required in the phase shift film 2 and also to secure a phase difference required in less thickness, the high nitrided layer 22 preferably has 50atom% or more nitrogen content. The high nitrided layer 22 preferably has 52atom% or more nitrogen content. Further, a nitrogen content of the high nitrided layer 22 is preferably 57atom% or less, and more preferably 55atom% or less.

[0038]

The low nitrided layer 21 preferably has a nitrogen content of less than 50atom%. The low nitrided layer 21 preferably has a nitrogen content of 48atom% or less, and more preferably 45atom% or less. Further, the low nitrided layer 21 preferably has a nitrogen content of 20atom% or more, and more preferably 25atom% or more. To secure a transmittance required in the phase shift film 2 and also to secure a phase difference required in less thickness, the low nitrided layer 21 preferably has a nitrogen content of 20atom% or more.

[0039]

The high nitrided layer 22 and the low nitrided layer 21 are preferably made of the same constituent elements. In the case where any of the high nitrided layer 22 and the low nitrided layer 21 includes a different constituent element and heat treatment or photoirradiation treatment was conducted or an ArF exposure light was irradiated while the layers are stacked in contact with each other, the different constituent element may migrate and disperse to the layer free of the constituent element. This may cause significant change in optical characteristics of the high nitrided layer 22 and the low nitrided layer 21 from the start of the film formation. Particularly, if the different constituent element is a metalloid element, it would be necessary to form the high nitrided layer 22 and the low nitrided layer 21 using different targets.

The high nitrided layer 22 of this embodiment preferably has a transmittance to an ArF exposure light higher than that of the low nitrided layer 21. In this case, the high nitrided layer 22 functions as a high transmitting layer, and the low nitrided layer 21 as a low transmitting layer.

[0040]

The high nitrided layer 22 and the low nitrided layer 21 are preferably formed of a material containing silicon, nitrogen, krypton, and xenon. Incidentally, noble gas such as krypton and xenon is an element that is difficult to detect even if the thin film is subjected to composition analysis such as RBS (Rutherford Back-Scattering Spectrometry) and XPS (X-ray Photoelectron Spectroscopy). The high nitrided layer 22 and the low nitrided layer 21 preferably contain krypton and xenon at a level that is detected by HR-RBS (high-resolution Rutherford backscattering spectroscopy). Further, the high nitrided layer 22 and the low nitrided layer 21 preferably contain krypton and xenon at a level that is detected by an ordinary RBS or XPS composition analysis.

[0041]

The high nitrided layer 22 preferably has a thickness of 20nm or less from the viewpoint of controllability, etc. of a pattern sidewall in patterning the high nitrided layer 22 by etching. A thickness of the high nitrided layer 22 is preferably 15nm or less, and more preferably 10nm or less. On the other hand, a thickness of the high nitrided layer 22 is preferably 3nm or more, more preferably 4nm or more, and even more preferably 5nm or more. When the high nitrided layer 22 has a thickness of less than 3nm, it would be necessary to form the low nitrided layer 21 thinner, as will be mentioned below. Such a thin low nitrided layer 21 will only include a mixed region containing a mixture of constituent elements of the low transmitting layer and constituent elements of the high transmitting layer (about 0.1 to 2nm), and may be unable to obtain optical characteristics desired for the low nitrided layer 21. Incidentally, a thickness of the high nitrided layer 22 herein includes the mixed region.

[0042]

The low nitrided layer 21 preferably has a thickness less than a thickness of the high nitrided layer 22. If the low nitrided layer 21 has more thickness than a thickness of the high nitrided layer 22, desired transmittance and phase difference are unlikely to be obtained from such a phase shift film 2. A thickness of the low nitrided layer 21 is preferably 15nm or less, and more preferably 10nm or less. A thickness of the low nitrided layer 21 is preferably 2nm or more, and more preferably 3nm or more.

[0043]

A thickness of the low nitrided layer 21 is preferably $1/2$ or less than a thickness of the high nitrided layer 22. The low nitrided layer 21 has a less refractive index n to an ArF exposure light than the high nitrided layer 22, and has a large extinction coefficient k to an ArF exposure light. Therefore, when a total film thickness of the low nitrided layer is greater than $1/2$ of a total film thickness of the high nitrided layer, it will be difficult to adjust the phase shift film 2 to desired transmittance and phase difference.

[0044]

The number of sets of the stacked structure of the high nitrided layer 22 and the low nitrided layer 21 of the phase shift film 2 is preferably two sets (total of four layers) or more, and more preferably four sets (total of eight layers) or more. Further, the number of sets of the stacked structure including the high nitrided layer 22 and the low nitrided layer 21 of the phase shift film 2 is preferably ten sets (total of 20 layers) or less, more preferably nine sets (total of 18 layers) or less, and even more preferably eight sets (total of 16 layers) or less. The high nitrided layer 22 and the low nitrided layer 21 of the phase shift film 2 are preferably of a structure where the layers are directly

stacked in contact with each other without any intervening film.

[0045]

From the viewpoint of end point detection precision of EB defect repair (this "EB defect repair" refers to a defect repair where electron beam is irradiated on a black defect portion of a thin film pattern while supplying gas containing fluorine such as XeF_2 to remove the black defect) on the phase shift film 2, the stacked structure of the high nitrided layer 22 and the low nitrided layer 21 is preferably stacked in the order of the high nitrided layer 22 and the low nitrided layer 21 from the transparent substrate 1 side.

[0046]

The transparent substrate 1 is formed of a material including silicon oxide as a main component. It is more advantageous for end point detection of EB defect repair to arrange the high nitrided layer 22 with a large amount of nitrogen content on the layer of the phase shift film 2 in contact with the transparent substrate 1.

[0047]

On the other hand, in forming a pattern in the phase shift film 2 of a silicon nitride-based material by dry etching, fluorine-based gas is generally used which has relatively small etching rate of dry etching to the transparent substrate 1 such as SF_6 . In dry etching using fluorine-based gas such as SF_6 , the low nitrided layer 21 with less nitrogen content can achieve higher etching selectivity between the transparent substrate 1. From the viewpoint of dry etching on the phase shift film 2, the stacked structure of the high nitrided layer 22 and the low nitrided layer 21 is preferably stacked in the order of the low nitrided layer 21 and the high nitrided layer 22 from the transparent substrate 1

side.

[0048]

The high nitrided layer 22 is preferably formed of a material where a refractive index n to an ArF exposure light is 2.5 or more (preferably 2.6 or more) and an extinction coefficient k is less than 1.0 (preferably 0.9 or less, more preferably 0.7 or less, further preferably 0.5 or less). Further, the low nitrided layer 21 is preferably formed of a material where a refractive index n is less than 2.5 (preferably 2.4 or less, more preferably 2.2 or less) and an extinction coefficient k is 1.0 or more (preferably 1.1 or more, more preferably 1.4 or more). This is because, in the case where the phase shift film 2 was formed with a stacked structure with six or more layers, it is difficult to satisfy a predetermined phase difference and a predetermined transmittance to an ArF exposure light which are optical characteristics required as the phase shift film 2, unless each of the high nitrided layer 22 and the low nitrided layer 21 is within a refractive index n and an extinction coefficient k of the above range.

[0049]

A refractive index n and an extinction coefficient k of a thin film are not determined only by the composition of the thin film. Film density and crystal condition of the thin film are also the factors that affect a refractive index n and an extinction coefficient k . Therefore, various conditions in forming the thin film by reactive sputtering are adjusted so that the thin film achieves desired refractive index n and extinction coefficient k . For allowing the high nitrided layer 22 and the low nitrided layer 21 to have a refractive index n and an extinction coefficient k of the above range, not only the ratio of mixed gas of noble gas and reactive gas is adjusted in forming the film by reactive sputtering,

but various other adjustments are made upon forming a film by reactive sputtering, such as pressure in a film forming chamber, power applied to the target, and positional relationship such as distance between the target and the transparent substrate. Further, these film forming conditions are unique to film forming apparatuses which are adjusted arbitrarily so that the thin film to be formed reaches desired refractive index n and extinction coefficient k .

[0050]

While the high nitrided layer 22 and the low nitrided layer 21 are formed by sputtering, any sputtering method is applicable such as DC sputtering, RF sputtering, and ion beam sputtering. In the case of using a target with low conductivity (silicon target, silicon compound target free of or including a small amount of metalloid element, etc.), application of RF sputtering and ion beam sputtering is preferable. However, application of RF sputtering is more preferable, considering the deposition rate.

[0051]

A total thickness of a thickness of the high nitrided layer 22 and a thickness of the low nitrided layer 21 is preferably 70% or more of a thickness of the phase shift film 2, and more preferably, 80% or more. Further, a total thickness of a thickness of the high nitrided layer 22 and a thickness of the low nitrided layer 21 is preferably 95% or less of a thickness of the phase shift film 2, considering providing an uppermost layer to be mentioned below. In the case where there is a plurality of layers of the high nitrided layers 22 and/or the low nitrided layers 21 in the phase shift film 2, a total thickness of a thickness of the high nitrided layers 22 and a thickness of the low nitrided layers 21 mentioned above is calculated as a total thickness of a

thickness of all high nitrided layers 22 in the phase shift film 2 combined and a thickness of all low nitrided layers 21 in the phase shift film 2 combined. On the other hand, a thickness of the phase shift film 2 is preferably 50nm or more. Further, a thickness of the phase shift film 2 is preferably 90nm or less, more preferably 80nm or less, and even more preferably 70nm or less.

[0052]

The method of manufacturing the mask blank 100 preferably includes a high nitrided layer forming step of forming the high nitrided layer 22 on the transparent substrate 1 by reactive sputtering using a silicon target or a target consisting of silicon and one or more elements selected from a metalloid element and a non-metallic element in sputtering gas including nitrogen-based gas and noble gas; and a low nitrided layer forming step of forming the low nitrided layer 21 on the transparent substrate 1 by reactive sputtering using a silicon target or a target consisting of silicon and one or more elements selected from a metalloid element and a non-metallic element in sputtering gas including nitrogen-based gas and noble gas which has a low mixing ratio of nitrogen-based gas than the high nitrided layer forming step.

[0053]

Further, in the method of manufacturing the mask blank 100, it is preferable that sputtering gas used in the high nitrided layer forming step is selected to have a mixing ratio of nitrogen gas that is more than the range of a mixing ratio of nitrogen gas of a transition mode in which film formation tends to be unstable, i.e., poison mode (reaction mode), and sputtering gas used in the low nitrided layer forming step is selected to have a mixing ratio of nitrogen-based gas that is less than the range of a mixing ratio of nitrogen-based gas of a transition mode, i.e., metal mode.

[0054]

Nitrogen-based gas used in the high nitrided layer forming step and the low nitrided layer forming step can be any gas as long as the gas contains nitrogen. As mentioned above, since it is preferable that the high nitrided layer 22 and the low nitrided layer 21 have less oxygen content, it is preferable to apply nitrogen-based gas free of oxygen, and it is preferable to apply nitrogen gas (N_2 gas). Further, noble gas used in the high nitrided layer forming step and the low nitrided layer forming step preferably includes krypton and xenon, and more preferably, only krypton and xenon.

[0055]

The phase shift film 2 is preferably provided with an uppermost layer 23 at a position farthest from the transparent substrate 1 and which is formed of a material containing silicon and oxygen. A silicon-based material film that does not positively contain oxygen but contains nitrogen has high light fastness to an ArF exposure light; however, it tends to have low chemical resistance compared to a silicon-based material film that positively contains oxygen. Further, in the case of a mask blank 100 where the high nitrided layer 22 or the low nitrided layer 21 that does not positively contain oxygen and which contains nitrogen is arranged as the uppermost layer 23 at an opposite side to the transparent substrate 1 of the phase shift film 2, it is difficult to avoid oxidization of the surface layer of the phase shift film 2 by subjecting the phase shift mask 200 manufactured from the mask blank 100 to mask cleaning and storage in the atmosphere. In the case of the phase shift film 2 of such a configuration, when a surface layer thereof is oxidized, the optical characteristics change significantly from those as of the thin film formation.

Particularly, in the case of a configuration where the low nitrided layer 21 is provided as the uppermost layer 23 of the phase shift film 2, there will be a significant increase of transmittance due to oxidization of the low nitrided layer 21. By further providing the phase shift film 2 with the uppermost layer 23 which is formed of a material containing silicon and oxygen on the stacked structure of the high nitrided layer 22 and the low nitrided layer 21, surface oxidization of the high nitrided layer 22 and the low nitrided layer 21 can be inhibited.

[0056]

On the other hand, the uppermost layer 23 can be formed of a material containing silicon, oxygen, krypton, and xenon. From the viewpoint of light fastness to an ArF exposure light, it is preferable that the uppermost layer 23 has a transition metal content of less than 1atom%, more preferably, free of transition metal. Further, it is preferable that the uppermost layer 23 is also free of metal elements excluding transition metal, in view of light fastness to an ArF exposure light. It is more preferable that the uppermost layer 23 further contains nitrogen. By the aforementioned configuration, surface oxidization of the high nitrided layer 22 and the low nitrided layer 21 can be inhibited, while reducing the thickness of the phase shift film 2 in entirety.

[0057]

The uppermost layer 23 is preferably formed of a material consisting of silicon, nitrogen, oxygen, krypton, and xenon, or a material consisting of silicon, nitrogen, oxygen, krypton, xenon, and one or more elements selected from a metalloid element and a non-metallic element. The uppermost layer 23 can contain any metalloid element in addition to silicon. The matters regarding the metalloid element and the non-metallic element are similar to

the case of the high nitrided layer 22 and the low nitrided layer 21 mentioned above. A total content of silicon, nitrogen, oxygen, krypton, and xenon of the uppermost layer 23 is preferably 90atom% or more, more preferably 95atom% or more, and even more preferably 98atom% or more.

[0058]

A thickness of the uppermost layer 23 is preferably 15nm or less, and more preferably 10nm or less. On the other hand, a thickness of the uppermost layer 23 is preferably 2nm or more, more preferably 3nm or more, and even more preferably 4nm or more. While the uppermost layer 23 is formed by sputtering, any sputtering method is applicable such as DC sputtering, RF sputtering, and ion beam sputtering. In the case of using a target with low conductivity (silicon target, silicon compound target free of or including a small amount of metalloid element, etc.), application of RF sputtering and ion beam sputtering is preferable. However, application of RF sputtering is more preferable, considering the deposition rate.

[0059]

The phase shift film 2 is preferably within a film stress where an absolute value of a flatness variation is 0.2 μ m or less, and more preferably 0.15 μ m or less, the flatness variation being calculated from a shape difference between the surface shape of the main surface of the transparent substrate 1 before formation of the phase shift film 2 and the surface shape of the phase shift film 2 after formation of the phase shift film 2 on the transparent substrate 1 and subjected to annealing treatment (heating treatment).

[0060]

The mask blank 100 preferably has a light shielding film 3

on the phase shift film 2. Generally in the phase shift mask 200 (see FIG. 2), an outer peripheral region of a region in which a transfer pattern is formed (transfer pattern forming region) is desired to secure a predetermined value or more optical density (OD) so that the resist film is not affected by an exposure light that is transmitted through the outer peripheral region when the resist film on a semiconductor wafer is exposure-transferred using an exposure apparatus. The outer peripheral region of the phase shift mask 200 is at least required have an optical density of more than 2.0. The phase shift film 2 has a function to transmit an exposure light at a predetermined transmittance as mentioned above, and it is difficult to ensure the above optical density with the phase shift film 2 alone. Therefore, it is preferable to stack the light shielding film 3 on the phase shift film 2 at the stage of manufacturing the mask blank 100 to ensure optical density that is lacking. With such a configuration of the mask blank 100, the phase shift mask 200 ensuring the above optical density on the outer peripheral region can be manufactured by removing the light shielding film 3 of the region using the phase shifting effect (basically, transfer pattern forming region) during manufacture of the phase shift film 2. Incidentally, in the mask blank 100, the optical density of the stacked structure of the phase shift film 2 and the light shielding film 3 is preferably 2.5 or more, and more preferably 2.8 or more. Further, for reducing the film thickness of the light shielding film 3, the stacked structure of the phase shift film 2 and the light shielding film 3 preferably has an optical density of 4.0 or less.

[0061]

A single layer structure and a stacked structure of two or more layers are applicable to the light shielding film 3. Further,

each layer in the light shielding film 3 of a single layer structure and the light shielding film 3 with a stacked structure of two or more layers can be configured by approximately the same composition in the thickness direction of the film or the layer, or with a composition gradient in the thickness direction of the layer.

[0062]

In the case where the light shielding film 3 has no intervening film between the phase shift film 2, it is necessary to apply a material having sufficient etching selectivity to etching gas used in forming a pattern in the phase shift film 2. The light shielding film 3 in this case is preferably formed of a material containing chromium. Materials containing chromium for forming the light shielding film 3 can include, in addition to chromium metal, a material containing chromium and one or more elements selected from oxygen, nitrogen, carbon, boron, and fluorine.

[0063]

While a chromium-based material is generally etched with mixed gas of chlorine-based gas and oxygen gas, the etching rate of chromium metal to the etching gas is not as high. Considering enhancing an etching rate of mixed gas of chlorine-based gas and oxygen gas to etching gas, the material forming the light shielding film 3 preferably includes chromium and one or more elements selected from oxygen, nitrogen, carbon, boron, and fluorine. Further, one or more elements among molybdenum and tin can be included in the material containing chromium for forming the light shielding film 3. Including one or more elements among molybdenum and tin can increase etching rate to mixed gas of chlorine-based gas and oxygen gas.

[0064]

On the other hand, in the case of a configuration where another film is interposed between the light shielding film 3 and the phase shift film 2 in the mask blank 100, it is preferable to form another film (etching stopper and etching mask film) from the material containing chromium, and form the light shielding film 3 from a material containing silicon. While the material containing chromium is etched by mixed gas of chlorine-based gas and oxygen gas, a resist film formed of an organic material is likely to be etched by this mixed gas. A material containing silicon is generally etched by fluorine-based gas or chlorine-based gas. Since these etching gases are basically free of oxygen, film reduction amount of a resist film made of an organic material can be reduced more than etching with mixed gas of chlorine-based gas and oxygen gas. Therefore, film thickness of the resist film can be reduced.

[0065]

A material containing silicon for forming the light shielding film 3 can include a transition metal, and can include metal elements other than the transition metal. The reason is that in the case where the phase shift mask 200 was manufactured from this mask blank 100, a pattern formed by the light shielding film 3 is basically a light shielding band pattern of an outer peripheral region having less accumulation of irradiation with an ArF exposure light compared to a transfer pattern forming region, and the light shielding film 3 rarely remains in a fine pattern so that substantial problems hardly occur even if ArF light fastness is low. Another reason is that when a transition metal is included in the light shielding film 3, light shielding performance is significantly improved compared to the case without the transition

metal, and a thickness of the light shielding film can be reduced. The transition metals to be included in the light shielding film 3 include any one of metals such as molybdenum (Mo), tantalum (Ta), tungsten (W), titanium (Ti), chromium (Cr), hafnium (Hf), nickel (Ni), vanadium (V), zirconium (Zr), ruthenium (Ru), rhodium (Rh), niobium (Nb), and palladium (Pd), or an alloy thereof.

[0066]

On the other hand, a material consisting of silicon and nitrogen, or a material consisting of silicon, nitrogen, and one or more elements selected from a metalloid element and a non-metallic element can be applied as a material containing silicon for forming the light shielding film 3.

[0067]

In the mask blank 100 having the light shielding film 3 stacked on the phase shift film 2, a preferable configuration is that a hard mask film 4 formed of a material having etching selectivity to etching gas used in etching the light shielding film 3 is further stacked on the light shielding film 3. Since the light shielding film 3 must have a function to secure a predetermined optical density, there is a limitation to reduce its thickness. The hard mask film 4 only needs to have a film thickness that can function as an etching mask until completion of dry etching for forming a pattern in the light shielding film 3 immediately below, and basically is not optically limited. Therefore, a thickness of the hard mask film 4 can be reduced significantly compared to a thickness of the light shielding film 3. The resist film of an organic-based material only needs to have a film thickness that can function as an etching mask until dry etching for forming a pattern in the hard mask film 4 is completed. Therefore, a thickness of a resist film can be reduced

significantly compared to conventional cases.

[0068]

In the case where the light shielding film 3 is formed of a material containing chromium, the hard mask film 4 is preferably formed of the material containing silicon given above. Since the hard mask film 4 in this case tends to have low adhesiveness with a resist film of an organic material, it is preferable to treat a surface of the hard mask film 4 with HMDS (Hexamethyldisilazane) to enhance surface adhesiveness. The hard mask film 4 in this case is more preferably formed of SiO_2 , SiN , SiON , etc. Further, in the case where the light shielding film 3 is formed of a material containing chromium, materials containing tantalum are also applicable as the materials of the hard mask film 4, in addition to the materials given above. The material containing tantalum in this case includes, in addition to tantalum metal, a material containing tantalum and one or more elements selected from nitrogen, oxygen, boron, and carbon, for example, Ta , TaN , TaON , TaBN , TaBON , TaCN , TaCON , TaBCN , and TaBOCN . On the other hand, in the case where the light shielding film 3 is formed of a material containing silicon, the hard mask film 4 is preferably formed of the material containing chromium given above.

[0069]

In the mask blank 100, an etching stopper film can be formed between the transparent substrate 1 and the phase shift film 2, which consists of a material having etching selectivity (the material containing chromium given above, e.g., Cr , CrN , CrC , CrO , CrON , CrC) together with the transparent substrate 1 and the phase shift film 2. Incidentally, this etching stopper film can be formed of a material containing aluminum.

[0070]

In the mask blank 100, a resist film of an organic material is preferably formed in contact with a surface of the hard mask film 4 at a film thickness of 100nm or less. In the case of a fine pattern applicable to DRAM hp32nm generation, a SRAF (Sub-Resolution Assist Feature) with 40nm line width may be provided on a transfer pattern (phase shift pattern) to be formed in the hard mask film 4. However, even in this case, the cross-sectional aspect ratio of the resist pattern can be reduced to 1:2.5 so that collapse and peeling of the resist pattern can be prevented in rinsing and developing, etc. of the resist film. Incidentally, the resist film preferably has a film thickness of 80nm or less.

[0071]

FIG. 2 is a schematic cross-sectional view showing the steps of manufacturing the phase shift mask 200 from the mask blank 100 of an embodiment of this invention.

[0072]

The phase shift mask 200 of this invention is featured in the phase shift mask 200 including a phase shift film 2 (phase shift pattern 2a) having a transfer pattern on a transparent substrate 1, in which the phase shift film 2 includes a high nitrided layer 22 and a low nitrided layer 21, and the high nitrided layer 22 and the low nitrided layer 21 contain silicon, nitrogen, krypton, and xenon.

[0073]

The phase shift mask 200 has a technical feature that is similar to the mask blank 100. The matters of the phase shift mask 200 regarding the transparent substrate 1, the high nitrided layer 22 and the low nitrided layer 21 of the phase shift film 2, and the light shielding film 3 are similar to the mask blank 100. Therefore, the phase shift mask 200 can be provided which has a

phase shift film 2 (phase shift pattern 2a) having a good in-plane uniformity of a transmittance and a phase difference and with a film stress of a tolerable range.

[0074]

Further, the method of manufacturing the phase shift mask 200 of this invention is featured in utilizing the mask blank 100 described above, including the steps of forming a transfer pattern to be formed in the phase shift film 2 in the later step in the light shielding film 3 by dry etching, forming a transfer pattern in the phase shift film 2 by dry etching with the light shielding film 3 (light shielding pattern 3a) having a transfer pattern as a mask, and forming a pattern including a light shielding band (light shielding pattern 3b) in the light shielding film 3 (light shielding pattern 3a) by dry etching with a resist film (resist pattern 6b) having a pattern including a light shielding band as a mask.

[0075]

One example of the method of manufacturing the phase shift mask 200 is explained below according to the manufacturing steps shown in FIG. 2. In this example, a material containing chromium is used for the light shielding film 3, and a material containing silicon is used for the hard mask film 4.

[0076]

First, a resist film was formed in contact with the hard mask film 4 of the mask blank 100 by spin coating. Next, a first pattern, which is a transfer pattern (phase shift pattern) to be formed in the phase shift film 2, was exposed and written in the resist film, and predetermined treatments such as developing were further conducted, to thereby form a first resist pattern 5a having a phase shift pattern (see FIG. 2(a)). Subsequently, dry etching

was conducted using fluorine-based gas with the first resist pattern 5a as a mask, and a first pattern (hard mask pattern 4a) was formed in the hard mask film 4 (see FIG. 2(b)).

[0077]

Next, after removing the resist pattern 5a, dry etching was conducted using mixed gas of chlorine-based gas and oxygen gas with the hard mask pattern 4a as a mask, and a first pattern (light shielding pattern 3a) was formed in the light shielding film 3 (see FIG. 2(c)). Subsequently, dry etching was conducted using fluorine-based gas with the light shielding pattern 3a as a mask, and a first pattern (phase shift pattern 2a) was formed in the phase shift film 2, and at the same time the hard mask pattern 4a was removed (see FIG. 2(d)).

[0078]

Next, a resist film was formed on the mask blank 100 by spin coating. Next, a second pattern, which is a pattern (light shielding pattern) to be formed in the light shielding film 3, was exposed and written in the resist film, and predetermined treatments such as developing were further conducted, to thereby form a second resist pattern 6b having a light shielding pattern. Subsequently, dry etching was conducted using mixed gas of chlorine-based gas and oxygen gas with the second resist pattern 6b as a mask, and a second pattern (light shielding pattern 3b) was formed in the light shielding film 3 (see FIG. 2(e)). Further, the second resist pattern 6b was removed, predetermined treatments such as cleaning were conducted, and the phase shift mask 200 was obtained (see FIG. 2(f)).

[0079]

There is no particular limitation to chlorine-based gas to be used for the dry etching described above, as long as Cl is

included. The chlorine-based gas includes, for example, Cl_2 , SiCl_2 , CHCl_3 , CH_2Cl_2 , CCl_4 , and BCl_3 . Further, there is no particular limitation to fluorine-based gas to be used for the dry etching described above, as long as F is included. The fluorine-based gas includes, for example, CHF_3 , CF_4 , C_2F_6 , C_4F_8 , and SF_6 . Particularly, fluorine-based gas free of C can further reduce damage on the transparent substrate 1 for having a relatively low etching rate to the transparent substrate 1 of a glass material.

[0080]

Moreover, the method of manufacturing a semiconductor device of this invention is featured in using the above-mentioned phase shift mask 200 or a phase shift mask 200 manufactured by using the above-mentioned mask blank 100, and exposure-transferring a pattern in a resist film on a semiconductor substrate. Since the phase shift mask 200 and the mask blank 100 of this invention exhibit the above effect, a pattern can be transferred in a resist film on a semiconductor substrate at a precision that sufficiently satisfies the design specification, when the phase shift mask 200 of this invention is set on a mask stage of an exposure apparatus using an ArF excimer laser as an exposure light and a phase shift pattern 2a is exposure-transferred in a resist film on a semiconductor substrate. Therefore, in the case where a lower layer film below the resist film was dry etched to form a circuit pattern using the pattern of the resist film as a mask, a highly precise circuit pattern without short-circuit of wiring and disconnection caused by insufficient precision can be formed.

[Example]

[0081]

The embodiment of this invention is described in greater detail below together with examples.

(Example 1)

[Manufacture of Mask Blank]

A transparent substrate 1 made of a synthetic quartz glass with a size of a main surface of about 152mm × about 152mm and a thickness of about 6.25mm was prepared. An end surface and the main surfaces of the transparent substrate 1 were polished to a predetermined surface roughness, and thereafter subjected to predetermined cleaning treatment and drying treatment.

[0082]

Next, the transparent substrate 1 was placed in a single-wafer RF sputtering apparatus, and by reactive sputtering (RF sputtering) using a silicon (Si) target with mixed gas of krypton (Kr), xenon (Xe), and nitrogen (N₂) (flow rate ratio Kr:Xe:N₂=4:3:10, pressure =0.13Pa) as sputtering gas and with 2.8kW electric power of RF power source, a high nitrided layer 22 consisting of silicon and nitrogen (Si:N=44atom%:56atom%) was formed on the transparent substrate 1 at a thickness of 8.0nm. On a main surface of another transparent substrate, only a high nitrided layer 22 was formed under the same condition and the optical characteristics of the high nitrided layer 22 were measured using a spectroscopic ellipsometer (M-2000D manufactured by J. A. Woollam), and a refractive index n was 2.64 and an extinction coefficient k was 0.36 at a wavelength of 193nm.

[0083]

Next, the transparent substrate 1 having the high nitrided layer 22 stacked thereon was placed in a single-wafer RF sputtering apparatus, and by reactive sputtering (RF sputtering) using a silicon (Si) target with mixed gas of krypton (Kr), xenon (Xe), and nitrogen (N₂) (flow rate ratio Kr:Xe:N₂=5:4:4, pressure=0.11 Pa) as sputtering gas and with 2.8kW electric power of RF power

source, a low nitrided layer 21 consisting of silicon and nitrogen (Si:N=62atom%:38atom%) was formed on the high nitrided layer 22 at a thickness of 3.5nm. On a main surface of another transparent substrate, only a low nitrided layer 21 was formed under the same condition. Optical characteristics of the low nitrided layer 21 were measured using a spectroscopic ellipsometer (M-2000D manufactured by J. A. Woollam). A refractive index n was 2.20 and an extinction coefficient k was 1.54 at a wavelength of 193nm.

[0084]

Through the above procedure, one set of a stacked structure was formed in contact with a surface of the transparent substrate 1, having the high nitrided layer 22 and the low nitrided layer 21 stacked in this order. Next, four sets of stacked structures of the high nitrided layer 22 and the low nitrided layer 21 were further formed through the similar procedure in contact with a surface of the low nitrided layer 21 of the transparent substrate 1 having formed the one set of a stacked structure. Further, an uppermost layer 23 was formed at a thickness of 8.0nm in contact with a surface of the low nitrided layer 21 that is the farthest from the transparent substrate 1 under the same film forming conditions as in forming the high nitrided layer 22. Through the above procedure, the phase shift film 2 having a total of eleven layers of stacked structures was formed.

[0085]

Next, in-plane distributions of a phase shift amount and a transmittance of the phase shift film 2 were measured, respectively. Further, prepared on another transparent substrate is a high nitrided SiN single layer film formed at a thickness corresponding to a total film thickness of all high nitrided layers in the phase shift film and the uppermost layer of Example 1, and a low nitrided

SiN single layer film formed at a thickness corresponding to a total film thickness of all low nitrided layers in the phase shift film of Example 1. In-plane distributions of a phase shift amount and a transmittance were measured, respectively, for each of the high nitrided SiN single layer film and the low nitrided SiN single layer film. The result is shown in FIG. 3 and FIG. 4.

As shown in FIG. 3, an in-plane distribution of a phase shift amount of those having the high nitrided SiN single layer film alone and the low nitrided SiN single layer film alone both exceeded 1.0 degree in an absolute value with respect to a reference of a target value. However, an in-plane distribution of a phase shift amount of the phase shift film 2 of Example 1 where the high nitrided layer 22 and the low nitrided layer 21 are stacked was 0.91 degree relative to the target value, satisfying the reference of 1.0 degree or less in an absolute value.

[0086]

Further, as shown in FIG. 4, an in-plane distribution of a transmittance of those having the high nitrided SiN single layer film alone and the low nitrided SiN single layer film alone in Example 1 both exceeded 0.2% in an absolute value with respect to the target value. However, an in-plane distribution of a transmittance of the phase shift film 2 of Example 1 where the high nitrided layer 22 and the low nitrided layer 21 are stacked was 0.16% relative to the target value, satisfying the reference of 0.2% or less in an absolute value.

Accordingly, the phase shift film 2 of Example 1 had a good in-plane uniformity in a transmittance and a phase difference. It is inferred that in-plane distributions of each of a portion of the high nitrided layer 22 and a portion of the low nitrided layer 21 are mutually offset by the stacked structure of the high

nitrided layer 22 and the low nitrided layer 21, and are improved in entirety. Further, it is inferred that the multiple reflections of the high nitrided layer 22 and the low nitrided layer 21 also worked well.

[0087]

Further, regarding the phase shift film 2 in Example 1, a shape difference between the surface shape of the main surface of the transparent substrate 1 before formation of the phase shift film 2 that has been measured previously and the surface shape of the phase shift film 2 after formation of the phase shift film 2 was derived, and a flatness variation was further calculated, which was 0.241 μ m (calculation area: 142mm x 142mm from the center of the substrate; same hereafter in Example 2 and Comparative Examples 1, 2). Next, the phase shift film 2 was subjected to heat treatment under the condition of 500°C heating temperature in the atmosphere for the processing time of one hour. Further, on the phase shift film 2 after the heat treatment, a shape difference between the surface shape of the main surface of the transparent substrate 1 before formation of the phase shift film 2 and the surface shape of the phase shift film 2 after the heat treatment was derived, and a flatness variation was further calculated, which was 0.103 μ m, a good result satisfying the reference of within 0.15 μ m.

Further, a transmittance and a phase difference of the phase shift film 2 after the heat treatment to a wavelength of an ArF excimer laser light (about 193nm) were measured using a phase shift measurement device (MPM-193 manufactured by Lasertec). A transmittance was 6.19% and a phase difference was 180.98 degrees.

[0088]

Next, the transparent substrate 1 having the phase shift film 2 after the heat treatment formed thereon was placed in a

single-wafer DC sputtering apparatus, and by reactive sputtering (DC sputtering) using a chromium (Cr) target, with mixed gas of argon (Ar), carbon dioxide (CO₂), nitrogen (N₂), and helium (He) (flow rate ratio Ar:CO₂:N₂:He=22:39:6:33, pressure=0.2Pa) as sputtering gas, and with 1.9kW electric power of DC power source, a lowermost layer of the light shielding film 3 consisting of CrOCN was formed in contact with a surface of the phase shift film 2 at a thickness of 30nm.

[0089]

Next, by reactive sputtering (DC sputtering) using the same chromium (Cr) target with mixed gas of argon (Ar) and nitrogen (N₂) (flow rate ratio Ar:N₂=83:17, pressure=0.1Pa) as sputtering gas, and with 1.4kW electric power of DC power source, a lower layer of the light shielding film 3 consisting of CrN was formed on the lowermost layer of the light shielding film 3 at a thickness of 4nm.

[0090]

Next, by reactive sputtering (DC sputtering) using the same chromium (Cr) target, with mixed gas of argon (Ar), carbon dioxide (CO₂), nitrogen (N₂), and helium (He) (flow rate ratio Ar:CO₂:N₂:He=21:37:11:31, pressure=0.2 Pa) as sputtering gas, and with 1.9kW electric power of DC power source, an upper layer of the light shielding film 3 consisting of CrOCN was formed on the lower layer of the light shielding film 3 at a thickness of 14nm. Through the above procedures, a light shielding film 3 of a chromium-based material consisting of a three-layer structure of the lowermost layer consisting of CrOCN, the lower layer consisting of CrN, and the upper layer consisting of CrOCN from the phase shift film 2 side was formed with a total film thickness of 48nm.

[0091]

Further, the transparent substrate 1 with the phase shift film 2 and the light shielding film 3 stacked thereon was placed in a single-wafer RF sputtering apparatus, and by RF sputtering using a silicon dioxide (SiO_2) target with argon (Ar) gas (pressure=0.03Pa) as sputtering gas, and with 1.5kW electric power of RF power source, a hard mask film 4 consisting of silicon and oxygen was formed on the light shielding film 3 at a thickness of 5nm. Through the above procedure, the mask blank 100 of Example 1 was manufactured, which includes a structure where the phase shift film 2 of the eleven layer structure, the light shielding film 3, and the hard mask film 4 are stacked on the transparent substrate 1.

[0092]

[Manufacture of Phase Shift Mask]

Next, a phase shift mask 200 of Example 1 was manufactured through the following procedure using the mask blank 100 of Example 1. First, a surface of the hard mask film 4 was subjected to HMDS treatment. Subsequently, a resist film of a chemically amplified resist for electron beam writing was formed in contact with a surface of the hard mask film 4 by spin coating at a film thickness of 80nm. Next, a first pattern, which is a phase shift pattern to be formed in the phase shift film 2, was written by an electron beam on the resist film, predetermined cleaning and developing treatments were conducted, and a first resist pattern 5a having the first pattern was formed (see FIG. 2(a)).

[0093]

Next, dry etching using CF_4 gas was conducted with the first resist pattern 5a as a mask, and a first pattern (hard mask pattern 4a) was formed in the hard mask film 4 (see FIG. 2(b)).

[0094]

Next, the first resist pattern 5a was removed. Subsequently, dry etching was conducted using mixed gas of chlorine and oxygen (gas flow rate ratio $\text{Cl}_2:\text{O}_2=4:1$) with the hard mask pattern 4a as a mask, and a first pattern (light shielding pattern 3a) was formed in the light shielding film 3 (see FIG. 2(c)).

[0095]

Next, dry etching was conducted using fluorine-based gas (mixed gas of SF_6 and He) with the light shielding pattern 3a as a mask, and a first pattern (phase shift pattern 2a) was formed in the phase shift film 2, and at the same time the hard mask pattern 4a was removed (see FIG. 2(d)).

[0096]

Next, a resist film of a chemically amplified resist for electron beam writing was formed on the light shielding pattern 3a by spin coating at a film thickness of 150nm. Next, a second pattern, which is a pattern (light shielding pattern) to be formed in the light shielding film 3, was exposed and written in the resist film, and predetermined treatments such as developing were conducted, to thereby form a second resist pattern 6b having a light shielding pattern. Subsequently, dry etching was conducted with mixed gas of chlorine and oxygen (gas flow rate ratio $\text{Cl}_2:\text{O}_2=4:1$) using the second resist pattern 6b as a mask, and a second pattern (light shielding pattern 3b) was formed in the light shielding film 3 (see FIG. 2(e)). Further, the second resist pattern 6b was removed, predetermined treatments such as cleaning were conducted, and the phase shift mask 200 was obtained (see FIG. 2(f)).

[0097]

Next, on the phase shift mask 200 of Example 1, a simulation of a transfer image was made when an exposure transfer was made on

a resist film on a semiconductor substrate at an exposure light of 193nm wavelength, using AIMS193 (manufactured by Carl Zeiss).

[0098]

The simulated exposure transfer image was inspected, and the design specification was fully satisfied. It can be considered from this result that a circuit pattern to be finally formed on the semiconductor substrate can be formed at a high precision, even if the phase shift mask 200 of Example 1 was set on a mask stage of an exposure apparatus and a resist film on the semiconductor substrate was subjected to exposure transfer.

[0099]

(Example 2)

[Manufacture of Mask Blank]

The mask blank 100 of Example 2 was manufactured through the same procedure as the mask blank 100 of Example 1, except for the change of the phase shift film 2. Concretely, the phase shift film 2 of Example 2 was manufactured as follows.

A transparent substrate 1 that is similar to Example 1 was placed in a single-wafer RF sputtering apparatus, and by reactive sputtering (RF sputtering) using a silicon (Si) target with mixed gas of krypton (Kr), xenon (Xe), and nitrogen (N₂) (flow rate ratio Kr:Xe:N₂=2:1:4, pressure=0.13Pa) as sputtering gas and with 2.8kW electric power of RF power source, a high nitrided layer 22 consisting of silicon and nitrogen (Si:N=44atom%:56atom%) was formed on the transparent substrate 1 at a thickness of 8.0nm. On a main surface of another transparent substrate, only a high nitrided layer 22 was formed under the same condition and the optical characteristics of the high nitrided layer 22 were measured using a spectroscopic ellipsometer (M-2000D manufactured by J. A. Woollam), and a refractive index n was 2.64 and an extinction

coefficient k was 0.36 at a wavelength of 193nm.

[0100]

Next, the transparent substrate 1 having the high nitrided layer 22 stacked thereon was placed in a single-wafer RF sputtering apparatus, and by reactive sputtering (RF sputtering) using a silicon (Si) target with mixed gas of krypton (Kr), xenon (Xe), and nitrogen (N_2) (flow rate ratio Kr:Xe: N_2 =7:3:4, pressure=0.11Pa) as sputtering gas and with 2.8kW electric power of RF power source, a low nitrided layer 21 consisting of silicon and nitrogen (Si:N=62atom%:38atom%) was formed on the high nitrided layer 22 at a thickness of 3.5nm. On a main surface of another transparent substrate, only a low nitrided layer 21 was formed under the same condition. Optical characteristics of the low nitrided layer 21 were measured using a spectroscopic ellipsometer (M-2000D manufactured by J. A. Woollam). A refractive index n was 2.20 and an extinction coefficient k was 1.54 at a wavelength of 193nm.

[0101]

Through the above procedure, one set of a stacked structure having the high nitrided layer 22 and the low nitrided layer 21 stacked in this order was formed in contact with a surface of the transparent substrate 1. Next, four sets of stacked structures, each set including the high nitrided layer 22 and the low nitrided layer 21, were further formed through the similar procedure in contact with a surface of the low nitrided layer 21 of the transparent substrate 1 having formed thereon the one set of a stacked structure. Further, an uppermost layer 23 was formed at a thickness of 8.0nm in contact with a surface of the low nitrided layer 21 that is the farthest from the transparent substrate 1 under the same film forming conditions as in forming the high nitrided layer 22. Through the above procedure, the phase shift

film 2 of Example 2 having a total of eleven layers of stacked structures was formed.

[0102]

Next, in-plane distributions of a phase shift amount and a transmittance of the phase shift film 2 were measured, respectively. Further, prepared on another transparent substrate is a high nitrided SiN single layer film formed at a thickness corresponding to a total film thickness of all high nitrided layers in the phase shift film and the uppermost layer of Example 2 and a low nitrided SiN single layer film formed at a thickness corresponding to a total film thickness of all low nitrided layers in the phase shift film of Example 2. In-plane distributions of a phase shift amount and a transmittance were measured, respectively, for each of the high nitrided SiN single layer film and the low nitrided SiN single layer film. The result is shown in FIG. 3 and FIG. 4.

As shown in FIG. 3, an in-plane distribution of a phase shift amount of those having the high nitrided SiN single layer film alone and the low nitrided SiN single layer film alone both exceeded 1.0 degree in an absolute value with respect to the target value. However, an in-plane distribution of a phase shift amount of the phase shift film 2 of Example 2 where the high nitrided layer 22 and the low nitrided layer 21 are stacked was 0.92 degree relative to the target value, satisfying the reference of 1.0 degree or less in an absolute value.

[0103]

Further, as shown in FIG. 4, an in-plane distribution of a transmittance of those having the high nitrided SiN single layer film alone and the low nitrided SiN single layer film alone in Example 2 both exceeded 0.2% in an absolute value with respect to the target value. However, an in-plane distribution of a

transmittance of the phase shift film 2 of Example 2 where the high nitrided layer 22 and the low nitrided layer 21 are stacked was 0.12% relative to the target value, satisfying the reference of 0.2% or less in an absolute value.

Accordingly, the phase shift film 2 of Example 2 had a good in-plane uniformity in a transmittance and a phase difference. It is inferred that in-plane distributions of a portion of the high nitrided layer 22 and a portion of the low nitrided layer 21 are offset by the stacked structure of the high nitrided layer 22 and the low nitrided layer 21, and are improved in entirety. Further, it is inferred that the multiple reflections of the high nitrided layer 22 and the low nitrided layer 21 also worked well.

[0104]

Further, on the phase shift film 2 in Example 2, a shape difference between the surface shape of the main surface of the transparent substrate 1 before formation of the phase shift film 2 that has been measured previously and the surface shape of the phase shift film 2 after formation of the phase shift film 2 was derived, and a flatness variation was further calculated, which was 0.324 μ m. Next, the phase shift film 2 was subjected to heat treatment under the condition of 500°C heating temperature in the atmosphere for the processing time of one hour. On the phase shift film 2 after the heat treatment, a shape difference between the surface shape of the main surface of the transparent substrate 1 before formation of the phase shift film 2 and the surface shape of the phase shift film 2 after the heat treatment was derived, and a flatness variation was further calculated, which was 0.128 μ m, a good result satisfying the reference of within 0.15 μ m.

Further, a transmittance and a phase difference of the phase shift film 2 after the heat treatment to wavelength of an ArF

excimer laser light (about 193nm) were measured using a phase shift measurement device (MPM-193 manufactured by Lasertec). A transmittance was 6.19% and a phase difference was 181.82 degrees.

[0105]

Further, the phase shift film 2 of Example 2 was formed on another transparent substrate 1, and measured by HR-RBS (high-resolution Rutherford backscattering spectroscopy). FIG. 5 is a graph showing an observation result of HR-RBS of Example 2 of this invention. More concretely, FIG. 5 is a graph showing observation data and a result of simulation fitting to the observation data. As shown in FIG. 5, krypton and xenon were detected in addition to silicon and nitrogen in the phase shift film 2 of Example 2. A depth profile of the phase shift film 2 in Example 2 was examined, and the presence of krypton and xenon was confirmed in both the high nitrided layer 22 and the low nitrided layer 21.

According to this result, it is estimated that krypton and xenon exist also in the phase shift film 2 of Example 1 in which a flow rate of xenon gas is larger than that of Example 2 and a flow rate of krypton gas is larger than that of xenon gas.

[0106]

Through the similar procedures as Example 1, a mask blank 100 of Example 2 having a structure where a phase shift film 2, a light shielding film 3, and a hard mask film 4 are stacked on a transparent substrate 1 was manufactured.

[0107]

[Manufacture of Phase Shift Mask]

Next, using the mask blank 100 of Example 2, a phase shift mask 200 of Example 2 was manufactured through the same procedure as Example 1.

[0108]

Next, on the phase shift pattern 2a of the phase shift mask 200 of Example 2, a simulation of a transfer image was made when an exposure transfer was made on a resist film on a semiconductor substrate at an exposure light of 193nm wavelength, using AIMS193 (manufactured by Carl Zeiss).

[0109]

The simulated exposure transfer image was inspected, and the design specification was fully satisfied. It can be considered from this result that a circuit pattern to be finally formed on the semiconductor substrate can be formed at a high precision, even if the phase shift mask 200 of Example 2 was set on a mask stage of an exposure apparatus and a resist film on the semiconductor substrate was subjected to exposure transfer.

[0110]

(Comparative Example 1)

[Manufacture of Mask Blank]

The mask blank of Comparative Example 1 was manufactured through the same procedure as the mask blank 100 of Example 1, except for the change of the phase shift film. Concretely, the phase shift film of Comparative Example 1 was manufactured as follows.

A transparent substrate that is similar to Example 1 was placed in a single-wafer RF sputtering apparatus, and by reactive sputtering (RF sputtering) using a silicon (Si) target with mixed gas of krypton (Kr), nitrogen (N₂), and helium (He) (flow rate ratio Kr:N₂:He=3:4:20, pressure=0.29Pa) as sputtering gas and with 2.8kW electric power of RF power source, a high nitrided layer consisting of silicon and nitrogen (Si:N=44atom%:56atom%) was formed on the transparent substrate at a thickness of 8.0nm. On a main surface of another transparent substrate, only a high nitrided

layer was formed under the same condition and the optical characteristics of the high nitrided layer were measured using a spectroscopic ellipsometer (M-2000D manufactured by J. A. Woollam), and a refractive index n was 2.64 and an extinction coefficient k was 0.36 at a wavelength of 193nm.

[0111]

Next, the transparent substrate having the high nitrided layer stacked thereon was placed in a single-wafer RF sputtering apparatus, and by reactive sputtering (RF sputtering) using a silicon (Si) target with mixed gas of krypton (Kr), nitrogen (N_2), and helium (He) (flow rate ratio Kr: N_2 :He=5:2:25, pressure=0.27Pa) as sputtering gas and with 2.8kW electric power of RF power source, a low nitrided layer consisting of silicon and nitrogen (Si:N=62atom%:38atom%) was formed on the high nitrided layer at a thickness of 3.5nm. On a main surface of another transparent substrate, only a low nitrided layer was formed under the same condition. Optical characteristics of the low nitrided layer were measured using a spectroscopic ellipsometer (M-2000D manufactured by J. A. Woollam). A refractive index n was 2.20 and an extinction coefficient k was 1.54 at a wavelength of 193nm.

[0112]

Through the above procedure, one set of a stacked structure having the high nitrided layer and the low nitrided layer stacked in this order was formed in contact with a surface of the transparent substrate. Next, four sets of stacked structures, each set including the high nitrided layer and the low nitrided layer, were further formed through the similar procedure in contact with a surface of the low nitrided layer of the transparent substrate having formed thereon the one set of a stacked structure. Further, an uppermost layer was formed at a thickness of 8.0nm in contact

with a surface of the low nitrided layer that is the farthest from the transparent substrate under the same film forming conditions as in forming the high nitrided layer. Through the above procedure, the phase shift film of Comparative Example 1 having a total of eleven layers of stacked structures was formed.

[0113]

Next, in-plane distributions of a phase shift amount and a transmittance of the phase shift film of the Comparative Example 1 were measured, respectively. Further, prepared on another transparent substrate is a high nitrided SiN single layer film formed at a thickness corresponding to a total film thickness of all high nitrided layers in the phase shift film and the uppermost layer of Comparative Example 1 and a low nitrided SiN single layer film formed at a thickness corresponding to a total film thickness of all low nitrided layers in the phase shift film of Comparative Example 1. In-plane distributions of a phase shift amount and a transmittance were measured, respectively, for each of the high nitrided SiN single layer film and the low nitrided SiN single layer film. The result is shown in FIG. 3 and FIG. 4.

As shown in FIG. 3, in-plane distributions of a phase shift amount of those having the high nitrided SiN single layer film alone and the low nitrided SiN single layer film alone in Comparative Example 1 both exceeded 1.0 degree in an absolute value with respect to the target value. An in-plane distribution of a phase shift amount of the phase shift film 2 of Comparative Example 1 where the high nitrided layer and the low nitrided layer are stacked was 2.59 degrees relative to the target value, which did not satisfy the reference of 1.0 degree or less in an absolute value.

[0114]

Further, as shown in FIG. 4, in-plane distributions of a transmittance of those having the high nitrided SiN single layer film alone and the low nitrided SiN single layer film alone in Comparative Example 1 both exceeded 0.2% in an absolute value with respect to the target value. An in-plane distribution of a transmittance of the phase shift film of Comparative Example 1 where the high nitrided layer and the low nitrided layer are stacked was 0.21% relative to the target value, which did not satisfy the reference of 0.2% or less in an absolute value.

Accordingly, the phase shift film 2 of Comparative Example 1 did not satisfy the reference on any of an in-plane uniformity of a transmittance and a phase difference.

[0115]

Further, on the phase shift film of Comparative Example 1, a shape difference between the surface shape of the main surface of the transparent substrate 1 before formation of the phase shift film that has been measured previously and the surface shape of the phase shift film after formation of the phase shift film was derived, and a flatness variation was further calculated, which was $0.169\mu\text{m}$. Next, the phase shift film was subjected to heat treatment under the condition of 500°C heating temperature in the atmosphere for the processing time of one hour. Further, on the phase shift film after the heat treatment, a shape difference between the surface shape of the main surface of the transparent substrate 1 before formation of the phase shift film and the surface shape of the phase shift film after the heat treatment was derived, and a flatness variation was further calculated, which was $-0.181\mu\text{m}$ where, although satisfying the reference of within $0.2\mu\text{m}$, did not satisfy the reference of within $0.15\mu\text{m}$.

A transmittance and a phase difference of the phase shift

film of Comparative Example 1 after the heat treatment to wavelength of an ArF excimer laser light (about 193nm) were measured using a phase shift measurement device (MPM-193 manufactured by Lasertec), and a transmittance was 6.35% and a phase difference was 179.54 degrees.

[0116]

Through the similar procedures as Example 1, a mask blank of Comparative Example 1 having a structure where a phase shift film, a light shielding film, and a hard mask film are stacked on a transparent substrate was manufactured.

[0117]

[Manufacture of Phase Shift Mask]

Next, using the mask blank of Comparative Example 1, a phase shift mask of Comparative Example 1 was manufactured through the same procedure as Example 1.

[0118]

Next, on the phase shift pattern of the phase shift mask of Comparative Example 1, a simulation of a transfer image was made when an exposure transfer was made on a resist film on a semiconductor substrate at an exposure light of 193nm wavelength, using AIMS193 (manufactured by Carl Zeiss).

[0119]

The simulated exposure transfer image was inspected, and the design specification was not fully satisfied, which was at a level causing an occurrence of transfer defect. It can be understood from this result that when the phase shift mask of Comparative Example 1 was set on a mask stage of an exposure apparatus and exposure-transferred on a resist film on a semiconductor substrate, generation of short-circuit or disconnection of circuit pattern is expected on a circuit pattern finally formed on the semiconductor

substrate.

[0120]

(Comparative Example 2)

[Manufacture of Mask Blank]

The mask blank of Comparative Example 2 was manufactured through the same procedure as the mask blank 100 of Example 1, except for the change of the phase shift film. Concretely, the phase shift film of Comparative Example 2 was manufactured as follows.

A transparent substrate that is similar to Example was placed in a single-wafer RF sputtering apparatus, and by reactive sputtering (RF sputtering) using a silicon (Si) target with mixed gas of krypton (Kr) and nitrogen (N₂) (flow rate ratio Kr:N₂=3:4, pressure=0.13Pa) as sputtering gas and with 2.8kW electric power of RF power source, a high nitrided layer consisting of silicon and nitrogen (Si:N=44atom%:56atom%) was formed on the transparent substrate 1 at a thickness of 8.0nm. On a main surface of another transparent substrate, only a high nitrided layer was formed under the same condition and the optical characteristics of the high nitrided layer were measured using a spectroscopic ellipsometer (M-2000D manufactured by J. A. Woollam), and a refractive index n was 2.64 and an extinction coefficient k was 0.36 at a wavelength of 193nm.

[0121]

Next, the transparent substrate having the high nitrided layer stacked thereon was placed in a single-wafer RF sputtering apparatus, and by reactive sputtering (RF sputtering) using a silicon (Si) target with mixed gas of krypton (Kr) and nitrogen (N₂) (flow rate ratio Kr:N₂=20:7, pressure=0.11Pa) as sputtering gas and with 2.8kW electric power of RF power source, a low

nitrided layer consisting of silicon and nitrogen (Si:N=62atom%:38atom%) was formed on the high nitrided layer at a thickness of 3.5nm. On a main surface of another transparent substrate, only a low nitrided layer was formed under the same condition. Optical characteristics of the low nitrided layer were measured using a spectroscopic ellipsometer (M-2000D manufactured by J. A. Woollam). A refractive index n was 2.20 and an extinction coefficient k was 1.54 at a wavelength of 193nm.

[0122]

Through the above procedure, one set of a stacked structure having the high nitrided layer and the low nitrided layer stacked in this order was formed in contact with a surface of the transparent substrate. Next, four sets of stacked structures, each set including the high nitrided layer and the low nitrided layer, were further formed through the similar procedure in contact with a surface of the low nitrided layer of the transparent substrate having formed thereon the one set of a stacked structure. Further, an uppermost layer was formed at a thickness of 8.0nm in contact with a surface of the low nitrided layer that is the farthest from the transparent substrate under the same film forming conditions as in forming the high nitrided layer. Through the above procedure, the phase shift film of Comparative Example 2 having a total of eleven layers of stacked structures was formed.

[0123]

Next, in-plane distributions of a phase shift amount and a transmittance of the phase shift film of Comparative Example 2 were measured, respectively. Further, prepared on another transparent substrate is a high nitrided SiN single layer film formed at a thickness corresponding to a total film thickness of all high nitrided layers in the phase shift film and the uppermost

layer of Comparative Example 2 and a low nitrided SiN single layer film formed at a thickness corresponding to a total film thickness of all low nitrided layers in the phase shift film of Comparative Example 2. In-plane distributions of a phase shift amount and a transmittance were measured, respectively, for each of the high nitrided SiN single layer film and the low nitrided SiN single layer film. The result is shown in FIG. 3 and FIG. 4.

As shown in FIG. 3, in-plane distributions of a phase shift amount of those having the high nitrided SiN single layer film alone and the low nitrided SiN single layer film alone in Comparative Example 2 both exceeded the reference of 1.0 degree in an absolute value with respect to the target value. However, an in-plane distribution of a phase shift amount of the phase shift film of Comparative Example 2 where the high nitrided layer and the low nitrided layer are stacked was 0.64 degree relative to the target value, which satisfied the reference of 1.0 degree or less in an absolute value.

[0124]

Further, as shown in FIG. 4, in-plane distributions of a transmittance of those having the high nitrided SiN single layer film alone and the low nitrided SiN single layer film alone in Comparative Example 2 both exceeded the reference of 0.2% in an absolute value with respect to the target value. However, an in-plane distribution of a transmittance of the phase shift film of Comparative Example 2 where the high nitrided layer and the low nitrided layer are stacked was 0.18% relative to the target value, which did satisfy the reference of 0.2% or less in an absolute value.

[0125]

However, on the phase shift film in Comparative Example 2,

a shape difference between the surface shape of the main surface of the transparent substrate 1 before formation of the phase shift film that has been measured previously and the surface shape of the phase shift film after formation of the phase shift film was derived, and a flatness variation was further calculated, which was 0.490 μ m. The phase shift film was subjected to heat treatment under the condition of 500°C heating temperature in the atmosphere for the processing time of one hour. On the phase shift film after the heat treatment, a shape difference between the surface shape of the main surface of the transparent substrate 1 before formation of the phase shift film and the surface shape of the phase shift film after the heat treatment was derived, and a flatness variation was further calculated, which was 0.246 μ m, satisfying neither the reference of within 0.15 μ m nor the reference of within 0.2 μ m.

A transmittance and a phase difference of the phase shift film of Comparative Example 2 after the heat treatment to wavelength of an ArF excimer laser light (about 193nm) were measured using a phase shift measurement device (MPM-193 manufactured by Lasertec), and a transmittance was 6.25% and a phase difference was 180.77 degrees.

[0126]

Further, the phase shift film of Comparative Example 2 was formed on another transparent substrate, and measured by HR-RBS (high-resolution Rutherford backscattering spectroscopy). FIG. 6 is a graph showing an observation result of HR-RBS of Comparative Example 2 of this invention. More concretely, FIG. 6 is a graph showing observation data and a result of simulation fitting to the observation data. As shown in FIG. 6, while krypton was detected in addition to silicon and nitrogen in the phase shift film of Comparative Example 2, xenon was confirmed undetected.

[0127]

Through the similar procedures as Example 1, a mask blank of Comparative Example 2 having a structure where a phase shift film, a light shielding film, and a hard mask film are stacked on a transparent substrate was manufactured.

[0128]

[Manufacture of Phase Shift Mask]

Next, using the mask blank of Comparative Example 2, a phase shift mask of Comparative Example 2 was manufactured through the same procedure as Example 1.

[0129]

Next, on the phase shift pattern of the phase shift mask of Comparative Example 2, a simulation of a transfer image was made when an exposure transfer was made on a resist film on a semiconductor substrate at an exposure light of 193nm wavelength, using AIMS193 (manufactured by Carl Zeiss).

[0130]

The simulated exposure transfer image was inspected, and an occurrence of position displacement of the pattern was found which is considered as caused by a film stress of the phase shift film, which did not sufficiently satisfy the design specification, and which was at a level causing an occurrence of transfer defect. It can be understood from this result that when the phase shift mask of Comparative Example 2 was set on a mask stage of an exposure apparatus and exposure-transferred on a resist film on a semiconductor substrate, generation of short-circuit or disconnection of circuit pattern is expected on a circuit pattern finally formed on the semiconductor substrate.

[Description of Reference Numerals]

[0131]

- 1. transparent substrate
- 2. phase shift film
- 2a. phase shift pattern
- 21. low nitrided layer
- 22. high nitrided layer
- 23. uppermost layer
- 3. light shielding film
- 3a, 3b. light shielding pattern
- 4. hard mask film
- 4a. hard mask pattern
- 5a. first resist pattern
- 6b. second resist pattern
- 100. mask blank
- 200. phase shift mask

[DOCUMENT] CLAIMS

[Claim 1]

A mask blank comprising a phase shift film on a transparent substrate,

wherein the phase shift film has a high nitrided layer and a low nitrided layer,

wherein the high nitrided layer and the low nitrided layer contain silicon, nitrogen, krypton, and xenon,

wherein the high nitrided layer has a nitrogen content of 50atom% or more,

wherein the low nitrided layer has a nitrogen content of less than 50atom%, and

wherein the high nitrided layer and the low nitrided layer contain krypton and xenon at a level that is detected by high-resolution Rutherford backscattering spectroscopy.

[Claim 2]

The mask blank according to claim 1, wherein the high nitrided layer and the low nitrided layer have a total content of silicon, nitrogen, krypton, and xenon of 90atom% or more.

[Claim 3]

The mask blank according to claim 1 or 2, wherein a total thickness of a thickness of the high nitrided layer and a thickness of the low nitrided layer is 70% or more of a thickness of the phase shift film.

[Claim 4]

The mask blank according to any of claims 1 to 3, wherein the phase shift film has a structure where two or more of the high nitrided layers and two or more of the low nitrided layers are stacked alternately.

[Claim 5]

The mask blank according to any of claims 1 to 4, wherein

the phase shift film has a function to transmit an exposure light of an ArF excimer laser at a transmittance of 2% or more, and a function to generate a phase difference of 150 degrees or more and 210 degrees or less between the exposure light transmitted through the phase shift film and the exposure light transmitted through the air for a same distance as a thickness of the phase shift film.

[Claim 6]

The mask blank according to any of claims 1 to 5 comprising a light shielding film on the phase shift film.

[Claim 7]

A phase shift mask comprising a phase shift film having a transfer pattern formed on a transparent substrate,

wherein the phase shift film has a high nitrided layer and a low nitrided layer,

wherein the high nitrided layer and the low nitrided layer contain silicon, nitrogen, krypton, and xenon,

wherein the high nitrided layer has a nitrogen content of 50atom% or more,

wherein the low nitrided layer has a nitrogen content of less than 50atom%, and

wherein the high nitrided layer and the low nitrided layer contain krypton and xenon at a level that is detected by high-resolution Rutherford backscattering spectroscopy.

[Claim 8]

The phase shift mask according to claim 7, wherein the high nitrided layer and the low nitrided layer have a total content of silicon, nitrogen, krypton, and xenon of 90atom% or more.

[Claim 9]

The phase shift mask according to claim 7 or 8, wherein a total thickness of a thickness of the high nitrided layer and a

thickness of the low nitrided layer is 70% or more of a thickness of the phase shift film.

[Claim 10]

The phase shift mask according to any of claims 7 to 9, wherein the phase shift film has a structure where two or more of the high nitrided layers and two or more of the low nitrided layers are stacked alternately.

[Claim 11]

The phase shift mask according to any of claims 7 to 10, wherein the phase shift film has a function to transmit an exposure light of an ArF excimer laser at a transmittance of 2% or more, and a function to generate a phase difference of 150 degrees or more and 210 degrees or less between the exposure light transmitted through the phase shift film and the exposure light transmitted through the air for a same distance as a thickness of the phase shift film.

[Claim 12]

The phase shift mask according to any of claims 7 to 11 comprising a light shielding film having a light shielding pattern formed on the phase shift film.

[Claim 13]

A method of manufacturing a semiconductor device comprising the step of using the phase shift mask according to any of claims 7 to 12 and exposure-transferring a transfer pattern in a resist film on a semiconductor substrate.