

patterning a thin film for pattern formation, further having a high transmittance to an exposure light. A further object is to provide a transfer mask manufactured using this mask blank. Moreover, an object of this invention is to provide a method of manufacturing a semiconductor device using the transfer mask.

[Means for Solving the Problem]

[0008]

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

(Configuration 1)

A mask blank having a structure where a transparent substrate has stacked thereon an etching stopper film and a thin film for pattern formation in this order,

in which the thin film includes a material containing silicon,

in which the etching stopper film includes a material containing hafnium, aluminum, and oxygen, and

in which an oxygen deficiency ratio of the etching stopper film is 6.4% or less.

[0009]

(Configuration 2)

The mask blank according to Configuration 1, in which a ratio by atom% of an amount of the hafnium to a total amount of the hafnium and the aluminum in the etching stopper film is 0.85 or less.

[0010]

(Configuration 3)

The mask blank according to Configuration 1 or 2, in which a ratio by atom% of an amount of the hafnium to a total amount of the hafnium and the aluminum in the etching stopper film is 0.60

the phase shift film.

[0016]

(Configuration 9)

The mask blank according to Configuration 8, in which a light shielding film is provided on the phase shift film.

[0017]

(Configuration 10)

The mask blank according to Configuration 9, in which the light shielding film includes a material containing chromium.

[0018]

(Configuration 11)

A transfer mask having a structure where a transparent substrate has stacked thereon an etching stopper film and a thin film having a transfer pattern in this order,

in which the thin film includes a material containing silicon,

in which the etching stopper film includes a material containing hafnium, aluminum, and oxygen, and

in which an oxygen deficiency ratio of the etching stopper film is 6.4% or less.

[0019]

(Configuration 12)

The transfer mask according to Configuration 11, in which a ratio by atom% of an amount of the hafnium to a total amount of the hafnium and the aluminum in the etching stopper film is 0.85 or less.

[0020]

(Configuration 13)

The transfer mask according to Configuration 11 or 12, in which a ratio by atom% of an amount of the hafnium to a total

that transmitted through the phase shift film and an exposure light that transmitted through air for a same distance as a thickness of the phase shift film.

[0026]

(Configuration 19)

The transfer mask according to Configuration 18 including a light shielding film having a light shielding pattern with a light shielding band on the phase shift film.

[0027]

(Configuration 20)

The transfer mask according to Configuration 19, in which the light shielding film includes a material containing chromium.

[0028]

(Configuration 21)

A method of manufacturing a semiconductor device including the step of using the transfer mask according to any of Configurations 11 to 20 and exposure-transferring the pattern on the transfer mask to a resist film on a semiconductor substrate.

[Effect of the Invention]

[0029]

The mask blank of this invention has a structure where an etching stopper film and a thin film for pattern formation are stacked in this order on a transparent substrate, featured in that the thin film includes a material containing silicon, the etching stopper film includes a material containing hafnium, aluminum, and oxygen, and an oxygen deficiency ratio of the etching stopper film is 6.4% or less. With the mask blank having such a structure, the etching stopper film can simultaneously achieve the functions of high durability to dry etching with fluorine-based gas used in

manufacturing step of the phase shift mask according to the third embodiment of this invention.

[FIG. 10] FIG. 10 is a graph showing a relationship between an oxygen deficiency ratio and a transmittance to an ArF exposure light of the etching stopper film.

[Embodiments for Carrying Out the Invention]

[0031]

First, the proceeding that has resulted in the completion of this invention is described. The inventors of this application diligently studied to solve the technical problem of an etching stopper film including a mixture of hafnium oxide and aluminum oxide. As a result, it was discovered that aluminum oxide is likely to generate oxygen deficiency compared to hafnium oxide. Further, the inventors found out that oxygen deficiency of aluminum oxide particularly affects reduction of transmittance to an ArF exposure light. Moreover, it was found that an etching stopper film formed of a mixture of hafnium oxide and aluminum oxide has a reduced transmittance to an ArF exposure light than an etching stopper film formed of hafnium oxide depending on mixture ratio. In addition, it was found that an etching stopper film formed of a mixture of hafnium oxide and aluminum oxide can have a higher transmittance to an ArF exposure light than an etching stopper film formed of hafnium oxide if an oxygen deficiency ratio of the etching stopper film is 6.4% or less.

[0032]

An etching stopper film formed of a mixture of hafnium oxide and aluminum oxide having less transmittance to an ArF exposure light than an etching stopper film formed of hafnium oxide is inferred as caused by the following mechanism. The study below is

based on the inference by the inventors of this invention as of the application, which by no means limits the scope of this invention.

[0033]

Conventionally, an etching stopper film including hafnium oxide is formed by sputtering. Even if a target is formed of hafnium oxide, a majority of hafnium oxide is released from the bond with oxygen and ejects out of the target in the state of hafnium particles and oxygen particles when plasma of noble gas such as argon collides the target and sputtering particles eject out of the target. Then the hafnium particles bond to surrounding oxygen particles again while flying in the sputtering chamber, deposit onto the transparent substrate, and construct an etching stopper film. However, due to gas in the sputtering chamber being replaced constantly, a part of hafnium oxide deposits onto the transparent substrate without the hafnium particles being stoichiometrically stably bonded to oxygen (HfO_2 bond), causing remaining oxygen to discharge out of the sputtering chamber. This is considered as the major reason of generation of an oxygen deficiency ratio in the hafnium oxide film formed by sputtering. For the same reason, an oxygen deficiency ratio is considered to generate in an aluminum oxide film when an etching stopper film including aluminum oxide is formed by sputtering.

[0034]

In forming an etching stopper film including a mixture of hafnium oxide and aluminum oxide by sputtering, plasma of noble gas collides a target formed of hafnium oxide and aluminum oxide (including the case where two targets, a target of hafnium oxide and a target of aluminum oxide, are placed in a sputtering chamber;

ArF exposure light of the etching stopper film is less than a transmittance to an ArF exposure light of an etching stopper film consisting only of hafnium oxide).

[0038]

The result of the diligent study is that, to solve the technical problem of the etching stopper film including a mixture of hafnium oxide and aluminum oxide, the mask blank of this invention has a structure where an etching stopper film and a thin film for pattern formation are stacked in this order on a transparent substrate, featured in that the thin film includes a material containing silicon, the etching stopper film includes a material containing hafnium, aluminum, and oxygen, and an oxygen deficiency ratio of the etching stopper film is 6.4% or less. An oxygen deficiency ratio [%] is calculated by $100 \times [O_I - O_R] / O_I$, where O_R is an oxygen content in the etching stopper film, and O_I is an oxygen content when all hafnium and aluminum present in the etching stopper film are in a stoichiometrically stable oxide state (i.e., state where hafnium and aluminum in the film exist only as oxides of HfO_2 and Al_2O_3). Next, each embodiment for carrying out this invention is explained.

[0039]

<First Embodiment>

[Mask Blank and its Manufacture]

A mask blank according to a first embodiment of this invention includes a phase shift film as a thin film for pattern formation which, provides predetermined transmittance and phase difference to an exposure light, which is used for manufacturing a phase shift mask (transfer mask). FIG. 1 shows a configuration of the mask blank of the first embodiment. A mask blank 100

[0042]

The etching stopper film 2 of the first embodiment is formed of a material containing hafnium, aluminum, and oxygen, and an oxygen deficiency ratio of the etching stopper film 2 is 6.4% or less. FIG. 10 shows a measured result in plots of a transmittance to an ArF exposure light of each of etching stopper films formed on a transparent substrate at film thicknesses of 2nm and 3nm with different oxygen deficiency ratios (relative transmittance when a transmittance of a transparent substrate of a synthetic quartz glass is 100%). Incidentally, an oxygen deficiency ratio of the etching stopper film herein is varied by adjusting the mixing ratio of hafnium and aluminum in the etching stopper film. The result of FIG. 10 shows that when an oxygen deficiency ratio of the etching stopper film is 6.4% or less, a transmittance is higher in the etching stopper films of any film thickness than the etching stopper film consisting only of hafnium oxide (FIG. 10: film of 8.70% oxygen deficiency ratio) (transmittance is 85% or more even in 3nm film thickness).

[0043]

Dry etching durability to fluorine-based gas was enhanced in any film thickness compared to an etching stopper film formed only of hafnium oxide. Therefore, over etching the phase shift film 3 does not cause elimination of the etching stopper film 2 and the micro trench that is likely to occur by high bias etching can be prevented. Incidentally, an oxygen deficiency ratio of the etching stopper film 2 is more preferably 4.2% or less. In this case, a transmittance to an ArF exposure light can be 90% or more even with 3nm film thickness of the etching stopper film.

While the etching stopper film 2 preferably has a higher

transmittance to an exposure light, since the etching stopper film 2 is simultaneously required to have sufficient etching selectivity to fluorine-based gas between the transparent substrate 1, it is difficult to apply a transmittance to an exposure light that is similar to a transmittance of the transparent substrate 1 (i.e., when a transmittance of the transparent substrate 1 (synthetic quartz glass) to an exposure light is 100%, a transmittance of the etching stopper film 2 is less than 100%). A transmittance of the etching stopper film 2 when a transmittance of the transparent substrate 1 to an exposure light is 100% is preferably 85% or more, and more preferably 90% or more.

[0045]

The oxygen content of the etching stopper film 2 is preferably 60atom% or more, more preferably 61.5atom% or more, and even more preferably 62atom% or less. This is because the etching stopper film 2 requires a large amount of oxygen, in addition to reducing an oxygen deficiency ratio, in order to make a transmittance to an exposure light equal to or greater than the aforementioned value. On the other hand, the oxygen content of the etching stopper film 2 is preferably 66atom% or less.

[0046]

The etching stopper film 2 preferably has a ratio by atom% of an amount of hafnium to a total amount of hafnium and aluminum (may hereafter be referred to as Hf/[Hf+Al] ratio) of 0.85 or less. In this case, an oxygen deficiency ratio of the etching stopper film 2 can be 6.4% or less. Further, Hf/[Hf+Al] ratio of the etching stopper film 2 is preferably 0.75 or less. In this case, an oxygen deficiency ratio of the etching stopper film 2 can be

4.2% or less.

[0047]

On the other hand, on the viewpoint of resistance to chemical cleaning (esp., alkali cleaning such as ammonium hydrogen peroxide mixture and TMAH), the etching stopper film 2 preferably has Hf/[Hf+Al] ratio of 0.40 or more. Further, on the viewpoint of chemical cleaning using a mixed solution of ammonia water, hydrogen peroxide, and deionized water referred to as SC-1 cleaning, the etching stopper film 2 preferably has Hf/[Hf+Al] ratio of 0.60 or more.

[0048]

The etching stopper film 2 preferably contains metals other than aluminum and hafnium of 2atom% or less, more preferably 1atom% or less, and even more preferably detection lower limit or less through analysis of X-ray photoelectron spectroscopy. This is because the etching stopper film 2 containing metals other than aluminum and hafnium causes reduction in a transmittance to an exposure light. Further, a total content of elements other than aluminum, hafnium, and oxygen of the etching stopper film 2 is preferably 5atom% or less, more preferably 3atom% or less, and even more preferably 1atom% or less. In other words, a total content of aluminum, hafnium, and oxygen of the etching stopper film 2 is preferably 95atom% or more, more preferably 97atom% or more, and even more preferably 99atom% or more.

[0049]

The etching stopper film 2 is preferably made of a material including hafnium, aluminum, and oxygen. The material including hafnium, aluminum, and oxygen indicates a material containing, in

krypton (Kr), and xenon (Xe). The phase shift film 3 of a silicon nitride-based material can contain oxygen. The phase shift film 3 of a silicon nitride-based material containing oxygen can achieve both of the function of having 20% or more transmittance to an exposure light of an ArF excimer laser and the function of having a phase difference of the above range.

[0066]

The phase shift film 3 of a silicon nitride-based material can be configured from a single layer except for the surface layer where oxidization is inevitable (oxidized layer), or a stack of multiple layers. In the case of the phase shift film 3 of a stacked structure of multiple layers, the stacked structure can be a combination of a layer of a silicon nitride-based material (SiN, SiON, etc.) with a layer of a silicon oxide-based material (SiO₂, etc.).

[0067]

While the phase shift film 3 of a silicon nitride-based material 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.), while application of RF sputtering and ion beam sputtering is preferable, application of RF sputtering is more preferable, considering the deposition ratio.

[0068]

Etching end point detection of EB defect repair is performed by detecting at least one of Auger electron, secondary electron, characteristic X-ray, and backscattered electron, which are discharged from an irradiated portion when an electron beam is

film 3 is preferably 0.01 or more. This is because in manufacturing the phase shift mask 200 from the mask blank 100, it is preferable that sheet resistance of the phase shift film 3 is low when applying defect repair by electron beam radiation and non-excitation gas such as XeF_2 on a black defect existing in the pattern of the phase shift film 3.

[0073]

On the other hand, by providing the etching stopper film 2 in contact with a main surface of the transparent substrate 1, further providing the phase shift film 3 in contact with an upper surface of the etching stopper film 2, and further adjusting conditions of the etching stopper film 2 and the phase shift film 3, a back surface reflectance to an ArF exposure light (reflectance to an ArF exposure light entered from the transparent substrate side) can be increased (e.g., 20% or more). For example, the conditions can be adjusted as follows. The etching stopper film 2 has a refractive index n to an ArF exposure light of 2.3 or more and 2.9 or less, an extinction coefficient k of 0.06 or more and 0.30 or less, and a film thickness of 2nm or more and 6nm or less. The phase shift film 3 has, in its entirety in the case of a single layer structure and a layer contacting the etching stopper film 2 in the case of a structure with two or more layers, a refractive index n to an ArF exposure light of 2.0 or more and 3.1 or less, an extinction coefficient k of 0.26 or more and 0.54 or less, and a film thickness of 50nm or more. Further, the etching stopper film 2 can have an oxygen deficiency ratio of 6.4% or less, and a film thickness of 2nm or more and 6nm or less. Further, the etching stopper film 2 can have an $\text{Hf}/[\text{Hf}+\text{Al}]$ ratio of 0.50 or more and 0.86 or less, an oxygen content of 61.5atom%, and a film thickness

SiON, etc.

[0085]

Further, in the case where the light shielding film 4 is formed of a material containing chromium, materials containing tantalum are also applicable as the materials of the hard mask film 5. 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.

[0086]

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 5 at a film thickness of 100nm or less.

[0087]

While the etching stopper film 2, the phase shift film 3, the light shielding film 4, and the hard mask film 5 are formed by sputtering, any sputtering method is applicable such as DC sputtering, RF sputtering, and ion beam sputtering. In the case where the target has low conductivity, while application of RF sputtering and ion beam sputtering is preferable, application of RF sputtering is more preferable considering the deposition ratio.

[0088]

In the method of forming the etching stopper film 2, it is preferable to arrange two targets, i.e., a mixed target of hafnium and oxygen and a mixed target of aluminum and oxygen in a film forming chamber to form the etching stopper film 2 on the transparent substrate 1. Concretely, the transparent substrate 1 is placed on a substrate stage in the film forming chamber, and a predetermined voltage is applied (preferably RF power source in this case) to each of the two targets under a noble gas atmosphere

such as argon gas (or mixed gas atmosphere with oxygen gas or oxygen-containing gas). As a result, plasmarized noble gas particles collide with the two targets, each causing a sputtering phenomenon, and the etching stopper film 2 containing hafnium, aluminum, and oxygen is formed on the surface of the transparent substrate 1. In this case, it is more preferable to apply HfO_2 target and Al_2O_3 target as the two targets.

[0089]

In addition to the above, the etching stopper film 2 can be formed only of a mixed target of hafnium, aluminum, and oxygen (preferably a mixed target of HfO_2 and Al_2O_3 ; same hereafter). Further, the etching stopper film 2 can be formed by simultaneously discharging a mixed target of hafnium, aluminum, and oxygen and a hafnium target, or a mixed target of hafnium and oxygen and an aluminum target. Moreover, the etching stopper film 2 can be formed by simultaneously discharging two targets, i.e., a hafnium target and an aluminum target, under a mixed gas atmosphere of noble gas and oxygen gas or oxygen-containing gas.

[0090]

As mentioned above, the mask blank 100 of the first embodiment includes an etching stopper film 2 containing hafnium, aluminum, and oxygen between the transparent substrate 1 and the phase shift film 3 which is a thin film for pattern formation, and an oxygen deficiency ratio of the etching stopper film 2 is 6.4% or less. The etching stopper film 2 simultaneously satisfies the properties of having higher durability to dry etching with fluorine-based gas performed in forming a pattern in the phase shift film 3 and having higher transmittance to an exposure light compared to an etching stopper film formed of hafnium oxide.

during manufacture of the phase shift mask 200.

[0093]

Namely, the transfer mask (phase shift mask) 200 of the first embodiment is featured in having a structure where an etching stopper film 2 and a phase shift pattern 3a which is a phase shift film having a transfer pattern are stacked in this order on a main surface of the transparent substrate 1, the phase shift pattern 3a is formed of a material containing silicon, and an oxygen deficiency ratio of the etching stopper film is 6.4% or less. An oxygen deficiency ratio [%] is calculated by $100 \times [O_I - O_R] / O_I$, where O_R is an oxygen content in the etching stopper film, and O_I is an oxygen content when all hafnium and aluminum present in the etching stopper film are in a stoichiometrically stable oxide state. Further, the phase shift mask 200 has a light shielding pattern 4b which is a light shielding film having a pattern including a light shielding band on the phase shift pattern 3a.

[0094]

The method of manufacturing the phase shift mask of the first embodiment uses the mask blank 100 mentioned above, which is featured in including the steps of forming a transfer pattern in the light shielding film 4 by dry etching; forming a transfer pattern in the phase shift film 3 by dry etching using fluorine-based gas with the light shielding film 4 having the transfer pattern as a mask; and forming a pattern including a light shielding band (light shielding band, light shielding patch, etc.) in the light shielding film 4 by dry etching. The method of manufacturing the phase shift mask 200 of the first embodiment is explained below according to the manufacturing steps shown in FIG. 3. Explained herein is the method of manufacturing the phase shift

verticality of the sidewall of the pattern of the phase shift pattern 3a and to enhance in-plane CD uniformity of the phase shift pattern 3a. Even after the over etching, a surface of the etching stopper film 2 is only slightly etched and a surface of the transparent substrate 1 is not exposed at the transmitting portion of the phase shift pattern 3a.

[0098]

Next, a resist film is formed on the mask blank 100 by spin coating. Thereafter, a second pattern, which is a pattern (light shielding pattern) to be formed in the light shielding film 4, is written with an electron beam in the resist film, and a predetermined treatment such as developing is conducted, to thereby form a second resist pattern 7b having a light shielding pattern (see FIG. 3(e)). Since the second pattern is rather large, it is possible to employ an exposure writing by a laser light using a laser writing apparatus having high throughput, in place of an electron beam writing.

[0099]

Subsequently, dry etching is conducted using mixed gas of chlorine-based gas and oxygen gas with the second resist pattern 7b as a mask, and a second pattern (light shielding pattern 4b) is formed in the light shielding film 4. Further, the second resist pattern 7b is removed, predetermined treatments such as cleaning are conducted, and the phase shift mask 200 is obtained (see FIG. 3(f)). While SC-1 cleaning was used in the cleaning step, variation was observed in the film reduction amount of the etching stopper film 2 depending on an oxygen deficiency ratio ($100 \times [O_I - O_R] / O_I$) as given below in Examples and Comparative Examples.

[0100]

containing chromium, and at least one or more metallic elements selected from indium (In), tin (Sn), and molybdenum (Mo) (these metallic elements are hereinafter referred to as "metallic element including indium, etc.>").

[0115]

In the mask blank 110, a resist film of an organic material is preferably formed in contact with a surface of the hard mask film 9 at a film thickness of 100nm or less.

[0116]

As mentioned above, the mask blank 110 of the second embodiment includes an etching stopper film 2 containing hafnium, aluminum, and oxygen between the transparent substrate 1 and the light shielding film 8 which is a thin film for pattern formation, and an oxygen deficiency ratio of the etching stopper film 2 is adjusted to be 6.4% or less. The etching stopper film 2 simultaneously satisfies the properties of having higher durability to dry etching with fluorine-based gas performed in forming a pattern in the light shielding film 8 and having a higher transmittance to an exposure light compared to an etching stopper film formed of hafnium oxide. Accordingly, since over etching can be made without digging a main surface of the transfer substrate 1 in forming a transfer pattern in the light shielding film 8 by dry etching with fluorine-based gas, verticality of the pattern sidewall can be enhanced, and in-plane CD uniformity of the pattern can be enhanced.

[0117]

On the other hand, when a transfer mask (binary mask) 210 was manufactured from the mask blank 110 of the second embodiment, since the etching stopper film 2 has a higher transmittance to an

an oxygen deficiency ratio of the etching stopper film 2 is 6.4% or less. An oxygen deficiency ratio [%] is calculated by $100 \times [O_I - O_R] / O_I$, where O_R is an oxygen content in the etching stopper film 2, and O_I is an oxygen content when all hafnium and aluminum present in the etching stopper film 2 are in a stoichiometrically stable oxide state.

[0120]

The manufacturing method of the transfer mask (binary mask) 210 of the second embodiment is featured in using the mask blank 110, and including the step of forming a transfer pattern in the light shielding film 8 by dry etching using fluorine-based gas. The method of manufacturing the transfer mask 210 according to the second embodiment is explained below according to the manufacturing steps shown in FIG. 6. Explained herein is the method of manufacturing the transfer mask 210 using the mask blank 110 having the hard mask film 9 stacked on the light shielding film 8. Further, an explanation is made in the case of applying a material containing a transition metal and silicon to the light shielding film 8, and applying a material containing chromium to the hard mask film 9.

[0121]

First, a resist film is formed in contact with the hard mask film 9 of the mask blank 110 by spin coating. Next, a transfer pattern (light shielding pattern) to be formed in the light shielding film 8 is written with an electron beam in the resist film, and a predetermined treatment such as developing is conducted, to thereby form a resist pattern 10a having a light shielding pattern (see FIG. 6(a)). Subsequently, dry etching is carried out using mixed gas of chlorine-based gas and oxygen gas with the

resist pattern 10a as a mask, and a transfer pattern (hard mask pattern 9a) is formed in the hard mask film 9 (see FIG. 6(b)).

[0122]

Next, after removing the resist pattern 10a, dry etching is conducted using fluorine-based gas with the hard mask pattern 9a as a mask, and a transfer pattern (light shielding pattern 8a) is formed in the light shielding film 8 (see FIG. 6(c)). In dry etching of the light shielding film 8 with fluorine-based gas, an additional etching (over etching) is done to enhance verticality of the sidewall of the pattern of the light shielding pattern 8a and to enhance in-plane CD uniformity of the light shielding pattern 8a. Even after the over etching, a surface of the etching stopper film 2 is only slightly etched and a surface of the transparent substrate 1 is not exposed at the transmitting portion of the light shielding pattern 8a.

[0123]

Further, the remaining hard mask pattern 9a is removed by dry etching using mixed gas of chlorine-based gas and oxygen gas, and through predetermined treatments such as cleaning, a transfer mask 210 is obtained (see FIG. 6(d)). While SC-1 cleaning was used in the cleaning step, variation was observed in the film reduction amount of the etching stopper film 2 depending on an oxygen deficiency ratio ($100 \times [O_I - O_R] / O_I$) as shown in the Examples and Comparative Examples given below. Incidentally, chlorine-based gas and fluorine-based gas used in the aforementioned dry etching are similar to those used in the first embodiment.

[0124]

The transfer mask 210 of the second embodiment is manufactured using the mask blank 110 mentioned above. The etching

thereafter, a phase shift pattern which should be formed in the phase shift film 3 is written with an electron beam in the resist film, and predetermined treatments such as developing are further conducted, to thereby form a resist pattern 18e (see FIG. 9(d)).

[0139]

Thereafter, dry etching is carried out using mixed gas of chlorine-based gas and oxygen gas with the resist pattern 18e as a mask, and a hard mask pattern 11e is formed in the hard mask film 11 (see FIG. 9(e)). Next, after removing the resist pattern 18e, dry etching is carried out using fluorine-based gas such as CF_4 , and a phase shift pattern 3e is formed in the phase shift film 3 (see FIG. 9(f)).

[0140]

Subsequently, dry etching is conducted using mixed gas of chlorine-based gas and oxygen gas with the light shielding pattern 4f as a mask, and a hard mask pattern 11f is formed. At this stage, the hard mask pattern 12f is removed simultaneously.

[0141]

Thereafter, a cleaning step is conducted and a mask defect inspection is performed as necessary. Further, depending on the result of the defect inspection, a defect repair is carried out as necessary and the transfer mask 220 is manufactured. While SC-1 cleaning was used in the cleaning step, variation was observed in the film reduction amount of the etching stopper film 2 depending on an oxygen deficiency ratio ($100 \times [O_I - O_R] / O_I$) as shown in the Examples and Comparative Examples given below.

[0142]

The transfer mask (CPL mask) 220 of the third embodiment was manufactured using the mask blank 120 mentioned above. Therefore,

which applies an extreme ultra violet (hereafter EUV) light as an exposure light source. Namely, the alternative form of mask blank has a structure where a multilayer reflective film, a protective film, and an absorber film are stacked in this order on a substrate, the protective film is formed of a material containing hafnium, aluminum, and oxygen, and an oxygen deficiency ratio of the protective film is 6.4% or less. Incidentally, an EUV light indicates a light of a wavelength range of soft x-ray region or vacuum ultraviolet region, specifically, a light having a wavelength of around 0.2 to 100nm.

[0147]

The configuration of the etching stopper film 2 of this invention given above can be applied as the configuration of the protective film of the mask blank of the alternative form of mask blank. Such a protective film has high durability to both of dry etching with fluorine-based gas and dry etching with chlorine-based gas. Therefore, not only a material containing tantalum, but various materials can be applied to the absorber film. For example, any of a material containing chromium, a material containing silicon, and a material containing a transition metal can be used for the absorber film.

[0148]

The substrate can be made from materials such as synthetic quartz glass, quartz glass, aluminosilicate glass, soda-lime glass, low thermal expansion glass (SiO_2 - TiO_2 glass, etc.), crystallized glass where β -quartz solid solution is precipitated, single crystal silicon, and SiC.

[0149]

The multilayer reflective film is a multilayer film where a

stacked in this order on a substrate, the absorber film includes a transfer pattern, the protective film is formed of a material containing hafnium, aluminum, and oxygen, and an oxygen deficiency ratio of the protective film is 6.4% or less.

(Example 1)

[0151]

The embodiment of this invention is described in greater detail below together with examples, referring to FIGS. 7 to 9.

(Example 1)

[Manufacture of Mask Blank]

A transparent substrate 1 formed of a synthetic quartz glass with a size of a main surface of about 152mm × about 152mm and a thickness of about 6.35mm was prepared. An end surface and the main surface of the transparent substrate 1 were polished to a predetermined surface roughness or less (0.2nm or less root mean square roughness Rq), and thereafter subjected to predetermined cleaning treatment and drying treatment.

[0152]

Next, an etching stopper film 2 formed of hafnium, aluminum, and oxygen (HfAlO film) was formed in contact with a surface of the transparent substrate 1 at a thickness of 3nm. Concretely, the etching stopper film 2 was formed by placing the transparent substrate 1 in a single-wafer RF sputtering apparatus, simultaneously discharging an Al₂O₃ target and an HfO₂ target, and by sputtering (RF sputtering) using argon (Ar) gas as sputtering gas. An etching stopper film formed on another transparent substrate under the same conditions was analyzed by X-ray photoelectron spectroscopy, and the result was Hf:Al:O=32.8:5.6 :61.6 (atom% ratio). Further, a composition ratio

in this etching stopper film when hafnium and aluminum present in this film are in a stoichiometrically stable oxide state was Hf:Al:O=29.2:5.0:65.8 (atom% ratio). Namely, the etching stopper film 2 is represented by $O_R:O_I=61.6:65.8$ (atom% ratio), and an oxygen deficiency ratio [%] calculated therefrom was 6.38.

Further, $Hf/[Hf+Al]$ of the etching stopper film 2 is 0.85. Incidentally, each optical characteristic of the etching stopper film was measured using the spectroscopic ellipsometer (M-2000D manufactured by J.A. Woollam), and a refractive index n was 2.851 and an extinction coefficient k was 0.278 in a light of 193nm wavelength.

[0153]

Next, a phase shift film (SiO_2 film) 3 including silicon and oxygen was formed in contact with a surface of the etching stopper film 2 at a thickness of 177nm. Concretely, the transparent substrate 1 having the etching stopper film 2 formed thereon was placed in a single-wafer RF sputtering apparatus, and by reactive sputtering (RF sputtering) using a silicon dioxide (SiO_2) target and argon (Ar) gas as sputtering gas, the phase shift film 3 was formed.

[0154]

Each optical characteristic of a phase shift film formed on another transparent substrate under the same conditions and subjected to heat treatment was measured using a spectroscopic ellipsometer (M-2000D manufactured by J. A. Woollam), and a refractive index n was 1.563 and an extinction coefficient k was 0.000 (lower limit measurable) at a light of 193nm wavelength.

[0155]

Next, a hard mask film (CrN film) 11 including chromium and

circuit pattern to be finally formed on the semiconductor device can be formed at a high precision, even if the phase shift mask 220 of Example 1 was set on a mask stage of an exposure apparatus and a resist film on the semiconductor device was subjected to an exposure transfer.

[0168]

(Example 2)

[Manufacture of Mask Blank]

A mask blank 120 of Example 2 was manufactured through the same procedure as the mask blank of Example 1, except for the etching stopper film 2. Explanation is made below on the points that differ from the mask blank of Example 1.

[0169]

In the etching stopper film 2 of Example 2, a HfAlO film (Hf:Al:O=28.0:9.5:62.5 (atom% ratio)) including hafnium, aluminum, and oxygen was applied, which was formed in contact with a surface of the transparent substrate 1 at a thickness of 3nm. Further, a composition ratio in this etching stopper film when hafnium and aluminum present in this film are in a stoichiometrically stable oxide state was Hf:Al:O=26.0:8.8:65.2 (atom% ratio). Namely, the etching stopper film 2 is represented by $O_R:O_I=62.5:65.2$ (atom% ratio), and an oxygen deficiency ratio [%] calculated therefrom was 4.14. Further, $Hf/[Hf+Al]$ of the etching stopper film 2 is 0.75. Further, a refractive index n of the etching stopper film 2 to a light of 193nm wavelength is 2.630, and an extinction coefficient k is 0.181.

[0170]

A transmittance of an etching stopper film formed on another transparent substrate at a film thickness of 3nm in a wavelength

thickness of 3nm. Further, a composition ratio in this etching stopper film when hafnium and aluminum present in this film are in a stoichiometrically stable oxide state was Hf:Al:O=23.1:12.3:64.6 (atom% ratio). Namely, the etching stopper film 2 is represented by $O_R:O_I=62.7:64.6$ (atom% ratio), and an oxygen deficiency ratio [%] calculated therefrom was 2.94. Further, $Hf/[Hf+Al]$ of the etching stopper film 2 is 0.65. Further, a refractive index n of the etching stopper film 2 to a light of 193nm wavelength is 2.434, and an extinction coefficient k is 0.094.

[0175]

A transmittance of an etching stopper film formed on another transparent substrate at a film thickness of 3nm in a wavelength of an ArF excimer laser (193nm) was measured using the phase shift measuring apparatus, and the transmittance was 94.0% when a transmittance of the transparent substrate is 100%. From this result, it was found that an influence of reduction in transmittance caused by providing the etching stopper film of Example 3 is small. Further, a transmittance of an etching stopper film formed on another transparent substrate at a film thickness of 2nm in a wavelength of an ArF excimer laser (193nm) was measured using the phase shift measuring apparatus, and a transmittance was 96.4% when a transmittance of the transparent substrate is 100%. The film reduction amount was 0.76nm in the etching stopper film measured after ten times the cleaning step on the transparent substrate on which the etching stopper film was formed through SC-1 cleaning explained in Example 1. From this result, it was confirmed that the etching stopper film 2 of Example 3 has sufficient resistance to chemical cleaning performed during manufacturing a phase shift mask from a mask blank.

220 of Example 3 was set on a mask stage of an exposure apparatus and a resist film on the semiconductor device was subjected to an exposure transfer.

[0179]

(Example 4)

[Manufacture of Mask Blank]

The mask blank 120 of Example 4 was manufactured through the same procedure as the mask blank of Example 1, except for the etching stopper film 2. In the etching stopper film 2 of Example 4, a HfAlO film (Hf:Al:O=22.5:14.6:62.9 (atom% ratio)) including hafnium, aluminum, and oxygen was applied, which was formed in contact with a surface of the transparent substrate 1 at a thickness of 3nm. Further, a composition ratio in this etching stopper film when hafnium and aluminum present in this film are in a stoichiometrically stable oxide state was Hf:Al:O=21.7:14.0:64.3 (atom% ratio). Namely, the etching stopper film 2 is represented by $O_R:O_I=62.9:64.3$ (atom% ratio), and an oxygen deficiency ratio [%] calculated therefrom was 2.18. $Hf/[Hf+Al]$ of the etching stopper film 2 is 0.61. Further, a refractive index n of the etching stopper film 2 to a light of 193nm wavelength is 2.366, and an extinction coefficient k is 0.070.

[0180]

A transmittance of an etching stopper film formed on another transparent substrate at a film thickness of 3nm in a wavelength of an ArF excimer laser (193nm) was measured using the phase shift measuring apparatus, and a transmittance was 95.1% when a transmittance of the transparent substrate is 100%. From this result, it was found that an influence of reduction in transmittance caused by providing the etching stopper film of

[0183]

On the phase shift mask (CPL mask) 220 of Example 4, a simulation of a transfer image was made when an exposure transfer was made on a resist film on a semiconductor device at an exposure light of 193nm wavelength, using AIMS193 (manufactured by Carl Zeiss). The simulated exposure transfer image was inspected, and the design specification was fully satisfied. There was little influence on the exposure transfer caused by the reduction of a transmittance of the transparent portion by providing the etching stopper film 2. It can be considered from this result that a circuit pattern to be finally formed on the semiconductor device can be formed at a high precision, even if the phase shift mask 220 of Example 4 was set on a mask stage of an exposure apparatus and a resist film on the semiconductor device was subjected to an exposure transfer.

[0184]

(Example 5)

[Manufacture of Mask Blank]

The mask blank 120 of Example 5 was manufactured through the same procedure as the mask blank of Example 1, except for the etching stopper film 2. In Example 5, an etching stopper film 2 including hafnium, aluminum, and oxygen (HfAlO film Hf:Al:O=19.9:16.9:63.2 (atom% ratio)) was applied, which was formed in contact with a surface of the transparent substrate 1 at a thickness of 3nm. Further, a composition ratio in this etching stopper film when hafnium and aluminum present in this film are in a stoichiometrically stable oxide state was Hf:Al:O=19.5:16.6:63.9 (atom% ratio). Namely, the etching stopper film 2 is represented by $O_R:O_I=63.2:63.9$ (atom% ratio), and an oxygen deficiency ratio

The mask blank of Comparative Example 1 has the same configuration as the mask blank of Example 1, except for the etching stopper film. In Comparative Example 1, an etching stopper film including hafnium and oxygen (HfO film) was formed in contact with a surface of a transparent substrate at a thickness of 3nm. Concretely, the etching stopper film was formed by placing the transparent substrate in a single-wafer RF sputtering apparatus, and by sputtering (RF sputtering) using HfO₂ target with argon (Ar) gas as sputtering gas. An etching stopper film formed on another transparent substrate under the same conditions was analyzed by X-ray photoelectron spectroscopy, and the result was Hf:Al:O=39.1:0.0:60.9 (atom% ratio). Further, a composition ratio in this etching stopper film when hafnium and aluminum present in this film are in a stoichiometrically stable oxide state was Hf:Al:O=33.3:0.0:66.7 (atom% ratio). Namely, the etching stopper film is represented by O_R:O_I=60.9:66.7 (atom% ratio), and an oxygen deficiency ratio [%] calculated therefrom was 8.70. Further, Hf/[Hf+Al] of the etching stopper film is 1.00. Further, a refractive index n of the etching stopper film to a light of 193nm wavelength is 2.949, and an extinction coefficient k is 0.274.

[0191]

Further, a transmittance of an etching stopper film formed on another transparent substrate in a wavelength of ArF excimer laser (193nm) was measured using the phase shift measuring apparatus, and the transmittance was 84.2% when a transmittance of the transparent substrate is 100%. Further, a transmittance of an etching stopper film formed on another transparent substrate at a film thickness of 2nm in a wavelength of an ArF excimer laser (193nm) was measured using the phase shift measuring apparatus,

[0194]

(Comparative Example 2)

[Manufacture of Mask Blank]

The mask blank of Comparative Example 2 has the same configuration as the mask blank of Example 1, except for the etching stopper film. In the etching stopper film of Comparative Example 2, a HfAlO film including hafnium, aluminum, and oxygen (Hf:Al:O=35.1:3.6:61.3 (atom% ratio)) was applied, which was formed in contact with a surface of a transparent substrate at a thickness of 3nm. Further, a composition ratio in this etching stopper film when hafnium and aluminum present in this film are in a stoichiometrically stable oxide state was Hf:Al:O=30.7:3.2:66.1 (atom% ratio). Namely, the etching stopper film is represented by $O_R:O_I=61.3:66.1$ (atom% ratio), and an oxygen deficiency ratio [%] calculated therefrom was 7.26. Further, $Hf/[Hf+Al]$ of the etching stopper film is 0.91. Further, a refractive index n of the etching stopper film to a light of 193nm wavelength is 2.908, and an extinction coefficient k is 0.309

[0195]

A transmittance of an etching stopper film formed on another transparent substrate in a wavelength of an ArF excimer laser (193nm) was measured using the phase shift measuring apparatus, and a transmittance was 83.4% when a transmittance of the transparent substrate is 100%. Further, a transmittance of an etching stopper film formed on another transparent substrate at a film thickness of 2nm in a wavelength of an ArF excimer laser (193nm) was measured using the phase shift measuring apparatus, and a transmittance was 89.2% when a transmittance of the transparent substrate is 100%. The film reduction amount was 0.20nm

CLAIMS

[Claim 1]

A mask blank having a structure where a transparent substrate has stacked thereon an etching stopper film and a thin film for pattern formation in this order,

wherein the thin film comprises a material containing silicon,

wherein the etching stopper film comprises a material containing hafnium, aluminum, and oxygen, and

wherein an oxygen deficiency ratio of the etching stopper film is 6.4% or less.

[Claim 2]

The mask blank according to claim 1, wherein a ratio by atom% of an amount of the hafnium to a total amount of the hafnium and the aluminum in the etching stopper film is 0.85 or less.

[Claim 3]

The mask blank according to claim 1 or 2, wherein a ratio by atom% of an amount of the hafnium to a total amount of the hafnium and the aluminum in the etching stopper film is 0.60 or more.

[Claim 4]

The mask blank according to any of claims 1 to 3, wherein the etching stopper film has an amorphous structure in a state including a bond of hafnium and oxygen and a bond of aluminum and oxygen.

[Claim 5]

The mask blank according to any of claims 1 to 4, wherein the etching stopper film consists of hafnium, aluminum, and oxygen.

[Claim 6]

The mask blank according to any of claims 1 to 5, wherein the etching stopper film is formed in contact with a main surface

of the transparent substrate.

[Claim 7]

The mask blank according to any of claims 1 to 6, wherein the etching stopper film has a thickness of 2nm or more.

[Claim 8]

The mask blank according to any of claims 1 to 7, wherein the thin film is a phase shift film, the phase shift film having a function to generate a phase difference of 150 degrees or more and 210 degrees or less between an exposure light that transmitted through the phase shift film and an exposure light that transmitted through air for a same distance as a thickness of the phase shift film.

[Claim 9]

The mask blank according to claim 8, wherein a light shielding film is provided on the phase shift film.

[Claim 10]

The mask blank according to claim 9, wherein the light shielding film comprises a material containing chromium.

[Claim 11]

A transfer mask having a structure where a transparent substrate has stacked thereon an etching stopper film and a thin film having a transfer pattern in this order,

wherein the thin film comprises a material containing silicon,
wherein the etching stopper film comprises a material containing hafnium, aluminum, and oxygen, and

wherein an oxygen deficiency ratio of the etching stopper film is 6.4% or less.

[Claim 12]

The transfer mask according to claim 11, wherein a ratio by

atom% of an amount of the hafnium to a total amount of the hafnium and the aluminum in the etching stopper film is 0.85 or less.

[Claim 13]

The transfer mask according to claim 11 or 12, wherein a ratio by atom% of an amount of the hafnium to a total amount of the hafnium and the aluminum in the etching stopper film is 0.60 or more.

[Claim 14]

The transfer mask according to any of claims 11 to 13, wherein the etching stopper film has an amorphous structure in a state including a bond of hafnium and oxygen and a bond of aluminum and oxygen.

[Claim 15]

The transfer mask according to any of claims 11 to 14, wherein the etching stopper film consists of hafnium, aluminum, and oxygen.

[Claim 16]

The transfer mask according to any of claims 11 to 15, wherein the etching stopper film is formed in contact with a main surface of the transparent substrate.

[Claim 17]

The transfer mask according to any of claims 11 to 16, wherein the etching stopper film has a thickness of 2nm or more.

[Claim 18]

The transfer mask according to any of claims 11 to 17, wherein the thin film is a phase shift film, the phase shift film having a function to generate a phase difference of 150 degrees or more and 210 degrees or less between an exposure light that transmitted through the phase shift film and an exposure light

that transmitted through air for a same distance as a thickness of the phase shift film.

[Claim 19]

The transfer mask according to claim 18 comprising a light shielding film having a light shielding pattern with a light shielding band on the phase shift film.

[Claim 20]

The transfer mask according to claim 19, wherein the light shielding film comprises a material containing chromium.

[Claim 21]

A method of manufacturing a semiconductor device comprising the step of using the transfer mask according to any of claims 11 to 20 and exposure-transferring the pattern on the transfer mask to a resist film on a semiconductor substrate.