

MASK BLANK, METHOD FOR MANUFACTURING TRANSFER MASK, AND METHOD FOR MANUFACTURING SEMICONDUCTOR DEVICE

Technical Field

[0001] The present invention relates to a mask blank, and a method for manufacturing a transfer mask manufactured by using the mask blank. Furthermore, the present invention relates to a method for manufacturing a semiconductor device with use of the transfer mask.

Background Art

[0002] At steps in manufacturing a semiconductor device, a fine pattern is formed by using a photolithography method. Furthermore, many transfer masks are usually used for forming the fine pattern. To make a semiconductor device pattern finer, it is necessary not only to make a mask pattern formed on a transfer mask finer, but also to shorten a wavelength of an exposure light source used in photolithography. In recent years, an ArF excimer laser (wavelength: 193 nm) has been employed increasingly in an exposure light source used in manufacturing a semiconductor device.

[0003] There are several types of transfer masks. In particular, a binary mask and a halftone phase shift mask are widely used. A conventional binary mask generally includes a light shielding film pattern made of a chromium based material on a transparent substrate. In recent years, a binary mask including a light shielding film formed of a transition metal silicide based material has come to be used. However, in recent years, the light shielding film made of a transition metal silicide based material has been found to have low resistance to exposure light of an ArF excimer laser (ArF exposure light) (that is, ArF light fastness), as disclosed in Patent Document 1. In Patent Document 1, ArF light fastness is enhanced by applying a material that contains carbon or hydrogen incorporated in transition metal silicide to a light shielding film.

[0004] On one hand, Patent Document 2 discloses a phase shift mask including a phase shift film of SiN_x. Patent Document 3 describes a phase shift film of SiN_x confirmed to have high ArF light fastness. On the other hand, Patent Document 4 discloses a defect repair technique for etching and removing a black defect portion of a light shielding film by irradiating the black defect portion with an electron beam while a xenon difluoride

(XeF₂) gas is supplied to the black defect portion (hereinafter, defect repair including irradiation with charged particles such as an electron beam will simply be referred to as EB defect repair).

Prior Art Documents

Patent Documents

[0005]

Patent Document 1: International Publication WO 2010/092899

Patent Document 2: Japanese Patent Application Publication 06-75361

Patent Document 3: Japanese Patent Application Publication 2014-137388

Patent Document 4: PCT Application Japanese Translation Publication 2004-537758

Summary of the Invention

Problems to be Solved by the Invention

[0006] The phase shift film made of a material containing silicon and nitrogen and containing no transition metal (hereinafter, will be referred to as a SiN based material) as disclosed in Patent Documents 2 and 3 is known to have high ArF light fastness. In examination by the present inventors, when the SiN based material is applied to a light shielding film of a binary mask, ArF light fastness of the light shielding film can be enhanced. However, when a black defect portion found in a pattern of the light shielding film made of the SiN based material is subjected to EB defect repair, two significant problems are found to occur.

[0007] One of the significant problems is that a surface of a transparent substrate at a region where a black defect has existed is significantly roughened (surface roughness significantly deteriorates) when the black defect portion of the light shielding film is removed by performing EB defect repair. The region including the roughened surface of the binary mask on which EB defect repair has been performed is a region serving as a transparent portion transmitting ArF exposure light. When the surface roughness of the substrate at the transparent portion significantly deteriorates, a decrease in transmittance of ArF exposure light and a diffuse reflection are likely to occur. When such a binary mask is installed on a mask stage of an exposure apparatus and used in transfer by exposure, transfer accuracy significantly decreases.

[0008] The other of the significant problems is that when the black defect portion of the light shielding film is removed by performing EB defect repair, the light shielding film pattern existing around the black defect portion is etched from a side wall of the pattern (this phenomenon will be referred to as spontaneous etching). When spontaneous etching occurs, the width of the light shielding film pattern becomes significantly smaller than the width of the light shielding film pattern on which EB defect repair is still not performed. When the light shielding film pattern on which EB defect repair is still not performed has a small width, the pattern may be fallen or deleted. When such a binary mask including the light shielding film pattern that is likely to undergo spontaneous etching is installed on a mask stage of an exposure apparatus and used in transfer by exposure, transfer accuracy significantly decreases.

[0009] Thus, the present invention has been made to solve the problems in the related art. An object of the present invention is to provide a mask blank capable of suppressing occurrence of roughening of a surface of a transparent substrate and suppressing occurrence of spontaneous etching of a light shielding film pattern when EB defect repair is performed on a black defect portion of a light shielding film formed of a SiN based material. Furthermore, an object of the present invention is to provide a method for manufacturing a transfer mask with use of such a mask blank. Further, an object of the present invention is to provide a method for manufacturing a semiconductor device with use of such a transfer mask.

Means for Solving the Problem

[0010] To solve the above-described problems, the present invention includes the following structures.

[0011]

(Structure 1)

A mask blank including a transparent substrate including a light shielding film for formation of a transfer pattern,

wherein the light shielding film is formed of a material containing silicon and nitrogen or a material containing one or more elements selected from a semimetal element and a non-metal element, silicon, and nitrogen,
the light shielding film is provided in contact with a main surface of the transparent

substrate,

the light shielding film has an optical density for exposure light of an ArF excimer laser of 2.5 or more,

a ratio of a content (atom%) of silicon to a content (atom%) of nitrogen at an internal region except for a neighborhood region near an interface between the light shielding film and the transparent substrate and a surface layer region on a side opposite to the transparent substrate is 2.4 or more and 4.0 or less, and

the internal region has a total content of silicon and nitrogen of 97 atom% or more.

[0012]

(Structure 2)

The mask blank according to structure 1, wherein a region except for the surface layer region of the light shielding film has an oxygen content of 3 atom% or less.

[0013]

(Structure 3)

The mask blank according to structure 1 or 2, wherein the surface layer region is a region ranging from a surface of the light shielding film on the side opposite to the transparent substrate to a depth of 5 nm in a direction toward the transparent substrate.

[0014]

(Structure 4)

The mask blank according to any one of structures 1 to 3, wherein the neighborhood region is a region ranging from the interface of the transparent substrate to a depth of 5 nm in a direction toward the surface layer region.

[0015]

(Structure 5)

The mask blank according to any one of structures 1 to 4, wherein the light shielding film is formed of a material containing silicon, nitrogen, and a non-metal element.

[0016]

(Structure 6)

The mask blank according to any one of structures 1 to 5, wherein the surface layer region has an oxygen content higher than the oxygen content of the region except for

the surface layer region of the light shielding film.

[0017]

(Structure 7)

The mask blank according to any one of structures 1 to 6, wherein the light shielding film has an extinction coefficient k for exposure light of an ArF excimer laser of 2.00 or more and 2.40 or less.

[0018]

(Structure 8)

The mask blank according to any one of structures 1 to 7, wherein the light shielding film has a refractive index n for exposure light of an ArF excimer laser of 1.25 or more and 1.55 or less.

[0019]

(Structure 9)

A method for manufacturing a transfer mask with use of the mask blank according to any one of structures 1 to 8, the method including a step of forming a transfer pattern on the light shielding film by dry etching.

[0020]

(Structure 10)

A method for manufacturing a semiconductor device, the method including a step of transferring by exposure a transfer pattern to a resist film on a semiconductor substrate with use of a transfer mask manufactured by the method for manufacturing a transfer mask according to structure 9.

Effect of Invention

[0021] A mask blank of the present invention is capable of suppressing occurrence of roughening of a surface of a transparent substrate and suppressing occurrence of spontaneous etching of a light shielding film pattern formed of a SiN based material when EB defect repair is performed on a black defect portion of the light shielding film pattern.

[0022] A method for manufacturing a transfer mask of the present invention is capable of suppressing occurrence of roughening of a surface of a transparent substrate and suppressing occurrence of spontaneous etching of a light shielding film pattern near a black defect portion even when EB defect repair is performed on the black defect portion

of the light shielding film pattern during the manufacturing of the transfer mask.

[0023] Therefore, a transfer mask manufactured by the method for manufacturing a transfer mask of the present invention is a transfer mask having high transfer accuracy.

Brief Description of Drawings

[0024]

FIG. 1 is a cross-sectional view illustrating a configuration of a mask blank according to an embodiment of the present invention.

FIG. 2A is a cross-sectional view illustrating a step in manufacturing a transfer mask according to an embodiment of the present invention.

FIG. 2B is a cross-sectional view illustrating a step in manufacturing a transfer mask according to the embodiment of the present invention.

FIG. 2C is a cross-sectional view illustrating a step in manufacturing a transfer mask according to the embodiment of the present invention.

FIG. 2D is a cross-sectional view illustrating a step in manufacturing a transfer mask according to the embodiment of the present invention.

FIG. 2E is a cross-sectional view illustrating a step in manufacturing a transfer mask according to the embodiment of the present invention.

FIG. 2F is a cross-sectional view illustrating a step in manufacturing a transfer mask according to the embodiment of the present invention.

Description of the Embodiments

[0025] First, the circumstances leading to the completion of the present invention will be described.

[0026] The present inventors have intensively studied a configuration of a light shielding film that suppresses occurrence of roughening of a surface of a transparent substrate and suppresses occurrence of spontaneous etching of a light shielding film pattern when EB defect repair is performed on a black defect portion of the light shielding film formed of a SiN based material. First, when EB defect repair is performed on a pattern of a phase shift film formed of the SiN based material, there is found a problem of a repair rate significantly reduced, but there is found no substantial problem involved in spontaneous etching.

[0027] An XeF_2 gas used in EB defect repair is known as an unexcited etching gas used in isotropic etching for a silicon based material. The etching is performed by a process including surface adsorption by the silicon based material of the unexcited XeF_2 gas, separation of the XeF_2 gas into Xe and F, and production and volatilization of a high-order fluoride of silicon. In EB defect repair for a thin film pattern made of the silicon based material, an unexcited fluorine-based gas such as an XeF_2 gas is supplied to a black defect portion of the thin film pattern, a surface of the black defect portion is caused to adsorb the fluorine-based gas, and then the black defect portion is irradiated with an electron beam. Accordingly, silicon at the black defect portion is excited to promote a bond of the silicon to fluorine, and volatilizes as a high-order fluoride of silicon produced significantly faster than in the case without irradiation with an electron beam. It is difficult to prevent the thin film pattern around the black defect portion from adsorbing the fluorine-based gas. Therefore, the thin film pattern around the black defect portion is also etched when EB defect repair is performed. In the case of etching silicon bonded to nitrogen, it is necessary to cleave the bond between silicon and nitrogen to produce a high-order fluoride of silicon by bonding fluorine in the XeF_2 gas to silicon. At the black defect portion irradiated with an electron beam, silicon is excited. Therefore, the bond between silicon and nitrogen is cleaved, and the silicon bonds to fluorine and becomes likely to volatilize. On the other hand, silicon not bonded to another element is likely to bond to fluorine. Therefore, even when the silicon not bonded to another element is silicon not excited without being irradiated with an electron beam or silicon that is a light shielding film pattern around the black defect portion and that is slightly influenced by irradiation with an electron beam, the silicon tends to bond to fluorine and is likely to volatilize. This is assumed to be an occurrence mechanism of spontaneous etching.

[0028] Since a silicon film has a significantly small refractive index n for ArF exposure light and a large extinction coefficient k , the silicon film is not appropriate as a material for the phase shift film. Among the SiN based materials, a SiN based material containing a large amount of nitrogen and having a large refractive index n and a small extinction coefficient k is appropriate as the material for the phase shift film. The phase shift film formed of such a SiN based material contains silicon bonded to nitrogen at a high ratio and silicon not bonded to another element at a significantly low ratio. It is considered that for this reason, the phase shift film formed of such a SiN based material does not

substantially have the problem involved in spontaneous etching when EB defect repair is performed. On the other hand, a light shielding film of a binary mask needs to have high light shielding performance against ArF exposure light, that is, an Optical Density (OD) equal to or more than a predetermined value, and needs to have a small thickness.

Therefore, it is necessary to use a material having a large extinction coefficient k as a material for the light shielding film. In these circumstances, a nitrogen content of the SiN based material used for the light shielding film is significantly lower than a nitrogen content of the SiN based material used for the phase shift film. Then, the light shielding film made of the SiN based material contains silicon bonded to nitrogen at a low ratio and silicon not bonded to another element at a high ratio. It is considered that for this reason, the light shielding film made of the SiN based material is likely to have the problem involved in spontaneous etching when EB defect repair is performed.

[0029] Next, the present inventors have investigated increasing the nitrogen content of the SiN based material forming the light shielding film. When the nitrogen content significantly increases as with the SiN based material for the phase shift film, the extinction coefficient k significantly decreases. Therefore, it is necessary to significantly increase the thickness of the light shielding film, and a repair rate during EB defect repair decreases. In consideration of the above, a light shielding film made of a SiN based material and having the nitrogen content increased to some extent is formed on a transparent substrate and is subjected to EB defect repair. As a result, in the light shielding film, a repair rate at the black defect portion is sufficiently high and occurrence of spontaneous etching can be suppressed, but a surface of the transparent substrate on which the repair has been performed is remarkably roughened. When the repair rate at the black defect portion of the light shielding film is sufficiently high, etching selectivity between the light shielding film and the transparent substrate is sufficiently high, and such remarkable roughening of the surface of the transparent substrate supposedly does not occur.

[0030] As a result of further intensive study of the present inventors, it has been found that the light shielding film made of the SiN based material has a relatively low nitrogen content and therefore, contains silicon generally in two nitrided states including unnitrided silicon and nitrided silicon. Further, it has been found that when the light shielding film made of such a SiN based material contains a certain amount or more of

nitrided silicon and has large dispersion in distribution of nitrided silicon, roughening of the surface of the transparent substrate when EB defect repair is performed becomes remarkable.

[0031] From these findings, the present inventors have hypothesized as follows. That is, when a black defect portion of a light shielding film containing a certain amount or more of nitrided silicon and having large dispersion in distribution of nitrided silicon is irradiated with an electron beam from above to perform EB defect repair on the black defect portion, a repair rate varies depending on the dispersion in distribution of nitrided silicon. Accordingly, a removal amount in a film thickness direction of the black defect portion in plan view largely varies. When EB defect repair is continued in a state where the removal amount in plan view varies at respective parts in the film thickness direction, the black defect portion irradiated with an electron beam includes a region where EB defect repair is early performed on the transparent substrate and the surface of the transparent substrate is exposed and a region where EB defect repair is not performed on the transparent substrate and the black defect portion still remains on the surface of the transparent substrate. Then, it is technically difficult to irradiate with an electron beam only the region where the black defect portion remains. Therefore, while EB defect repair is continued to remove the region where the black defect portion remains, the region where the surface of the transparent substrate is exposed is also continuously irradiated with an electron beam. Since the transparent substrate is etched to some extent by EB defect repair, the surface of the transparent substrate is roughened until EB defect repair is completed.

[0032] The phase shift film made of the SiN based material has a significantly high nitrogen content and hardly contains unnitrided silicon. Accordingly, nitrided silicon is relatively uniformly distributed in the phase shift film and is unlikely to be dispersed. On the other hand, the light shielding film needs to secure an optical density equal to or more than a predetermined value for ArF exposure light with a small film thickness. Therefore, the nitrogen content of the light shielding film made of the SiN based material is significantly lower than the nitrogen content of the phase shift film made of the SiN based material. In the case of the light shielding film made of the SiN based material and having such a significantly low nitrogen content that causes spontaneous etching when EB defect repair is performed, an existence ratio of nitrided silicon is very low. In this case,

dispersion in distribution of nitrided silicon in the light shielding film is large. However, since the existence ratio of nitrided silicon is very low, the problem of roughening of the surface of the transparent substrate is unlikely to occur even when EB defect repair is performed. In contrast, when the nitrogen content of the light shielding film made of the SiN based material is increased to prevent occurrence of spontaneous etching, an existence ratio of unnitrided silicon is higher than the existence ratio of nitrided silicon, but the existence ratio of nitrided silicon is relatively high. In this case, dispersion in distribution of nitrided silicon in the light shielding film is likely to be large, and a repair rate is likely to vary depending on dispersion in distribution of unnitrided silicon and nitrided silicon. Therefore, the problem of roughening of the surface of the transparent substrate is likely to occur when EB defect repair is performed.

[0033] As a result of intensive study based on the hypothesis, it has been found that in a case where the SiN based material forming the light shielding film has a ratio of contents of silicon and nitrogen equal to or more than a certain value, when EB defect repair is performed on a black defect portion of the light shielding film, roughening of a surface of the transparent substrate at a region where the black defect portion has existed can be reduced to such an extent that the surface roughening has substantially no influence at the time of transfer by exposure using the light shielding film as a transfer mask. In the light shielding film made of the SiN based material, a surface layer region on a side exposed to air (a surface layer region on a side opposite to the transparent substrate) is inevitably oxidized. However, the oxidation of the surface layer proceeds substantially uniformly in plan view and oxidized silicon needs a larger amount of energy than nitrided silicon to cleave a bond and bond to fluorine. Therefore, ununiform distribution of nitrided silicon in plan view at the oxidized surface layer region has little influence on an ununiform removal amount in plan view when EB defect repair is performed. Further, a neighborhood region near an interface between the transparent substrate and the light shielding film is assumed to have the same composition as composition of an internal region except for the neighborhood region and the surface layer region. However, since the neighborhood region is inevitably influenced by composition of the transparent substrate, it is difficult to determine values of the composition and the number of existing bonds by composition analysis such as Rutherford Back-Scattering Spectrometry (RBS) and X-ray Photoelectron Spectroscopy (XPS). Furthermore, even when the distribution of

nitrided silicon is ununiform at the neighborhood region, a ratio to the total film thickness of the light shielding film is low, and therefore the ununiform distribution of nitrided silicon at the neighborhood region has little influence. Accordingly, when a ratio of a content (atom%) of silicon to a content (atom%) of nitrogen at the internal region except for the neighborhood region near the interface between the light shielding film and the transparent substrate and the surface layer region on the side opposite to the transparent substrate is 2.4 or more, the roughening of the surface of the transparent substrate involved in EB defect repair can be suppressed significantly.

[0034] Further, it has also been found that when a ratio of a content (atom%) of silicon to a content (atom%) of nitrogen at the internal region of the light shielding film is 4.0 or lower, nitrided silicon exists at a certain ratio or more at the internal region of the light shielding film, and that when EB defect repair is performed on the black defect portion of the light shielding film, occurrence of spontaneous etching of a pattern side wall of the light shielding film around the black defect portion can also be suppressed significantly.

Based on the above intensive investigation, the present invention has been completed.

[0035] Next, embodiments of the present invention will be described.

FIG. 1 is a cross-sectional view illustrating a configuration of a mask blank 100 according to an embodiment of the present invention.

The mask blank 100 illustrated in FIG. 1 includes a structure where a light shielding film 2 and a hard mask film 3 are layered in this order on a transparent substrate 1.

[0036]

Transparent Substrate

The transparent substrate 1 is made of a material containing silicon and oxygen. The transparent substrate 1 can be formed of a glass material such as synthetic quartz glass, quartz glass, aluminosilicate glass, soda-lime glass, and low thermal expansion glass (SiO_2 - TiO_2 glass, etc.). Among these, synthetic quartz glass has a high transmittance for ArF exposure light and is particularly preferable as a material forming a transparent substrate of a mask blank.

[0037]

Light Shielding Film

The light shielding film 2 is a monolayer film formed of a silicon nitride based material. The silicon nitride based material in the present invention is a material containing silicon and nitrogen or a material containing one or more elements selected from a semimetal element and a non-metal element, silicon, and nitrogen. Furthermore, since the light shielding film 2 is a monolayer film, the number of manufacturing steps decreases, production efficiency increases, and control of quality including defects during manufacturing becomes facilitated. Furthermore, since the light shielding film 2 is formed of the silicon nitride based material, the light shielding film 2 has high ArF light fastness.

[0038] The light shielding film 2 may contain any semimetal element in addition to silicon. Among the semimetal elements, the light shielding film 2 preferably contains one or more elements selected from boron, germanium, antimony, and tellurium, and in this case, an increase in conductivity of silicon used as a sputtering target can be expected.

[0039] Furthermore, the light shielding film 2 may contain any non-metal element in addition to nitrogen. The non-metal element in the present invention includes a non-metal element in a narrower definition (nitrogen, carbon, oxygen, phosphorus, sulfur, selenium, and hydrogen), halogen (fluorine, chlorine, bromine, iodine, etc.), and a rare gas. Among the non-metal elements, the light shielding film 2 preferably contains one or more elements selected from carbon, fluorine, and hydrogen. The light shielding film 2 except a surface layer region 23 described below preferably has an oxygen content of 3 atom% or less, and further preferably contains substantially no oxygen (at a detection lower limit value or less as determined by composition analysis using X-ray photoelectron spectroscopy). When an oxygen content of the light shielding film 2 is high, a repair rate when EB defect repair is performed significantly decreases.

[0040] The rare gas is an element existing in a film forming chamber when the light shielding film 2 is formed by reactive sputtering and accordingly being capable of increasing a deposition rate to improve productivity. The rare gas becomes plasma and collides with a target. Accordingly, a target constituent element is emitted from the target. While the target constituent element incorporates a reactive gas, the light shielding film 2 is formed on the transparent substrate 1. The rare gas in the film forming chamber is slightly incorporated until the target constituent element adheres to the transparent substrate 1 after the target constituent element is emitted from the target. Preferable examples of the rare gas necessary for the reactive sputtering include argon, krypton, and

xenon. Furthermore, to relax a stress of the light shielding film 2, helium and neon having a small atomic weight may be incorporated positively in the light shielding film 2.

[0041] The light shielding film 2 is preferably formed of a material containing silicon, nitrogen, and the non-metal element. The rare gas is slightly incorporated when the light shielding film 2 is formed by reactive sputtering, as described above. However, the rare gas is an element difficult to detect by performing composition analysis such as RBS and XPS on the light shielding film 2. Therefore, the material containing silicon and nitrogen can be considered to include a material containing the rare gas.

[0042] The inside of the light shielding film 2 includes three regions including a substrate neighborhood region (neighborhood region) 21, an internal region 22, and the surface layer region 23 from the transparent substrate 1 side. The substrate neighborhood region 21 is a region ranging from an interface between the light shielding film 2 and the transparent substrate 1 to a depth of 5 nm (more preferably 4 nm, and further preferably 3 nm) in a direction toward a surface on a side opposite to the transparent substrate 1 (that is, on the surface layer region 23 side). When the substrate neighborhood region 21 is subjected to X-ray photoelectron spectroscopy, the substrate neighborhood region 21 is likely to be influenced by the transparent substrate 1 existing under the substrate neighborhood region 21, and accuracy of a maximum peak of obtained photoelectron intensity in a Si2p narrow spectrum of the substrate neighborhood region 21 is low.

[0043] The surface layer region 23 is a region ranging from the surface on the side opposite to the transparent substrate 1 to a depth of 5 nm (more preferably 4 nm, and further preferably 3 nm) in the direction toward the transparent substrate 1. The surface layer region 23 is a region containing oxygen incorporated from the surface of the light shielding film 2. Therefore, the surface layer region 23 includes a structure where an oxygen content has a composition gradient in a thickness direction of the film (a structure having a composition gradient in which the oxygen content of the film increases as the surface layer region 23 is farther from the transparent substrate 1). That is, the surface layer region 23 has a higher oxygen content than an oxygen content of the internal region 22. Therefore, a removal amount in plan view when EB defect repair is performed on the oxidized surface layer region 23 is unlikely to become ununiform.

[0044] The internal region 22 is a region of the light shielding film 2 except for the substrate neighborhood region 21 and the surface layer region 23. A ratio of a silicon

content (atom%) to a nitrogen content (atom%) at the internal region 22 is 2.4 or more and 4.0 or lower. Here, the internal region 22 needs to have a total content of silicon and nitrogen of 97 atom% or more and is preferably formed of a material having a total content of silicon and nitrogen of 98 atom% or more. That is, to exclude an element such as oxygen having an adverse effect on a binary mask from the internal region 22, the internal region 22 includes silicon and nitrogen in addition to an inevitably introduced element and an intentionally introduced element (semimetal element and non-metal element). On the other hand, a difference in the film thickness direction of a content of each element constituting the internal region 22 is preferably less than 10%. In this case, dispersion in a repair rate when the internal region 22 is removed by EB defect repair decreases.

[0045] Since the substrate neighborhood region 21 near the interface between the transparent substrate 1 and the light shielding film 2 is inevitably influenced by composition of the transparent substrate 1, it is difficult to determine values of the composition and the number of existing bonds by composition analysis such as RBS and XPS. However, the substrate neighborhood region 21 is assumed to have the same composition as the composition of the internal region 22 as described above.

[0046] The light shielding film 2 most preferably includes an amorphous structure because of favorable pattern edge roughness of a pattern formed by etching and the like. When the light shielding film 2 has composition difficult to form the amorphous structure, the light shielding film 2 preferably includes the amorphous structure together with a microcrystal structure.

[0047] The thickness of the light shielding film 2 is 80 nm or less, preferably 70 nm or less, and more preferably 60 nm or less. When the thickness of the light shielding film 2 is 80 nm or less, a fine pattern of the light shielding film is likely to be formed. Furthermore, a load in manufacturing a transfer mask with use of a mask blank including this light shielding film decreases. Furthermore, the thickness of the light shielding film 2 is preferably 40 nm or more, and more preferably 45 nm or more. When the thickness of the light shielding film 2 is less than 40 nm, sufficient light shielding performance against ArF exposure light is unlikely to be obtained. On the other hand, a ratio of the thickness of the internal region 22 to the total thickness of the light shielding film 2 is preferably 0.7 or more, and more preferably 0.75 or more.

[0048] An optical density of the light shielding film 2 for ArF exposure light needs to be 2.5 or more and is preferably 3.0 or more. When the optical density is 2.5 or more, sufficient light shielding performance is obtained. Therefore, when a transfer mask manufactured with use of the mask blank is used in exposure, sufficient contrast of a projected optical image (transfer image) of the transfer mask is likely to be obtained. Furthermore, the optical density of the light shielding film 2 for ArF exposure light is preferably 4.0 or less, and more preferably 3.5 or less. When the optical density is more than 4.0, the film thickness of the light shielding film 2 increases and a fine light shielding film pattern is unlikely to be formed.

[0049] A refractive index n of the light shielding film 2 for ArF exposure light is preferably 1.25 or more. To obtain the refractive index n of less than 1.25, it is necessary to significantly decrease a nitrogen content of the light shielding film 2. Therefore, when the refractive index is less than 1.25, spontaneous etching is likely to occur when EB defect repair is performed. Furthermore, the refractive index n is preferably 1.55 or less from the viewpoint of decreasing an Electro Magnetic Field (EMF) bias of the light shielding film 2.

[0050] An extinction coefficient k of the light shielding film 2 for ArF exposure light is preferably 2.40 or less. To obtain the extinction coefficient k of more than 2.40, it is necessary to significantly decrease the nitrogen content of the light shielding film 2. Therefore, when the extinction coefficient k is more than 2.40, spontaneous etching is likely to occur when EB defect repair is performed. Furthermore, the extinction coefficient k is more preferably 2.00 or more from the viewpoint of decreasing the thickness of the light shielding film 2.

[0051] Note that in the light shielding film 2, oxidation of a surface layer on the side opposite to the transparent substrate 1 proceeds. Therefore, the surface layer of the light shielding film 2 has different composition and different optical characteristics from composition and optical characteristics of a region of the light shielding film 2 except for the surface layer.

Furthermore, on a top of the light shielding film 2, an anti-reflective film may be layered. The anti-reflective film contains oxygen incorporated from a surface and has a content of oxygen higher than the content of oxygen of the light shielding film 2. Therefore, a removal amount in plan view when EB defect repair is performed is unlikely

to become ununiform in the anti-reflective film.

[0052] The light shielding film 2 is formed by sputtering, and any type of sputtering such as DC sputtering, RF sputtering, and ion beam sputtering is applicable. When a target having low conductivity (such as a silicon target, a silicon compound target containing no or a little semimetal element) is used, RF sputtering or ion beam sputtering is preferably applied, while RF sputtering is more preferably applied from the viewpoint of a film forming rate. A method for manufacturing the mask blank 100 preferably includes at least a step of forming the light shielding film 2 on the transparent substrate 1 by reactive sputtering in a sputtering gas containing a nitrogen-based gas and a rare gas with use of a silicon target or a target made of a material containing one or more elements incorporated in silicon and selected from a semimetal element and a non-metal element.

[0053] The refractive index n and the extinction coefficient k of the light shielding film 2 are not determined by the composition of the light shielding film 2 alone. A film density and a crystal state of the light shielding film 2 are also factors affecting the refractive index n and the extinction coefficient k . Therefore, conditions under which the light shielding film 2 is formed by reactive sputtering are adjusted to form the light shielding film 2 having the refractive index n and the extinction coefficient k for ArF exposure light falling within defined values. One way to obtain the refractive index n and the extinction coefficient k of the light shielding film 2 falling within the defined range is to adjust a ratio of a rare gas and a reactive gas in a mixed gas when the film formation is performed by reactive sputtering. Furthermore, there are various ways to obtain the refractive index n and the extinction coefficient k of the light shielding film 2 falling within the defined range, including adjusting a pressure within the film forming chamber when the film formation is performed by reactive sputtering, adjusting electric power applied to the target, and adjusting a positional relationship such as a distance between the target and the transparent substrate. Furthermore, these film forming conditions are specific to a film forming device and are adjusted appropriately to form the light shielding film 2 having a desired refractive index n and a desired extinction coefficient k .

[0054] As the nitrogen-based gas used as a sputtering gas when the light shielding film 2 is formed, any gas is applicable as long as the gas is a gas containing nitrogen. As described above, the light shielding film 2 except for the surface layer preferably has a low oxygen content. Therefore, a nitrogen-based gas containing no oxygen is preferably

applied, and a nitrogen gas (N_2 gas) is more preferably applied. Furthermore, a type of rare gas used as a sputtering gas when the light shielding film 2 is formed is not limited. Argon, krypton, or xenon is preferably used. Furthermore, to relax a stress of the light shielding film 2, helium and neon having a small atomic weight can be incorporated positively in the light shielding film 2.

[0055]

Hard Mask Film

In the mask blank 100 including the light shielding film 2, the hard mask film 3 formed of a material having etching selectivity for the etching gas used when the light shielding film 2 is etched may further be layered on the light shielding film 2. Since the light shielding film 2 needs to ensure a predetermined optical density, the light shielding film 2 has a lower limit of the thickness. The hard mask film 3 has a film thickness sufficient to be capable of functioning as an etching mask until end of dry etching for forming a pattern on the light shielding film 2 located immediately under the hard mask film 3, and the thickness of the hard mask film 3 is not basically limited by optical characteristics. Therefore, the hard mask film 3 can have the thickness significantly smaller than the thickness of the light shielding film 2. Then, since a resist film made of an organic material has a film thickness sufficient to be capable of functioning as an etching mask until end of dry etching for forming a pattern on this hard mask film 3, the resist film can have the thickness significantly smaller than the thickness of a known resist film. Therefore, occurrence of a problem such as resist pattern collapse can be suppressed.

[0056] The hard mask film 3 is preferably formed of a chromium (Cr)-containing material. The chromium-containing material has particularly high dry etching resistance to dry etching using a fluorine-based gas such as SF_6 . A thin film made of the chromium-containing material is generally patterned by dry etching using a mixed gas of a chlorine-based gas and an oxygen gas. However, this dry etching does not have sufficiently high anisotropy. Therefore, when the thin film made of the chromium-containing material is patterned by dry etching, etching in a side wall direction of the pattern (side etching) is likely to proceed.

When the chromium-containing material is used for a light shielding film, the light shielding film 2 has a relatively large film thickness. Therefore, a problem involved

in side etching occurs during dry etching of the light shielding film 2. However, when the chromium-containing material is used as the hard mask film 3, the hard mask film 3 has a relatively large film thickness. Therefore, a problem due to side etching is unlikely to occur.

[0057] Examples of the chromium-containing material include a chrome metal and a material containing one or more elements incorporated in chromium and selected from oxygen, nitrogen, carbon, boron, and fluorine, such as CrN, CrC, CrON, CrCO, and CrCON. A film made of the material containing these elements added to the chrome metal is likely to include an amorphous structure and is preferable because surface roughness of the film and line edge roughness in dry etching of the light shielding film 2 are suppressed.

[0058] Furthermore, from the viewpoint of dry etching of the hard mask film 3, a material containing one or more elements incorporated in chromium and selected from oxygen, nitrogen, carbon, boron, and fluorine is preferably used as a material forming the hard mask film 3.

A chromium based material is etched with a mixed gas of a chlorine-based gas and an oxygen gas. However, a chromium metal has an etching rate relatively low for this etching gas. When one or more elements selected from oxygen, nitrogen, carbon, boron, and fluorine is incorporated in chromium, an etching rate for the etching mixed gas of a chlorine-based gas and an oxygen gas can be enhanced.

[0059] Note that the hard mask film 3 made of CrCO contains no nitrogen being likely to increase side etching and contains carbon suppressing side etching and oxygen enhancing an etching rate, and therefore is particularly preferable for dry etching using a mixed gas of a chlorine-based gas and an oxygen gas. Furthermore, the chromium-containing material forming the hard mask film 3 may contain one or more elements of indium, molybdenum, and tin. When the chromium-containing material forming the hard mask film 3 contains one or more elements of indium, molybdenum, and tin, an etching rate for a mixed gas of a chlorine-based gas and an oxygen gas can be more enhanced.

[0060] In the mask blank 100, a resist film made of an organic material having a film thickness of 100 nm or less is preferably formed in contact with a surface of the hard mask film 3. In the case of a fine pattern supporting the hp 32 nm generation of DRAMs, a Sub-Resolution Assist Feature (SRAF) having a line width of 40 nm may be provided on

a transfer pattern to be formed on the hard mask film 3. However, since even in such a case, an aspect ratio of a cross section of a resist pattern can be as low as 1:2.5, collapsing or peeling off of the resist pattern during development, rinsing, or the like of the resist film can be suppressed. Note that the film thickness of the resist film is more preferably 80 nm or less.

[0061] In the mask blank 100, a resist film can also be formed directly in contact with the light shielding film 2 without the hard mask film 3 being provided. In this case, the mask blank 100 includes a simple structure and dry etching of the hard mask film 3 becomes unnecessary when a transfer mask is manufactured. Therefore, the number of manufacturing steps can be decreased. Note that in this case, the resist film is preferably formed after the light shielding film 2 is subjected to surface treatment such as hexamethyldisilazane (HMDS).

[0062] Furthermore, the mask blank of the present invention is a mask blank suitable for application of a binary mask, as described below. However, the mask blank is not limited to the application of a binary mask. The mask blank can be used as a mask blank for a Levenson phase shift mask or a mask blank for a Chromeless Phase Lithography (CPL) mask.

[0063]

Transfer Mask

FIGS. 2A to 2F are schematic cross-sectional views illustrating steps in manufacturing a transfer mask (binary mask) 200 with use of the mask blank 100 according to an embodiment of the present invention.

[0064] In a method for manufacturing the transfer mask 200 illustrated in FIGS. 2A to 2F, the mask blank 100 is used. The method includes steps of forming a transfer pattern on the hard mask film 3 by dry etching, forming a transfer pattern on the light shielding film 2 by dry etching using the hard mask film 3 having the transfer pattern (hard mask pattern 3a) as a mask, and removing the hard mask pattern 3a.

[0065] Hereinafter, the method for manufacturing the transfer mask 200 will be described as an example according to the manufacturing steps illustrated in FIGS. 2A to 2F. Note that in this example, a material containing silicon and nitrogen is applied to the light shielding film 2 and a chromium-containing material is applied to the hard mask film 3.

[0066] First, the mask blank 100 (see FIG. 2A) is prepared and a resist film is formed in contact with the hard mask film 3 by a spin coating method. Next, a transfer pattern to be formed on the light shielding film 2 is written by exposure on the resist film and predetermined treatment such as development is further performed to form a resist pattern 4a (see FIG. 2B). Note that at that time, to form a black defect on the light shielding film 2, a programmed defect in addition to a light shielding film pattern to be originally formed is added to the resist pattern 4a obtained by writing with an electron beam.

[0067] Subsequently, dry etching using a chlorine-based gas such as a mixed gas of chlorine and oxygen is performed by using the resist pattern 4a as a mask, to form a pattern (hard mask pattern 3a) on the hard mask film 3 (see FIG. 2C). The chlorine-based gas is not particularly limited as long as the chlorine-based gas contains Cl. Examples of the chlorine-based gas can include Cl_2 , SiCl_2 , CHCl_3 , CH_2Cl_2 , and BCl_3 . When the mixed gas of chlorine and oxygen is used, a flow rate ratio of the gas may be, for example, $\text{Cl}_2:\text{O}_2 = 4:1$.

Next, the resist pattern 4a is removed by ashing or using a resist stripper (see FIG. 2D).

[0068] Subsequently, dry etching using a fluorine-based gas is performed by using the hard mask pattern 3a as a mask, to form a pattern (light shielding film pattern 2a) on the light shielding film 2 (see FIG. 2E). As the fluorine-based gas, any gas containing F can be used, and SF_6 is favorable. In addition to SF_6 , examples of the fluorine-based gas can include CHF_3 , CF_4 , C_2F_6 , and C_4F_8 . A fluorine-based gas containing C has an etching rate relatively high for the transparent substrate 1 made of a glass material. SF_6 is preferable because SF_6 causes little damage to the transparent substrate 1. Note that He or the like may further preferably be added to SF_6 .

[0069] Thereafter, the hard mask pattern 3a is removed by using a chromium etching liquid and predetermined treatment such as washing is performed to obtain the transfer mask 200 (see FIG. 2F). Note that in the step of removing the hard mask pattern 3a, dry etching using a mixed gas of chlorine and oxygen may be performed. Here, an example of the chromium etching liquid can include a mixture containing diammonium cerium nitrate and perchloric acid.

[0070] The transfer mask 200 manufactured by the manufacturing method illustrated in FIGS. 2A to 2F is a binary mask including the transparent substrate 1 including the light

shielding film 2 having the transfer pattern (light shielding film pattern 2a). As a result of inspection by a mask inspection device of a mask pattern of the transfer mask 200 manufactured in Example 1, a black defect is confirmed to exist on the light shielding pattern 2a at a location where a programmed defect has been disposed. Therefore, the black defect portion is removed by EB defect repair.

[0071] In the transfer mask 200 manufactured as described above, even when EB defect repair is performed on the black defect portion of the light shielding film pattern 2a during the manufacturing of the transfer mask 200, occurrence of roughening of a surface of the transparent substrate 1 near the black defect portion can be suppressed and occurrence of spontaneous etching of the light shielding film pattern 2a can be suppressed.

[0072] Note that the case where the transfer mask 200 is a binary mask is described here; however, the transfer mask of the present invention is not limited to a binary mask and can be applied to a Levenson phase shift mask and a CPL mask. That is, when the transfer mask is a Levenson phase shift mask, the light shielding film of the present invention can be used for a light shielding film of the transfer mask. When the transfer mask is a CPL mask, the light shielding film of the present invention can be used at a region mainly including an outer circumferential light shielding band.

[0073] Further, a method for manufacturing a semiconductor device of the present invention includes transferring by exposure a transfer pattern to a resist film on a semiconductor substrate with use of the above-described transfer mask 200 or the transfer mask 200 manufactured with use of the above-described mask blank 100.

[0074] The transfer mask 200 and the mask blank 100 of the present invention have the effects described above. Therefore, when the transfer mask 200 is set on a mask stage of an exposure apparatus using an ArF excimer laser as exposure light and a transfer pattern is transferred by exposure to a resist film on a semiconductor device, the transfer pattern can be transferred to the resist film on the semiconductor device with high CD accuracy. Therefore, in a case where a circuit pattern is formed by subjecting an underlayer film of the resist film to dry etching using a pattern of the resist film as a mask, the circuit pattern can be formed with high accuracy without shortcut and disconnection of wiring due to insufficient accuracy.

Examples

[0075] Hereinafter, embodiments of the present invention will be described more specifically by way of examples.

(Example 1)

[Manufacture of Mask Blank]

A transparent substrate 1 having a main surface dimension of approximately 152 mm x approximately 152 mm and made of synthetic quartz glass having a thickness of approximately 6.35 mm was prepared. An end surface and a main surface of this transparent substrate 1 were polished to predetermined surface roughness and then subjected to predetermined washing treatment and drying treatment.

[0076] Next, the transparent substrate 1 was installed in a single-wafer RF sputtering device. A light shielding film 2 made of silicon and nitrogen and having a thickness of 41.5 nm was formed on the transparent substrate 1 by reactive sputtering (RF sputtering) using a silicon (Si) target and using a mixed gas of argon (Ar), nitrogen (N₂), and helium (He) as a sputtering gas, and an RF power supply. Note that the same single-wafer RF sputtering device as the single-wafer RF sputtering device used in Example 1 was used in Examples 2 to 4 and Comparative Examples 1 and 2.

[0077] Next, the transparent substrate 1 on which the light shielding film 2 was formed was subjected to heating treatment under conditions of a heating temperature of 500°C and treatment time of 1 hour in air to adjust a stress of the film.

[0078] An optical density (OD) at a wavelength of 193 nm of the light shielding film 2 having subjected to the heating treatment was measured by a spectrophotometer (Cary4000 available from Agilent Technologies), and a value of the optical density was 2.58. According to the results, the mask blank in Example 1 has necessary light shielding performance.

Furthermore, a refractive index n and an extinction coefficient k at a wavelength of 193 nm of the light shielding film 2 having subjected to the heating treatment were measured by a spectroscopic ellipsometer (M-2000D available from J. A. Woollam Co., Inc.). At a wavelength of 193 nm, the refractive index n was 1.29 and the extinction coefficient k was 2.39.

[0079] Another light shielding film was formed on a main surface of another transparent substrate under the same film forming conditions as the conditions for the light shielding

film 2 in Example 1 and further subjected to heating treatment under the same conditions. Next, after the heating treatment, the light shielding film on said another transparent substrate was subjected to X-ray photoelectron spectroscopy. The X-ray photoelectron spectroscopy included a step of irradiating a surface of the light shielding film with an X ray (AlK α ray: 1486 eV) to measure intensity of photoelectron discharged from the light shielding film, digging the surface of the light shielding film by Ar gas sputtering to a depth of approximately 0.65 nm for predetermined time, and irradiating the light shielding film at the dug region with an X ray to measure intensity of photoelectron discharged from the dug region. The step was repeated to obtain composition at each depth of the light shielding film. As a result, average composition at an internal region of the light shielding film was found to be Si:N:O = 78.7:19.7:1.6 (atom% ratio). Accordingly, a ratio of a silicon content (atom%) to a nitrogen content (atom%) at the internal region was found to be 3.995, and was found to satisfy a condition (2.4 or more and 4.0 or less) of the ratio of the silicon content (atom%) to the nitrogen content (atom%) at the internal region. Note that the composition at each depth of the internal region was substantially the same as the above-described average composition and a ratio of a silicon content (atom%) to a nitrogen content (atom%) at each depth was also substantially the same as a value calculated from the average composition.

[0080] Next, the transparent substrate 1 on which the light shielding film 2 having subjected to the heating treatment was formed was installed in a single-wafer DC sputtering device and a hard mask film 3 made of a CrN film having a film thickness of 5 nm was formed by reactive sputtering (DC sputtering) using a chromium (Cr) target in an atmosphere of a mixed gas of argon (Ar) and nitrogen (N₂). A film composition ratio of this film was measured by XPS, and had Cr of 75 atom% and N of 25 atom%. Then, heat treatment was performed at a temperature (280°C) lower than the temperature in the heating treatment performed on the light shielding film 2 and a stress of the hard mask film 3 was adjusted.

[0081] A mask blank 100 including a structure in which the light shielding film 2 and the hard mask film 3 were layered on the transparent substrate 1 was manufactured by the above-described procedure.

[0082]

[Manufacture of Transfer Mask]

Next, a transfer mask (binary mask) 200 in Example 1 was manufactured by the following procedure with use of the mask blank 100 in Example 1.

First, the mask blank 100 in Example 1 (see FIG. 2A) was prepared. A resist film made of a chemically amplified resist for electron beam lithography and having a thickness of 80 nm was formed in contact with a surface of the hard mask film 3. Next, a transfer pattern to be formed on the light shielding film 2 was written with an electron beam on the resist film and predetermined development treatment and washing treatment were performed to form a resist pattern 4a (see FIG. 2B). Note that at that time, to form a black defect on the light shielding film 2, a programmed defect in addition to a light shielding film pattern to be originally formed was added to the resist pattern 4a obtained by writing with an electron beam.

[0083] Next, dry etching using a mixed gas of chlorine and oxygen (gas flow rate ratio $\text{Cl}_2:\text{O}_2 = 4:1$) was performed by using the resist pattern 4a as a mask, to form a pattern (hard mask pattern 3a) on the hard mask film 3 (see FIG. 2C).

[0084] Next, the resist pattern 4a was removed (see FIG. 2D). Subsequently, dry etching using a fluorine-based gas (mixed gas of SF_6 and He) was performed by using the hard mask pattern 3a as a mask, to form a pattern (light shielding film pattern 2a) on the light shielding film 2 (see FIG. 2E).

[0085] Thereafter, the hard mask pattern 3a was removed by using a chromium etching liquid containing diammonium cerium nitrate and perchloric acid and was subjected to predetermined treatment such as washing to obtain the transfer mask 200 (see FIG. 2F).

[0086] A mask pattern of the transfer mask 200 manufactured in Example 1 was inspected by a mask inspection device, and a black defect was confirmed to exist on the light shielding pattern 2a at a location where the programmed defect had been disposed. EB defect repair was performed on the black defect portion. A repair rate ratio of the light shielding film pattern 2a to the transparent substrate 1 (namely, a repair rate of the light shielding film pattern 2a to a repair rate of the transparent substrate 1) was sufficiently high and etching of a surface of the transparent substrate 1 was able to be minimized.

[0087] Next, the transfer mask 200 in Example 1 on which the EB defect repair had been performed was subjected to a simulation using AIMS 193 (available from Carl Zeiss) of transfer images transferred by exposure to a resist film on a semiconductor device with exposure light having a wavelength of 193 nm. According to verification of the images

transferred by exposure in this simulation, design specifications were sufficiently satisfied. Furthermore, the transfer image at the portion on which EB defect repair had been performed was comparable to the transfer image at a region other than the portion. According to the results, when EB defect repair is performed on the black defect portion of the light shielding film pattern 2a in the transfer mask 200 in Example 1, occurrence of roughening of the surface of the transparent substrate 1 can be suppressed and occurrence of spontaneous etching of the light shielding film pattern 2a can be suppressed. Furthermore, even when the transfer mask 200 in Example 1 on which EB defect repair has been performed is set on a mask stage of an exposure apparatus and transferred by exposure to a resist film on a semiconductor device, a circuit pattern finally formed on the semiconductor device can be formed with high accuracy. Therefore, the transfer mask 200 manufactured by the method for manufacturing a transfer mask in Example 1 is a transfer mask having high transfer accuracy.

[0088]

(Example 2)

[Manufacture of Mask Blank]

A mask blank in Example 2 was manufactured by the same procedure as the procedure for the mask blank 100 in Example 1 except that a light shielding film was formed as follows.

[0089] A method of forming a light shielding film in Example 2 is as follows.

A transparent substrate 1 was installed in a single-wafer RF sputtering device. A light shielding film 2 made of silicon and nitrogen and having a thickness of 50.0 nm was formed on the transparent substrate 1 by reactive sputtering (RF sputtering) using a silicon (Si) target, and using a mixed gas of argon (Ar), nitrogen (N₂), and helium (He) as a sputtering gas, and an RF power supply.

[0090] As with Example 1, the transparent substrate 1 on which the light shielding film 2 was formed was subjected to heating treatment, and an optical density (OD) of the light shielding film 2 having subjected to the heating treatment was measured. A value of the optical density was 3.02. According to the results, the mask blank in Example 2 has necessary high light shielding performance.

Furthermore, a refractive index n and an extinction coefficient k at a wavelength of 193 nm of the light shielding film 2 having subjected to the heating treatment were

measured by a spectroscopic ellipsometer (M-2000D available from J. A. Woollam Co., Inc.). At a wavelength of 193 nm, the refractive index n was 1.40 and the extinction coefficient k was 2.25.

[0091] As with Example 1, another light shielding film was formed on a main surface of another transparent substrate under the same film forming conditions as the conditions for the light shielding film 2 in Example 2 and subjected to heating treatment under the same conditions. Furthermore, as with Example 1, after the heating treatment, the light shielding film on said another transparent substrate was subjected to X-ray photoelectron spectroscopy. According to the results of the X-ray photoelectron spectroscopy, average composition at an internal region of the light shielding film was found to be Si:N:O = 75.4:23.5:1.1 (atom% ratio). Accordingly, a ratio of a silicon content (atom%) to a nitrogen content (atom%) at the internal region was found to be 3.208, and was found to satisfy a condition (2.4 or more and 4.0 or less) of the ratio of the silicon content (atom%) to the nitrogen content (atom%) at the internal region. Furthermore, composition at each depth of the internal region was substantially the same as the above-described average composition and a ratio of a silicon content (atom%) to a nitrogen content (atom%) at each depth was also substantially the same as a value calculated from the average composition.

Thereafter, a mask blank 100 including a structure in which the light shielding film 2 and the hard mask film 3 were layered on the transparent substrate 1 was manufactured by the same procedure as in Example 1.

[0092]

[Manufacture of Transfer Mask]

Next, a transfer mask (binary mask) in Example 2 was manufactured by the same procedure as in Example 1 with use of the mask blank in Example 2.

A mask patter of the transfer mask 200 manufactured in Example 2 was inspected by a mask inspection device, and a black defect was confirmed to exist on a light shielding pattern 2a at a location where a programmed defect had been disposed. EB defect repair was performed on the black defect portion. A ratio of a repair rate of the light shielding film pattern 2a to a repair rate of the transparent substrate 1 was sufficiently high and etching of a surface of the transparent substrate 1 was able to be minimized.

The transfer mask 200 in Example 2 on which the EB defect repair had been performed was subjected to a simulation using AIMS 193 (available from Carl Zeiss) of transfer images transferred by exposure to a resist film on a semiconductor device with an exposure light having a wavelength of 193 nm. According to verification of the images transferred by exposure in this simulation, design specifications were sufficiently satisfied. Furthermore, the transfer image of the portion on which EB defect repair had been performed was comparable to the transfer image of a region other than the portion. According to the results, when EB defect repair is performed on the black defect portion of the light shielding film pattern 2a in the transfer mask 200 in Example 2, occurrence of roughening of the surface of the transparent substrate 1 can be suppressed and occurrence of spontaneous etching of the light shielding film pattern 2a can be suppressed. Furthermore, even when the transfer mask 200 in Example 2 on which EB defect repair has been performed is set on a mask stage of an exposure apparatus and transferred by exposure to a resist film on a semiconductor device, a circuit pattern finally formed on the semiconductor device can be formed with high accuracy. Therefore, the transfer mask 200 manufactured by the method for manufacturing the transfer mask in Example 2 is a transfer mask having high transfer accuracy.

[0093]

(Example 3)

[Manufacture of Mask Blank]

A mask blank in Example 3 was manufactured by the same procedure as the procedure for the mask blank 100 in Example 1 except that a light shielding film was formed as follows.

[0094] A method of forming a light shielding film in Example 3 is as follows.

A transparent substrate 1 was installed in a single-wafer RF sputtering device. A light shielding film 2 made of silicon and nitrogen and having a thickness of 52.4 nm was formed on the transparent substrate 1 by reactive sputtering (RF sputtering) using a silicon (Si) target, and using a mixed gas of argon (Ar), nitrogen (N₂), and helium (He) as a sputtering gas, and an RF power supply.

[0095] As with Example 1, the transparent substrate 1 on which the light shielding film 2 was formed was subjected to heating treatment, and an optical density (OD) of the light shielding film 2 having subjected to the heating treatment was measured. A value of the

optical density was 3.05. According to the results, the mask blank in Example 3 has necessary light shielding performance.

Furthermore, a refractive index n and an extinction coefficient k at a wavelength of 193 nm of the light shielding film 2 having subjected to the heating treatment were measured by a spectroscopic ellipsometer (M-2000D available from J. A. Woollam Co., Inc.). At a wavelength of 193 nm, the refractive index n was 1.52 and the extinction coefficient k was 2.09.

[0096] As with Example 1, another light shielding film was formed on a main surface of another transparent substrate under the same film forming conditions as the conditions for the light shielding film 2 in Example 3, and heating treatment was performed on the other light shielding film under the same conditions. Further, as with Example 1, after the heating treatment, the light shielding film of said another transparent substrate was subjected to X-ray photoelectron spectroscopy. According to the results of the X-ray photoelectron spectroscopy, average composition at an internal region of the light shielding film was found to be Si:N:O = 71.1:27.8:1.1 (atom% ratio). Accordingly, a ratio of a silicon content (atom%) to a nitrogen content (atom%) at the internal region was found to be 2.555, and found to satisfy a condition (2.4 or more and 4.0 or less) of the ratio of the silicon content (atom%) to the nitrogen content (atom%) at the internal region. Furthermore, composition at each depth of the internal region was substantially the same as the above-described average composition and a ratio of a silicon content (atom%) to a nitrogen content (atom%) at each depth was also substantially the same as a value calculated from the average composition.

Thereafter, a mask blank 100 including a structure in which the light shielding film 2 and the hard mask film 3 were layered on the transparent substrate 1 was manufactured by the same procedure as in Example 1.

[0097]

[Manufacture of Transfer Mask]

Next, a transfer mask (binary mask) in Example 3 was manufactured by the same procedure as in Example 1 with use of the mask blank in Example 3.

A mask pattern of the transfer mask 200 manufactured in Example 3 was inspected by a mask inspection device, and a black defect was confirmed to exist on a light shielding pattern 2a at a location where a programmed defect had been disposed. EB

defect repair was performed on the black defect portion. A ratio of a repair rate of the light shielding film pattern 2a to a repair rate of the transparent substrate 1 was sufficiently high and etching of a surface of the transparent substrate 1 was able to be minimized.

The transfer mask 200 in Example 3 on which the EB defect repair had been performed was subjected to a simulation using AIMS 193 (available from Carl Zeiss) of transfer images transferred by exposure to a resist film on a semiconductor device with an exposure light having a wavelength of 193 nm. According to verification of the images transferred by exposure in this simulation, design specifications were sufficiently satisfied. Furthermore, the transfer image of the portion on which EB defect repair had been performed was comparable to the transfer image of a region other than the portion. According to the results, when EB defect repair is performed on the black defect portion of the light shielding film pattern 2a in the transfer mask 200 in Example 3, occurrence of roughening of the surface of the transparent substrate 1 can be suppressed, and occurrence of spontaneous etching of the light shielding film pattern 2a can be suppressed. Furthermore, even when the transfer mask 200 in Example 3 on which EB defect repair has been performed is set on a mask stage of an exposure apparatus and transferred by exposure to a resist film on a semiconductor device, a circuit pattern finally formed on the semiconductor device can be formed with high accuracy. Therefore, the transfer mask 200 manufactured by the method for manufacturing the transfer mask in Example 3 is a transfer mask having high transfer accuracy.

[0098]

(Example 4)

[Manufacture of Mask Blank]

A mask blank in Example 4 was manufactured by the same procedure as the procedure for the mask blank 100 in Example 1 except that a light shielding film was formed as follows.

[0099] A method of forming a light shielding film in Example 4 is as follows.

A transparent substrate 1 was installed in a single-wafer RF sputtering device. A light shielding film 2 made of silicon and nitrogen and having a thickness of 45.1 nm was formed on the transparent substrate 1 by reactive sputtering (RF sputtering) using a silicon (Si) target, and using a mixed gas of argon (Ar), nitrogen (N₂), and helium (He) as

a sputtering gas, and an RF power supply.

[0100] As with Example 1, the transparent substrate 1 on which the light shielding film 2 was formed was subjected to heating treatment, and an optical density (OD) of the light shielding film 2 having subjected to the heating treatment was measured. A value of the optical density was 2.54. According to the results, the mask blank in Example 4 has necessary light shielding performance.

Furthermore, a refractive index n and an extinction coefficient k at a wavelength of 193 nm of the light shielding film 2 having subjected to the heating treatment were measured by a spectroscopic ellipsometer (M-2000D available from J. A. Woollam Co., Inc.). At a wavelength of 193 nm, the refractive index n was 1.54 and the extinction coefficient k was 2.05.

[0101] As with Example 1, another light shielding film was formed on a main surface of another transparent substrate under the same film forming conditions as the conditions for the light shielding film 2 in Example 4, and heating treatment was performed on the other light shielding film under the same conditions. Furthermore, as with Example 1, after the heating treatment, the light shielding film on said another transparent substrate was subjected to X-ray photoelectron spectroscopy. According to the results of the X-ray photoelectron spectroscopy, average composition at an internal region of the light shielding film was found to be Si:N:O = 69.0:28.2:2.8 (atom% ratio). Accordingly, a ratio of a silicon content (atom%) to a nitrogen content (atom%) at the internal region was found to be 2.447 and found to satisfy a condition (2.4 or more and 4.0 or less) of the ratio of the silicon content (atom%) to the nitrogen content (atom%) at the internal region. Furthermore, composition at each depth of the internal region was substantially the same as the above-described average composition and a ratio of a silicon content (atom%) to a nitrogen content (atom%) at each depth was also substantially the same as a value calculated from the average composition.

Thereafter, a mask blank 100 including a structure in which the light shielding film 2 and the hard mask film 3 were layered on the transparent substrate 1 was manufactured by the same procedure as in Example 1.

[0102]

[Manufacture of Transfer Mask]

Next, a transfer mask (binary mask) in Example 4 was manufactured by the same

procedure as in Example 1 with use of the mask blank in Example 4.

A mask pattern of the transfer mask 200 manufactured in Example 4 was inspected by a mask inspection device, and a black defect was confirmed to exist on a light shielding pattern 2a at a location where a programmed defect had been disposed. EB defect repair was performed on the black defect portion. A ratio of a repair rate of the light shielding film pattern 2a to a repair rate of the transparent substrate 1 was sufficiently high and etching of a surface of the transparent substrate 1 was able to be minimized.

The transfer mask 200 in Example 4 on which the EB defect repair had been performed was subjected to a simulation using AIMS 193 (available from Carl Zeiss) of transfer images transferred by exposure to a resist film on a semiconductor device with exposure light having a wavelength of 193 nm. According to verification of the images transferred by exposure in this simulation, design specifications were sufficiently satisfied. Furthermore, the transfer image of the portion on which EB defect repair had been performed was comparable to a transfer image of a region other than the portion. According to the results, when EB defect repair is performed on the black defect portion of the light shielding film pattern 2a in the transfer mask 200 in Example 4, occurrence of roughening of the surface of the transparent substrate 1 can be suppressed and occurrence of spontaneous etching of the light shielding film pattern 2a can be suppressed. Furthermore, even when the transfer mask 200 in Example 4 on which EB defect repair has been performed is set on a mask stage of an exposure apparatus and transferred by exposure to a resist film on a semiconductor device, a circuit pattern finally formed on the semiconductor device can be formed with high accuracy. Accordingly, the transfer mask 200 manufactured by the method for manufacturing a transfer mask in Example 4 is a transfer mask having high transfer accuracy.

[0103]

(Comparison Example 1)

[Manufacture of Mask Blank]

A mask blank in Comparative Example 1 was manufactured by the same procedure as the procedure for the mask blank 100 in Example 1 except that a light shielding film was formed as follows.

[0104] A method of forming a light shielding film in Comparative Example 1 is as

follows.

A transparent substrate was installed in a single-wafer RF sputtering device. A light shielding film made of silicon and nitrogen and having a thickness of 52.8 nm was formed on the transparent substrate by reactive sputtering (RF sputtering) using a silicon (Si) target, and using a mixed gas of argon (Ar), nitrogen (N₂), and helium (He) as a sputtering gas, and an RF power supply.

[0105] As with Example 1, the transparent substrate on which the light shielding film was formed was subjected to heating treatment, and an optical density (OD) of the light shielding film having subjected to the heating treatment was measured. A value of the optical density was 2.98. According to the results, the mask blank in Comparative Example 1 has necessary light shielding performance.

Furthermore, a refractive index n and an extinction coefficient k at a wavelength of 193 nm of the light shielding film having subjected to the heating treatment were measured by a spectroscopic ellipsometer (M-2000D available from J. A. Woollam Co., Inc.). At a wavelength of 193 nm, the refractive index n was 1.58 and the extinction coefficient k was 1.99.

[0106] As with Example 1, another light shielding film was formed on a main surface of another transparent substrate under the same film forming conditions as the conditions for the light shielding film in Comparative Example 1 and subjected to heating treatment under the same conditions. Further, as with Example 1, after the heating treatment, the light shielding film of said another transparent substrate was subjected to X-ray photoelectron spectroscopy. According to the results of the X-ray photoelectron spectroscopy, average composition at an internal region of the light shielding film was found to be Si:N:O = 68.3:28.5:3.2 (atom% ratio). Accordingly, a ratio of a silicon content (atom%) to a nitrogen content (atom%) at the internal region was 2.396 and did not satisfy a condition (2.4 or more and 4.0 or less) of the ratio of the silicon content (atom%) to the nitrogen content (atom%) at the internal region. Furthermore, composition at each depth of the internal region was substantially the same as the above-described average composition and a ratio of a silicon content (atom%) to a nitrogen content (atom%) at each depth were also substantially the same as a value calculated from the average composition.

Thereafter, a mask blank including a structure in which the light shielding film

and the hard mask film were layered on the transparent substrate was manufactured by the same procedure as in Example 1.

[0107]

[Manufacture of Transfer Mask]

Next, a transfer mask (binary mask) in Comparative Example 1 was manufactured by the same procedure as in Example 1 with use of the mask blank in Comparative Example 1.

A mask pattern of the transfer mask manufactured in Comparative Example 1 was inspected by a mask inspection device, and a black defect was confirmed to exist on the light shielding pattern at a location where a programmed defect had been disposed. EB defect repair was performed on the black defect portion. A ratio of a repair rate of the light shielding film pattern to a repair rate of the transparent substrate was low and etching of the surface of the transparent substrate (roughening of the surface) proceeded.

[0108] The transfer mask in Comparative Example 1 on which the EB defect repair had been performed was subjected to a simulation using AIMS 193 (manufactured by Carl Zeiss) of transfer images transferred by exposure to a resist film on a semiconductor device with exposure light having a wavelength of 193 nm. According to verification of the images transferred by exposure in this simulation, a decrease in CD of the light shielding film pattern that seemed to be caused by a slow etching rate when the pattern was formed on the light shielding film by dry etching occurred even at a portion other than the portion on which EB defect repair had been performed. Further, the transfer image at the portion on which EB defect repair had been performed was an image at a level where a transfer defect was caused by influence of roughening of the surface of the transparent substrate and the like. According to the results, when the transfer mask in Comparative Example 1 on which EB defect repair has been performed is set on a mask stage of an exposure apparatus and transferred by exposure to a resist film on a semiconductor device, disconnection and a short circuit of a circuit pattern finally formed on the semiconductor device are expected to occur.

[0109]

(Comparison Example 2)

[Manufacture of Mask Blank]

A mask blank in Comparative Example 2 was manufactured by the same

procedure as the procedure for the mask blank 100 in Example 1 except that a light shielding film was formed as follows.

[0110] A method of forming a light shielding film in Comparative Example 2 is as follows.

A transparent substrate was installed in a single-wafer RF sputtering device. A light shielding film made of silicon and nitrogen and having a thickness of 48.0 nm was formed on the transparent substrate by reactive sputtering (RF sputtering) using a silicon (Si) target, and using a mixed gas of argon (Ar), nitrogen (N₂), and helium (He) as a sputtering gas, and an RF power supply.

[0111] As with Example 1, the transparent substrate on which the light shielding film was formed was subjected to heating treatment, and an optical density (OD) of the light shielding film having subjected to the heating treatment was measured. A value of the optical density was 3.04. According to the results, the mask blank in Comparative Example 2 has necessary high light shielding performance.

Furthermore, a refractive index n and an extinction coefficient k at a wavelength of 193 nm of the light shielding film having subjected to the heating treatment were measured by a spectroscopic ellipsometer (M-2000D available from J. A. Woollam Co., Inc.). At a wavelength of 193 nm, the refractive index n was 1.23 and the extinction coefficient k was 2.48.

[0112] As with Example 1, another light shielding film was formed on a main surface of another transparent substrate under the same film forming conditions as the conditions for the light shielding film in Comparative Example 2, and heating treatment was performed on the other light shielding film under the same conditions. Further, as with Example 1, after the heating treatment, the light shielding film on said another transparent substrate was subjected to X-ray photoelectron spectroscopy. According to the results of the X-ray photoelectron spectroscopy, average composition at an internal region of the light shielding film was found to be Si:N:O = 80.9:16.7:2.4 (atom% ratio). Accordingly, a ratio of a silicon content (atom%) to a nitrogen content (atom%) at the internal region was 4.844 and did not satisfy a condition (2.4 or more and 4.0 or less) of the ratio of the silicon content (atom%) to the nitrogen content (atom%) at the internal region. Furthermore, composition at each depth of the internal region was substantially the same as the above-described average composition and a ratio of a silicon content (atom%) to a

nitrogen content (atom%) at each depth was also substantially the same as a value calculated from the average composition.

Thereafter, a mask blank including a structure in which the light shielding film and the hard mask film were layered on the transparent substrate was manufactured by the same procedure as in Example 1.

[0113]

[Manufacture of Transfer Mask]

Next, a transfer mask (binary mask) in Comparative Example 2 was manufactured by the same procedure as in Example 1 with use of the mask blank in Comparative Example 2.

A mask pattern of the transfer mask manufactured in Comparative Example 2 was inspected by a mask inspection device, and a black defect was confirmed to exist on the light shielding pattern at a location where a programmed defect had been disposed. EB defect repair was performed on the black defect portion. A repair rate was too high and undercut occurred. Further, a phenomenon where an unexcited XeF_2 gas supplied during EB defect repair comes into contact with a side wall of the light shielding film pattern around the black defect portion and the side wall is etched, that is, spontaneous etching proceeded.

[0114] The transfer mask in Comparative Example 2 on which the EB defect repair had been performed was subjected to a simulation using AIMS 193 (manufactured by Carl Zeiss) of transfer images transferred by exposure to a resist film on a semiconductor device with exposure light having a wavelength of 193 nm. According to verification of the images transferred by exposure in this simulation, roughening of the surface of the transparent substrate at a portion other than the portion on which EB defect repair had been performed did not occur. However, the transfer image around the portion where EB defect repair had been performed was an image at a level where a transfer defect was caused by influence of spontaneous etching and the like. According to the results, when the phase shift mask in Comparison Example 2 on which EB defect repair has been performed is set on a mask stage of an exposure apparatus and transferred by exposure to a resist film on a semiconductor device, disconnection and a short circuit of a circuit pattern finally formed on the semiconductor device are expected to occur.

Description of Reference Numerals

[0115]

1 Transparent substrate

2 Light shielding film

2a Light shielding film pattern

21 Substrate neighborhood region

22 Internal region

23 Surface layer region

3 Hard mask film

3a Hard mask pattern

4a Resist pattern

100 Mask blank

200 Transfer mask (binary mask)

CLAIMS

1. A mask blank comprising a transparent substrate including a light shielding film for formation of a transfer pattern,

wherein the light shielding film is formed of a material containing silicon and nitrogen or a material containing one or more elements selected from a semimetal element and a non-metal element, silicon, and nitrogen,

the light shielding film is provided in contact with a main surface of the transparent substrate,

the light shielding film has an optical density for exposure light of an ArF excimer laser of 2.5 or more,

a ratio of a content (atom%) of silicon to a content (atom%) of nitrogen at an internal region except for a neighborhood region near an interface between the light shielding film and the transparent substrate and a surface layer region on a side opposite to the transparent substrate is 2.4 or more and 4.0 or less, and

the internal region has a total content of silicon and nitrogen of 97 atom% or more, wherein the light shielding film has an extinction coefficient k for exposure light of an ArF excimer laser of 2.00 or more and 2.40 or less.

2. The mask blank according to claim 1, wherein a region except for the surface layer region of the light shielding film has an oxygen content of 3 atom% or less.

3. The mask blank according to claim 1 or 2, wherein the surface layer region is a region ranging from a surface of the light shielding film on the side opposite to the transparent substrate to a depth of 5 nm in a direction toward the transparent substrate.

4. The mask blank according to any one of claims 1 to 3, wherein the neighborhood region is a region ranging from the interface of the transparent substrate to a depth of 5 nm in a direction toward the surface layer region.

5. The mask blank according to any one of claims 1 to 4, wherein the light shielding film is formed of a material containing silicon, nitrogen, and a non-metal element.

6. The mask blank according to any one of claims 1 to 5, wherein the surface layer region has an oxygen content higher than the oxygen content of the region except for the surface layer region of the light shielding film.
7. The mask blank according to any one of claims 1 to 6, wherein the light shielding film has a refractive index n for exposure light of an ArF excimer laser of 1.25 or more and 1.55 or less.
8. A method for manufacturing a transfer mask with use of the mask blank according to any one of claims 1 to 7, the method comprising a step of forming a transfer pattern on the light shielding film by dry etching.
9. A method for manufacturing a semiconductor device, the method comprising a step of transferring by exposure a transfer pattern to a resist film on a semiconductor substrate with use of a transfer mask manufactured by the method for manufacturing a transfer mask according to claim 8.