oxygen-containing chlorine-based gas. In the mask blank, a pattern is formed on the hard mask film by dry etching using a resist pattern as a mask. Then, using, as a mask, the hard mask film provided with the pattern, the light-shielding film is dry etched using the oxygen-containing chlorine-based gas to form a pattern on the light-shielding film. Generally, the hard mask film is formed of a material which can be patterned by dry etching using a fluorine-based gas. The dry etching using the fluorine-based gas is ion-based etching and, therefore, has a high tendency toward anisotropic etching. Accordingly, in the hard mask film provided with the pattern, a side etching amount of a pattern sidewall is small. In case of the dry etching using the fluorine-based gas, the side etching amount tends to be small also in the resist pattern for forming the pattern on the hard mask film. Therefore, for the light-shielding film of the chromium-based material also, it is desired that the side etching amount is small in the dry etching using the oxygen-containing chlorine-based gas.

[0010]

As means for reducing the side etching amount in the light-shielding film of the chromium-based material, it is considered to significantly increase, in the dry etching using the oxygen-containing chlorine-based gas, a mixing ratio of a chlorine-based gas in the oxygen-containing chlorine-based gas. This is because the chlorine-based gas has a high tendency to generate ionic plasma. In the dry etching using the oxygen-containing chlorine-based gas with an increased ratio of the chlorine-based gas, an etching rate of the light-shielding film of the chromium-based material inevitably decreases. In order to supplement the decrease in etching rate of the light-shielding film of the chromium-based material, it is also considered to significantly increase a bias voltage applied during the dry etching (hereinafter, the dry etching, which uses the oxygen-containing chlorine-based gas with an increased ratio of the chlorine-based gas and which is performed under a condition where a high bias voltage is applied, will be called "high-bias etching with the oxygen-containing chlorine-based gas").

[0011]

The etching rate of the light-shielding film of the chromium-based material by the high-bias etching with the oxygen-containing chlorine-based gas has a

In order to obtain the above-mentioned two effects, i.e., the first and the second effects, the content of nitrogen in the hard mask film made of the material containing silicon, oxygen, and nitrogen is preferably at least 2 atomic%, more preferably at least 3 atomic%, further preferably at least 4 atomic%, yet further preferably at least 5 atomic%. If the content of nitrogen is too small, the above-mentioned two effects are hardly obtained.

In the hard mask film made of the material containing silicon, oxygen, and nitrogen according to this invention, the N1s narrow spectrum obtained by analysis of X-ray photoelectron spectroscopy has a maximum peak at a binding energy of at least 398 eV.

[0029]

Next, the present inventors studied about deterioration in function as a hard mask and degradation in pattern transfer performance.

As a result, thirdly, it has been found out that a hard mask film made of a material containing silicon, oxygen, and nitrogen tends to be deteriorated in function as the hard mask (slightly decreased in etching resistance against a chlorine-based gas) as the content of nitrogen is increased. It has been found out that, if the content of nitrogen is at most 18 atomic%, deterioration in function as the hard mask can be inhibited and degradation in pattern transfer performance can be avoided. In addition, it has been found to be necessary that, in the hard mask film made of the material containing silicon, oxygen, and nitrogen, an Si2p narrow spectrum obtained by analysis of X-ray photoelectron spectroscopy has the maximum peak at a binding energy of at least 103 eV. With a high existence ratio of SiO_2 bonds and Si-O bonds in the hard mask film, it is possible to assure the function as the hard mask. By providing the hard mask film with these characteristics, it is possible to reduce the third tendency mentioned above while maintaining the above-mentioned two effects, i.e., the first and the second effects.

[0030]

It has been found out that the third tendency mentioned above is increased under a high-bias etching condition with an oxygen-containing chlorine-based gas and the function as the hard mask is deteriorated (etching resistance against the chlorine-based gas is decreased). Thus, it has been found out that, because an

patterning is possible by the dry etching using the fluorine-based gas.

Among others, the metalloid elements may be, in addition to silicon, any metalloid elements. The non-metal elements may be, in addition to nitrogen, any non-metal elements. For example, at least one element selected from oxygen (O), carbon (C), fluorine (F), and hydrogen (H) is preferably contained. The metal elements are exemplified by molybdenum (Mo), tungsten (W), titanium (Ti), tantalum (Ta), zirconium (Zr), hafnium (Hf), niobium (Nb), vanadium (V), cobalt (Co), chromium (Cr), nickel (Ni), ruthenium (Ru), tin (Sn), boron (B), and germanium (Ge).

[0047]

The phase shift film 2 is formed of, for example, MoSiN. In order to satisfy a predetermined phase difference (phase shift amount) (for example, 150 [deg] to 210 [deg], preferably 160 [deg] to 200 [deg]) and a predetermined transmittance (for example, 1% to 30%) for the exposure light (for example, ArF excimer laser light), a refractive index n, an extinction coefficient k, and a film thickness of the phase shift film 2 are selected. A composition of a film material and a film-forming condition are adjusted so that the refractive index n and the extinction coefficient k mentioned above are obtained.

[0048]

[Light-Shielding Film]

The light-shielding film 3 preferably contains at least one element selected from chromium and tantalum. A film structure of the light-shielding film 3 may be a single-layer structure or a layered structure of two or more layers. In case of the layered structure, it is possible to provide a reflection reduction effect of reducing a reflectance for exposure light or inspection light upon defect inspection. The light-shielding film of the single-layer structure or each layer of the light-shielding film of the layered structure of two or more layers may have a substantially same composition in a thickness direction of the film or the layer, or may have a composition gradient in the thickness direction of the film or the layer. The film containing at least one element selected from chromium and tantalum can be patterned by dry etching using an oxygen-containing chlorine-based gas or a chlorine-based gas containing substantially no oxygen gas.

In the hard mask film 4, the content of oxygen is preferably at least 50 atomic%, more preferably at least 55 atomic%. In order that the hard mask film 4 has respective characteristics of the Si2p narrow spectrum mentioned above, a large content of oxygen must be contained. In the hard mask film 4, the content of oxygen is preferably at most 65 atomic%, more preferably at most 63 atomic%. This is to make the hard mask film 4 have the respective characteristics of the N1s narrow spectrum mentioned above.

[0056]

The hard mask film 4 is formed in contact with a surface of the light-shielding film 3. The hard mask film 4 is a film formed of a material having an etching selectivity for the etching gas used upon etching the light-shielding film 3. It is sufficient that the hard mask film 4 has a film thickness enough to serve as an etching mask until the end of the dry etching for forming a pattern on the light-shielding film 3, basically without limitation in terms of optical characteristics. Therefore, a thickness of the hard mask film 4 can be considerably small as compared with a thickness of the light-shielding film 3.

[0057]

The thickness of the hard mark film 4 is required to be at most 20 nm, preferably at most 15 nm, more preferably at most 10 nm. This is because, if the thickness of the hard mask film 4 is too large, a resist film to serve as an etching mask in dry etching for forming the pattern on the hard mask film 4 must have a large thickness. The thickness of the hard mask film 4 is required to be at least 2 nm, preferably at least 3 nm. This is because, if the thickness of the hard mask film 4 is too small, the pattern of the hard mask film 4 may possibly disappear before the end of the dry etching for forming the light-shielding pattern on the light-shielding film 3, depending on the condition of the high-bias etching with the oxygen-containing chlorine-based gas.

[0058]

As regards the resist film of an organic material used as the etching mask in the dry etching by a fluorine-based gas to form the pattern on the hard mask film 4, it is sufficient that the resist film has a film thickness enough to serve as the etching mask until the end of the dry etching of the hard mask film 4. Therefore,

cross-section aspect ratio of the resist pattern formed by the resist film can be lowered to 1 : 2.5. Therefore, it is possible to prevent the resist pattern from being collapsed or detached during development or rinsing of the resist film. More preferably, the resist film has a film thickness of at most 80 nm. The resist film is preferably a resist for electron beam writing and exposure. More preferably, the resist is of a chemically-amplified type.

[0063]

[Manufacturing Steps of Mask Blank]

The mask blank 100 of the above-mentioned structure is manufactured through the following steps. At first, the transparent substrate 1 is prepared. In the transparent substrate 1, an end face and a main surface have been polished to predetermined surface roughness (for example, root mean square roughness Rq of at most 0.2 nm in an inside region of a 1μm square). Thereafter, the transparent substrate has been subjected to predetermined cleaning and drying.

[0064]

Next, on the transparent substrate 1, the phase shift film 2 is formed by sputtering. After the phase shift film 2 is formed, annealing is carried out at a predetermined heating temperature. Next, the above-mentioned light-shielding film 3 is formed on the phase shift film 2 by sputtering. Then, the above-mentioned hard mask film 4 is formed on the light-shielding film 3 by sputtering. In formation of each layer by sputtering, a sputtering target containing the materials forming each layer at a predetermined composition ratio and a sputtering gas are used. Furthermore, film formation using a gas mixture of a noble gas and a reactive gas as a sputtering gas may be performed as necessary. Thereafter, in case where the mask blank 100 has the resist film, the surface of the hard mask film 4 is subjected to HMDS (Hexamethyldisilazane) treatment as necessary. Then, by a coating method such as spin coating, the resist film is formed on the surface of the hard mask film 4 having been subjected to the HMDS treatment to complete the mask blank 100.

[0065]

(Manufacturing Method of Phase Shift Mask)

Next, referring to Fig. 2, a method for manufacturing a phase shift mask

contains substantially no oxygen" means that the content of oxygen in the etching gas is at most 5 atomic%.

[0114]

There is also a method in which, without removing the resist pattern 17a immediately after formation of the etching mask pattern 15a, the absorber film 14 is etched using, as a mask, the etching mask pattern 15a with the resist pattern 17a. In this case, there is provided a characteristic that the resist pattern 17a is automatically removed during etching of the absorber film 14 so that the process is simplified. On the other hand, in the method of etching the absorber film 14 using, as a mask, the etching mask pattern 15a after removing the resist pattern 17a, there is provided a characteristic that stable etching can be performed without change of an organic product (outgas) from the resist which disappears during etching.

[0115]

By the above-mentioned process, it is possible to obtain the reflective mask 400 having a high-accuracy fine pattern with a less shadowing effect and less sidewall roughness.

[0116]

(Method for Manufacturing Semiconductor Device)

By performing EUV exposure using the reflective mask 400 in this embodiment, a desired transfer pattern based on the absorber pattern 14a on the reflective mask 400 can be formed on a semiconductor substrate.

[Examples]

[0117]

Now, the embodiment of this invention will be described more in detail with reference to examples.

[0118]

<Example 1>

[Manufacture of Mask Blank]

Referring to Fig. 1, the transparent substrate 1 made of synthetic quartz glass with the main surface having a size of about 152 mm x about 152 mm and a thickness of about 6.35 mm was prepared. In the transparent substrate 1, the end

Furthermore, in each depth-direction chemical bond state analysis in Figs. 3 to 5, an analysis result of the phase shift film 2 at a position in the film thickness direction after erosion from the uppermost surface of the hard mask film 4 for 21.00 min by Ar gas sputtering is shown in a "plot at 21.00 min." An analysis result of the phase shift film 2 at a position in the film thickness direction after erosion from the uppermost surface of the hard mask film 4 for 26.00 min by Ar gas sputtering is shown in a "plot at 26.00 min." An analysis result of the phase shift film 2 at a position in the film thickness direction after erosion from the uppermost surface of the hard mask film 4 for 30.00 min by Ar gas sputtering is shown in a "plot at 30.00 min."

[0130]

In the narrow spectra in Figs. 3 to 5, scales on a vertical axis are not same. Among the Si2p narrow spectra in Fig. 3, in each of the narrow spectra of the "plot at 9.00 min" and the "plot at 14.00 min", the scales on the vertical axis are enlarged as compared with the narrow spectra of the other plots. Thus, a wave of vibration in each of the narrow spectra of the "plot at 9.00 min" and the "plot at 14.00 min" in Fig. 3 does not represent presence of peaks but merely represents noise. This result shows that the content of silicon is below a detection lower limit value at a position in the film thickness direction that corresponds to each Si2p narrow spectrum of the light-shielding film 3.

[0131]

The analysis result of the hard mask film 4 at the position in the film thickness direction after erosion from the uppermost surface of the hard mask film 4 for 1.00 min by Ar gas sputtering is a measurement result for a portion of the hard mask film 4 except a surface layer portion.

[0132]

From the result of the Si2p narrow spectra in Fig. 3, it is understood that the hard mask film 4 in Example 1 has a maximum peak at a binding energy between 103 and 104 eV. This result means that Si-O bonds are present at a predetermined ratio or more (SiO_2 is predominant).

It is also understood that there is no substantial difference (smaller than 0.1 eV) between the position of the binding energy at which the maximum peak of the