formed on a resist film is designed in anticipation of a declining amount due to the side etching. Furthermore, the width of the pattern to be formed on the resist film is designed also in anticipation of the side etching amount of the light-shielding film of the chromium-based material.

[0009]

In recent years, a mask blank has begun to be used which is provided with an etching mask film (hard mask film) formed on a light-shielding film of a chromium-based material and made of a material having a sufficient etching selectivity over the chromium-based material with respect to dry etching using an 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 comparable level to that in dry etching under a conventional etching condition. The side etching amount of the light-shielding film during the etching can also be reduced as compared with that in the past.

[0012]

Furthermore, by examining and adjusting bonds and compositions in the light-shielding film of the chromium-based material, it is possible to considerably reduce the side etching amount of the pattern formed on the light shielding film in case where the light-shielding film is patterned using, as a mask, the hard mask film with the pattern formed thereon, using the oxygen-containing chlorine-based gas as an etching gas, and under a high-bias etching condition. As a result, a fine pattern can be formed on the phase shift film with high accuracy (Patent Literature 2).

[0013]

However, the pattern to be formed on the phase shift film is required to be further miniaturized. For this purpose, only the above-mentioned technique of considerably reducing the side etching amount of the pattern of the light-shielding film is not sufficient. Also, the pattern to be formed on the pattern-forming thin

possible to form a pattern of the hard mask film, which has an excellent (flat and smooth) sidewall with small sidewall roughness and small line edge roughness. As a result, it is possible to improve a pattern quality of the hard mask film.

[0037]

When an etching rate of a certain film is increased, an etching time required to pattern the film is shortened. When the etching time required to pattern the film is shortened, a sidewall of the film is exposed to an etching gas for a shorter time duration, resulting in reduction of a side etching amount.

In addition, in case where the etching rate of the certain film is increased, the etching time in a film thickness direction is shortened so that the sidewall of the certain film is exposed to the etching gas for a shorter time duration. Thus, it is possible to form the pattern having an excellent (flat and smooth) sidewall with small sidewall roughness.

[0038]

In order to obtain the above-mentioned effects and states, the content of oxygen in the hard mask film made of the material containing silicon and oxygen is preferably at most 66.5 atomic%, more preferably at most 66.0 atomic%, further preferably at most 65.5 atomic%. If the content of oxygen is too large, the above-mentioned effects and states are difficult to obtain.

[0039]

In order to obtain the above-mentioned effects and states, the content of oxygen in the hard mask film made of the material containing silicon and oxygen is preferably at least 60 atomic%, more preferably at least 62 atomic%, further preferably at least 64 atomic%. If the content of oxygen is too small, the above-mentioned effects and states are difficult to obtain.

[0040]

In order to obtain the above-mentioned effects and states, the content of silicon in the hard mask film made of the material containing silicon and oxygen is

hard mask film, a difference between the binding energies thereof is preferably smaller (preferably, substantially same) in the film thickness direction (depth direction) in order to achieve high controllability during etching of the hard mask film.

[0049]

Now, a detailed structure of this invention mentioned above will be described with reference to the drawings. Description will be made using same reference numerals assigned to similar components in the figures.

[0050]

<First Embodiment>

[Mask Blank and Manufacture Thereof]

(Mask Blank)

Fig. 1 is a view illustrating a schematic structure of a mask blank according to a first embodiment. The mask blank 100 illustrated in Fig. 1 has a structure in which a phase shift film 2, a light-shielding film 3 (pattern-forming thin film), and a hard mask film 4 are formed as layers in this order on one main surface of a transparent substrate 1. The mask blank 100 may have a structure including a resist film formed on the hard mask film 4 as necessary. Hereinafter, details of main constituent parts of the mask blank 100 will be described.

[0051]

[Transparent Substrate]

The transparent substrate 1 is made of a material excellent in transmissivity for exposure light used in an exposure process in lithography. As the material of the type, synthetic quartz glass, aluminosilicate glass, soda lime glass, low-thermal-expansion glass (SiO_2-TiO_2 glass or the like), and other various types of glass substrates may be used. In particular, a substrate using synthetic quartz glass has a high transmissivity for ArF excimer laser light (having a wavelength of about 193 nm) and, therefore, may suitably be used as the transparent substrate 1 of the mask blank 100.

[0052]

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).

[0056]

The phase shift film 2 is formed of, for example, MoSiN. In order to satisfy a predetermined phase difference (for example, 140 [deg] to 190 [deg], preferably 150 [deg] to 180 [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.

[0057]

[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 a gas mixture of a chlorine-based gas and an

The hard mask film 4 is formed of a material containing silicon and oxygen or a material containing silicon, oxygen, and at least one element selected from non-metal elements except nitrogen and metalloid elements. The hard mask film 4 in this case may contain any metalloid elements. Among the metalloid elements, at least one element selected from boron, germanium, antimony, and tellurium is preferably contained because it is expected to increase a conductivity of silicon used as a target upon forming the hard mask film 4 by sputtering. The non-metal elements are exemplified by carbon (C), fluorine (F), and hydrogen (H).

[0064]

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.

[0065]

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 is increased in 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.

[0066]

mask film 4 for 44.00 min by Ar gas sputtering is shown in a "plot at 44.00 min."

[0139]

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 Si2p 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 thickness direction that corresponds to each Si2p narrow spectrum of the light-shielding film 3.

[0140]

Among the narrow spectra in Fig. 4, in each of the narrow spectra of the "plot at 0.00 min", the "plot at 1.00 min", and the "plot at 44.00 min", scales on the vertical axis are enlarged as compared with the N1s narrow spectra of the other plots. Thus, a wave of vibration in each of the N1s narrow spectra of the "plot at 0.00 min", the "plot at 1.00 min", and the "plot at 44.00 min" in Fig. 4 does not represent presence of peaks but merely represents noise (that is, below a detection lower limit value). This result shows that the content of nitrogen is below a detection lower limit value at a position in the thickness direction that corresponds to each of the N1s narrow spectra of the hard mask film 4 and the transparent substrate 1.

[0141]

In the Si2p narrow spectrum of the "plot at 4.00 min" in Fig. 3, scales on the vertical axis are enlarged as compared with the narrow spectra of the "plot at 0.00 min" and the "plot at 1.00 min". Thus, it is shown that a small peak is detected in the Si2p narrow spectrum of the "plot at 4.00 min". This result shows that, at the position of the light-shielding film 3 in the thickness direction that corresponds to the "plot at 4.00 min", the peak is detected under a little influence

of the hard mask film 5 which has been present thereon.

[0142]

The analysis result of the hard mask film 4 at the position in the 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.

[0143]

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 (103.4 eV) between 103 and 103.5 eV. This result means that Si-O bonds are present at a predetermined ratio or more (Si-O bonds with a high oxidation degree is predominant) and that an existence ratio of Si-O bonds or Si-Si bonds with a low oxidation degree is low.

[0144]

From the result of the Si2p narrow spectra (narrow spectra of the "plot at 0.00 min" and the "plot at 1.00 min") of the hard mask film 4 in Fig. 3, it is understood that the hard mask film 4 in Example 1 has a substantially flat waveform at the binding energy between 97 eV and 100 eV and has no peak (below a detection lower limit value). This result means that presence of Si-Si bonds was not detected from the hard mask film 4.

[0145]

From the result of the Si2p narrow spectra in Fig. 3, it is understood that, in the hard mask film 4 in Example 1, a difference between a maximum peak position of the uppermost surface (0.00 min) and a maximum peak position of the inside of the film (1.00 min) is slightly less than 0.2 eV. It has been found out that the difference being relatively small is preferable in order to achieve high controllability during etching of the hard mask film.

[0146]

From the result of the N1s narrow spectra in Fig. 4, it has been found out

an N1s narrow spectrum, and an O1s narrow spectrum of the mask blank in Comparative Example 2 were obtained, respectively. From the result of the Si2p narrow spectrum (not shown), it has been found out that the hard mask film 4 in Comparative Example 2 has peaks at a binding energy (99.2 eV) between at least 97 eV and at most 100 eV and at a binding energy (102.7 eV) less than 103 eV, respectively.

[0174]

Furthermore, as regards the hard mask film 4 in Comparative Example 2, it has also been found out that, in the Si2p narrow spectrum, an integrated intensity of Si-Si bonds ranges from at least half of an integrated intensity of Si-O bonds to a level equivalent thereto and both the Si-O bonds and the Si-Si bonds are present in significant proportions.

[0175]

[Manufacture of Phase Shift Mask]

Next, using the mask blank 100 in Comparative Example 2, the halftone phase shift mask 200 was manufactured in the manner similar to Example 1. At first, a surface of the hard mask film 4 was subjected to HMDS treatment.

[0176]

Next, in the manner similar to Example 1, the resist pattern 5a having the first pattern was formed (see Fig. 2(a)).

[0177]

Next, dry etching using the resist pattern 5a as a mask and using a CF_4 gas was carried out to form the first pattern (hard mask pattern 4a) on the hard mask film 4 (see Fig. 2 (b)).

[0178]

At this time, the hard mask film 4 was higher in etching rate for the fluorine-based gas than the hard mask film 4 in Example 1. Thus, it has been found out that the hard mask film 4 can be rapidly etched with high accuracy.

[0179]