and since $CO_2$ gas can be distributed uniformly through a wide range in a chamber for being less reactive than oxygen gas, it is preferable in view of maintaining uniform film quality of the light shielding film 30 to be formed. As for the introduction method, the gas can be introduced separately into the chamber, or some gas can be introduced together or all gas can be introduced in mixture.

[0042]

Materials of the target can include, not only a simple chromium, but also chromium as a major substance, and chromium including any one of oxygen and carbon, or a combination of oxygen and carbon added to chromium can be used as the target.

[0043]

Incidentally, the mask blank of the present invention is not limited to those shown in FIG. 1, but can be configured to have an additional film (etching stopper film) intervening between the phase shift film 20 and the light shielding film 30. In this case, a preferable configuration is that the etching stopper film is formed from the material containing chromium given above, and that the light shielding film 30 is formed from a material containing silicon or a material containing tantalum.

The mask blank of the present invention is not limited to the mask blank for the phase shift mask described above, and can be applied to a mask blank for a binary mask. The mask blank in this case has a configuration without the phase shift film 20 between the main surface 11a of the transparent substrate 10 and the light shielding film 30. Further, the predetermined optical density is secured by the light shielding film 30 alone. A binary mask (transfer mask) can be formed by forming a transfer pattern in the light shielding film 30 of such a mask blank.

Further, the mask blank of the present invention can be a reflective mask blank for EUV lithography (Extreme Ultraviolet Lithography). In this case, an absorber film is preferably configured from the thin film in this embodiment.

[0044]

A material containing silicon for forming the light

10 or more: 1, more preferably 15 or more: 1, and further preferably 20 or more: 1. By using etching gas with high mixing ratio of chlorine-based gas, anisotropic property of dry etching can be enhanced. Further, in dry etching of the light shielding film 30, mixing ratio of mixed gas of chlorine-based gas and oxygen gas is, at gas flow ratio in an etching chamber, preferably chlorine-based gas: oxygen gas = 40 or less: 1.

[0058]

Subsequently, dry etching is carried out using fluorine-based gas with the light shielding pattern 30a as a mask, a phase shift pattern 20a as a first pattern is formed in the phase shift film 20, and the hard mask pattern 31a is removed (see FIG. 3(d)). Next, a resist film is formed on the light shielding pattern 30a by spin coating. On the resist film, a light shielding pattern as a second pattern to be formed in the light shielding film 30 is written by exposure with electron beam. Thereafter, predetermined treatments such as a developing treatment are carried out, and a resist film having a resist pattern 40b as a second pattern corresponding to the light shielding pattern is formed (see FIG. 3(e)).

[0059]

Next, dry etching is carried out using mixed gas of chlorine-based gas and oxygen gas with the resist pattern 40b as a mask, and a light shielding pattern 30b as a second pattern is formed in the light shielding film 30 (see FIG. 3(f)). Further, the resist pattern 40b is removed, predetermined treatments such as cleaning are carried out, and the phase shift mask 200 is obtained (see FIG. 3(g)).

[0060]

Incidentally, there is no particular limitation to chlorine-based gas used in the dry etching in the manufacturing process described above, as long as Cl is included. Examples of chlorine-based gas include $Cl_2$, $SiCl_2$, $CHCl_3$, $CH_2Cl_2$, $CCl_4$, $BCl_3$, and the like. Further, there is no particular limitation to fluorine-based gas used in the dry etching in the manufacturing process described above, as long as F is included. Examples of

target and in a mixed gas atmosphere of argon (Ar) and nitrogen monoxide (NO), a hard mask film 31 consisting of silicon, nitrogen, and oxygen was formed with the thickness of 5nm, on the light shielding film 30 and inside the edge of the light shielding film 30. At this stage, a masking plate was used which has a square opening having a 146mm side based on the center of the substrate. Further, a predetermined cleaning treatment was carried out to form a mask blank 100 of Example 1.

[0073]

Another transparent substrate 10 was prepared, which has a light shielding film 30 formed on a main surface 11a under the same conditions without the other films, and which was subjected to heat treatment. The sheet resistance of the light shielding film 30 was measured, resulting in 0.246kΩ/Square, which was 0.5kΩ/Square or less. Further, the refractive index n and extinction coefficient k of the light shielding film 30 to the light of 400nm to 700nm wavelength were measured using a spectroscopic ellipsometer. As a result, the extinction coefficient k to the light of 400nm wavelength was 2.33, the extinction coefficient k to the light of 550nm wavelength was 2.53, and the extinction coefficient k to the light of 700nm wavelength was 3.01, and the values were confirmed as 2.0 or more. The refractive index n to the light of 400nm wavelength was 2.52, the refractive index n to the light of 550nm wavelength was 2.96, and refractive index n to the light of 700nm wavelength was 3.57.

[0074]

Further, the light shielding film 30 was analyzed by an X-ray photoelectron spectroscopy (XPS; with RBS corrections). As a result, it was confirmed that the region near the surface that is opposite to the transparent substrate 10 side of the light shielding film 30 (region up to about 2nm depth from the surface) has a composition gradient portion having more oxygen content (40atom% or more oxygen content) than the other regions. Further, the content of each constituent element in the region of the light shielding film 30 excluding the composition

conditions as above without the other films, and which was subjected to heat treatment. The sheet resistance of the light shielding film of Comparative Example 1 was measured, resulting in 168kΩ/Square, which was significantly above 1.0kΩ/Square. Further, the refractive index n and extinction coefficient k of the light shielding film to the light of 400nm to 700nm wavelength were measured using a spectroscopic ellipsometer. As a result, the extinction coefficient k to the light of 400nm wavelength was 1.23, the extinction coefficient k to the light of 550nm wavelength was 1.27, and the extinction coefficient k to the light of 700nm wavelength was 1.2, and the values were below 2.0. The refractive index n to the light of 400nm wavelength was 2.42, the refractive index n to the light of 550nm wavelength was 2.64, and refractive index n to the light of 700nm wavelength was 2.67.

[0086]

Further, the light shielding film was analyzed by an X-ray photoelectron spectroscopy (XPS; with RBS corrections). As a result, it was confirmed that the region near the surface that is opposite to the transparent substrate side of the light shielding film (region up to about 2nm depth from the surface) has a composition gradient portion having more oxygen content (40atom% or more oxygen content) than other regions. Further, the content of each constituent element in the region of the light shielding film excluding the composition gradient portion was found to be, at an average value, Cr:56atom%, O:29atom%, and C:15atom%. Moreover, it was confirmed that the difference of each constituent element in the thickness direction of the region of the light shielding film excluding the composition gradient portion was 3atom% or less in all cases, and there was substantially no composition gradient in the thickness direction.

Since it was difficult to visually identify the boundary between the region where the main surface is exposed and the region where the light shielding film was formed in the light shielding film of Comparative Example 1, it was difficult to finely adjust the position to dispose the masking plate with