

BLANK MASK AND PHOTOMASK USING THE SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the priority benefit of Korean Patent Application No. 10-2021-0117417 filed on September 3, 2021 in the Korean Intellectual Property Office, the entire disclosure of which is incorporated herein by reference for all purposes.

BACKGROUND

[0002] 1. Field

[0003] The present disclosure relates to a blank mask and a photomask using the same.

[0004] 2. Description of Related Art

[0005] Due to high integration of semiconductor devices or the like, miniaturization of circuit patterns of semiconductor devices is on demand. For this reason, the importance of a lithography technique, which is a technique for developing a circuit pattern on a wafer surface using a photomask is being further emphasized.

[0006] To develop a miniaturized circuit pattern, a light source of exposure used in an exposure process (photolithography) is required to have a short wavelength. As the light source of exposure used recently, there is ArF excimer laser (wavelength of 193 nm) or the like.

[0007] On the other hand, there are Binary mask, Phase shift mask, and the like as photomasks.

[0008] The Binary mask has a structure in which a light shielding layer pattern is formed on a transparent substrate. On a surface where a pattern is formed from the Binary mask, a transmissive portion not including a light shielding layer allows exposure light to be transmitted, and a light shielding portion including a light shielding layer blocks exposure light, to transfer a pattern on resist film of the surface of a wafer. However, the Binary mask may cause a problem in the development of a minute pattern due to diffraction of light occurring at the edge of the transmissive portion as the pattern is being more miniaturized.

[0009] As a phase shift mask, there are Levenson type, Outrigger type, and Half-tone type. Among the above, Half-tone type phase shift mask has a structure, in which a pattern formed

with semi-transmissive films, is formed on a transparent substrate. On a surface where a pattern is formed from the Half-tone type phase shift mask, a transmissive portion not including a semi-transmissive layer allows exposure light to be transmitted, and a semi-transmissive portion including a semi-transmissive layer allows attenuated exposure light to be transmitted. The attenuated exposure light is allowed to have a phase difference compared to exposure light, which has gone through the transmissive portion. Accordingly, diffraction light occurring at the edge of the transmissive portion is counteracted by the exposure light, which has penetrated the semi-transmissive portion, and thereby the phase shift mask can form a further refined minute pattern on the surface of a wafer.

SUMMARY

[0010] A blank mask according to one embodiment of the present disclosure includes a transparent substrate and a light shielding film disposed on the transparent substrate, wherein the light shielding film includes a transition metal and at least one selected from the group consisting of oxygen and nitrogen, and wherein a surface of the light shielding film has a first contact angle of 40 ° to 45 ° measured by using diiodo-methane as a first liquid contacting the surface of the light shielding film.

[0011] The surface of the light shielding film may have an Rsk value, which is a skewness value, of -1 to 0.

[0012] The surface of the light shielding film may have an Rku value, which is kurtosis value, of 7 or less.

[0013] A ratio of a dispersion component of a surface energy of the surface of the light shielding film to the surface energy of the surface of the light shielding film may be 0.84 to 0.865.

[0014] The dispersion component of the surface energy of the surface of the light shielding film may be 37 mN/m to 40 mN/m.

[0015] The light shielding film may have the surface energy of 43 mN/m to 47 mN/m.

[0016] The first contact angle divided by a second contact angle of the light shielding film measured by using pure water as a second liquid contacting the surface of the light shielding film may be 0.58 to 0.604.

[0017] The surface of the light shielding film may have an Rku value of 2 or more.

[0018] The light shielding film may include a first light shielding layer and a second light shielding layer disposed on the first light shielding layer.

[0019] An amount of the transition metal in the second light shielding layer may be greater than an amount of the transition metal in the first light shielding layer.

[0020] The transition metal may further include at least one selected from the group consisting of Cr, Ta, Ti, and Hf.

[0021] A photomask according to another embodiment of the present disclosure includes a transparent substrate and a light shielding pattern film disposed on the transparent substrate, wherein the light shielding pattern film includes a transition metal and at least one selected from the group consisting of oxygen and nitrogen, and wherein an upper surface of the light shielding pattern film has a contact angle of 40 ° to 45 ° measured by using diiodo-methane as a liquid contacting the surface of the light shielding film.

[0022] The upper surface of the light shielding pattern film may have an Rsk value, which is a skewness value, of -1 to 0.

[0023] The upper surface of the light shielding pattern film may have an Rku value, which is kurtosis value, of 7 or less.

[0024] A method of manufacturing a semiconductor element according to another embodiment of the present disclosure includes: preparing a light source, a photomask, and a semiconductor wafer, onto which a resist film has been applied; selectively transmitting a light incident from the light source through the photomask onto the semiconductor wafer; and developing a pattern on the semiconductor wafer, wherein the photomask includes a transparent substrate and a light shielding pattern film disposed on the transparent substrate, wherein the light shielding pattern film includes a transition metal and at least one selected from the group consisting of oxygen and nitrogen, and wherein an upper surface of the light shielding pattern film has a contact angle of 40 ° to 45 ° measured by using diiodo-methane as a liquid contacting the surface of the light shielding film.

[0025] The upper surface of the light shielding pattern film may have an Rsk value, which is a skewness value, of -1 to 0.

[0026] The upper surface of the light shielding pattern film may have an Rku value, which is kurtosis value, of 7 or less.

[0027] Other features and aspects will be apparent from the following detailed description, the drawings, and the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0028] Hereinafter, example embodiments of the present disclosure will be described in detail with reference to the accompanying drawings so that they can be easily practiced by those skilled in the art to which the present invention pertains. However, the example embodiments may be embodied in many different forms and is not to be construed as being limited to the embodiments set forth herein.

[0029] FIG. 1 is a conceptual view for illustrating the blank mask according to one embodiment of the present disclosure.

[0030] FIG. 2 is a conceptual view for illustrating the blank mask according to another embodiment of the present disclosure.

[0031] FIG. 3 is a conceptual view for illustrating the blank mask according to another embodiment of the present disclosure.

[0032] FIG.4 is a conceptual view for illustrating the photomask according to another embodiment of the present disclosure.

[0033] Throughout the drawings and the detailed description, the same reference numerals refer to the same or like elements. The drawings may not be to scale, and the relative size, proportions, and depiction of elements in the drawings may be exaggerated for clarity, illustration, and convenience.

DETAILED DESCRIPTION

[0034] Hereinafter, example embodiments of the present disclosure will be described in detail with reference to the accompanying drawings so that they can be easily practiced by those skilled in the art to which the present invention pertains. However, the example embodiments may be embodied in many different forms and is not to be construed as being limited to the embodiments set forth herein.

[0035] In this disclosure, the term for degree like “about”, “substantially” and the like is used for meaning values approximative from/to the value when a tolerance to be proper to referred meaning for manufacture and substance is presented. Additionally, these terms for degree are used to help understanding of example embodiments and to prevent that an

unconscionable trespasser unjustly uses the presented content in which exact or absolute number is referred.

[0036] Throughout this disclosure, the phrase “combination(s) thereof” included in a Markush-type expression denotes one or more mixtures or combinations selected from the group consisting of components stated in the Markush-type expression, that is, denotes one or more components selected from the group consisting of the components are included.

[0037] Throughout this disclosure, the description of “A and/or B” means “A, B, or A and B.”

[0038] Throughout this disclosure, terms such as “first”, “second”, “A”, or “B” are used to distinguish the same terms from each other unless specially stated otherwise.

[0039] In this disclosure, “B being placed on A” means that B is placed in direct contact with A or placed over A with another layer or structure interposed therebetween and thus should not be interpreted as being limited to B being placed in direct contact with A.

[0040] In this disclosure, a singular form is contextually interpreted as including a plural form as well as a singular form unless specially stated otherwise.

[0041] In this disclosure, the surface profile refers to an outline observed at the surface.

[0042] The Rsk value is a value evaluated based on ISO_4287. The Rsk value shows skewness of the surface profile as a measuring target.

[0043] The Rku value is a value evaluated based on ISO_4287. The Rku value shows kurtosis of the surface profile as a measuring target.

[0044] The peak is a portion placed on the upper portion of a reference line (referring a height average line from the surface profile) from the surface profile of a light shielding film.

[0045] The valley is a portion placed on the lower portion of a reference line (referring a height average line from the surface profile) from the surface profile of a light shielding film.

[0046] The present disclosure illustrates a resist film for an example of a thin film formed in contact with a light shielding film. However, the characteristics of the present disclosure can be applied to all thin films that can be formed in contact with a light shielding film and be removed in subsequent processes. Therefore, the thin film formed in contact with a light shielding film is not limited to a resist film.

[0047] Due to high integration of semiconductor devices, a further miniaturized circuit pattern is required to be formed on a semiconductor wafer. As the critical dimension (CD) of a

pattern developed on a semiconductor wafer is more decreased, issues related to degradation of resolution of a photomask are increasing.

[0048] A light shielding film included in a blank mask may be formed into a light shielding pattern film by processes including cleaning the light shielding film for removal of particles, coating a resist film on the light shielding film, and patterning thereof. In these processes, some particles may remain on the surface of the light shielding film after cleaning, and a problem of failing to elaborately pattern the light shielding film in a predesigned pattern shape may occur.

[0049] The inventors of the present disclosure confirmed that the above problems can be solved by controlling the surface energy and roughness characteristics of a light shielding film, and completed the embodiments.

[0050] Hereinafter, detailed descriptions of the present disclosure will be made.

[0051] FIG.1 is a conceptual view for illustrating the blank mask according to one embodiment of the present disclosure. With reference to the FIG.1, the blank mask of the embodiment is described.

[0052] The blank mask 100 includes a transparent substrate 10 and a light shielding film disposed on the transparent substrate 10.

[0053] The material of the transparent substrate is not limited, and any material having a light transmissive characteristic with respect to an exposure light and being applicable to a blank mask may be used. In detail, the transmittance of the transparent substrate 10 with respect to an exposure light having a wavelength of 193 nm may be 85 % or more. The transmittance may be 87 % or more. The transmittance may be 99.99 % or less. For example, the transparent substrate 10 may be a synthetic quartz substrate. In such a case, the transparent substrate 10 may suppress attenuation of a light transmitting the transparent substrate 10.

[0054] Additionally, surface characteristics such as smoothness and roughness of the transparent substrate 10 may be adjusted and thereby the occurrence of optical distortion may be suppressed.

[0055] The light shielding film 20 may be disposed on the top side of the light transmitting substrate 10.

[0056] The light shielding film 20 may have a characteristic of blocking at least some of an exposure light incident to the bottom side of the transparent substrate 10. Also, when a phase shift film 30 (refer to FIG.3) is disposed between the transparent substrate 10 and the

light shielding film 20, the light shielding film 20 may be used as an etching mask in a process of etching the phase shift film 30 and the like to be the pattern shape.

[0057] The light shielding film 20 includes a transition metal, and at least one selected from the group consisting of oxygen and nitrogen.

[0058] Characteristics Related to Surface Energy of Light shielding film

[0059] The light shielding film 20 may have a contact angle of 40 ° to 45 ° measured by using diiodo-methane as a liquid contacting the surface of the light shielding film.

[0060] Organic particles present in air or caused from a worker during processes of storage and movement may be absorbed to a blank mask. For removing such particles, a resist film may be coated on a light shielding film 20 after a cleaning process is performed for the surface of the light shielding film 20. Coating of the resist film may be performed on the surface of the light shielding film 20 without a separate treatment, or may be performed after application of a material as an adhesion improver such as HMDS (Hexamethyldisilazane) and other organic silane-based compounds.

[0061] Even though a cleaning process is performed by applying the same cleaning solution and cleaning method, the cleaning effect may be different depending on the surface characteristic of the light shielding film 20. The embodiment can control roughness characteristics, compositions, process conditions of thermal treatment and cooling treatment, and the like. At the same time, the embodiment can control the contact angle of the light shielding film measured by using diiodo-methane as a liquid contacting the surface of the light shielding film within a predetermined range. Through the above, the repulsive force between the particles and the surface of the light shielding film 20 can be increased and thereby particles can be easily removed from the surface of the light shielding film 20. At the same time, even though the surface of the light shielding film 20 is not processed by adhesion improver, the light shielding film 20 may have more stable adhesive force with respect to a resist film having a hydrophobicity.

[0062] The contact angle of the light shielding film 20 measured by using diiodo-methane as a liquid contacting the surface of the light shielding film may be measured through Goniometer method by using a surface analyzer. In detail, the surface of the light shielding film 20 is divided into a total of nine sectors by trisecting vertically and horizontally. Diiodo-methane of 0.8 to 1.2 μL , for example, diiodo-methane of 1 μL is dropped onto the center of each sector, and the contact angle of diiodo-methane of each sector is measured, and the average value of measured contact angles of each sector is calculated as a contact angle of the light shielding

film 20 measured by using diiodo-methane as a liquid contacting the surface of the light shielding film.

[0063] The diiodo-methane used for the measurement of the contact angle has a surface energy of 50.8 mN/m, among which polar component is 0 mN/m and dispersion component is 50.8 mN/m.

[0064] For example, the contact angle of the light shielding film 20 measured by diiodo-methane is measured through a MSA (Mobile Surface Analyzer) double type model available from KRÜSS corporation.

[0065] For example, the contact angle of the light shielding film 20 measured by diiodo-methane may be 40 ° to 45 °. The contact angle may be 42 ° or more. The contact angle may be 42.5 ° or more. The contact angle may be 44.8 ° or less. The contact angle may be 43.8 ° or less. In such a case, organic particles present on the surface of the light shielding film 20 may be easily removed. Also, when a resist film is coated on the light shielding film 20 not additionally treated for the surface, the adhesive force between the light shielding film 20 and the resist film may have a stable adhesive strength.

[0066] The ratio of the dispersion component of the surface energy of the light shielding film 20 compared to the surface energy of the light shielding film 20 may be 0.84 to 0.865.

[0067] The cleaning solution applied in a process for cleaning the light shielding film 20 may be SC-1 solution, ammonia water, oxygenated water, or the like, and a solution having a relatively high polarity may be used. The cleaning solution may be in contact with the surface of the light shielding film 20 activated through light irradiation or the like, and thereby can remove organic matters absorbed on the surface of the light shielding film 20. However, such a cleaning solution has a high reactivity, and when remaining on the surface of the light shielding film 20, may cause damage of the surface of the light shielding film 20. Therefore, the cleaning solution is required to be removed from the surface of the light shielding film 20 after completion of a cleaning process.

[0068] The surface energy value is the sum of the dispersion component and polar component of the surface energy. Even though having the same surface energy value, the light shielding film 20 may have different characteristics on the surface depending on the value of dispersion component compared to the surface energy. By controlling the ratio of the dispersion component of the surface energy compared to the surface energy, the resist film may be stably coated on the light shielding film 20, which has not been surface-treated. At the same time, the activated surface of the light shielding film 20 is allowed to have further

high affinity with respect to a cleaning solution, thus particles remaining on the surface of the light shielding film 20 may be more efficiently removed.

[0069] The surface energy of the light shielding film 20 and the dispersion component of the surface energy is measured through Goniometer method by using a surface analyzer. In detail, the surface of the light shielding film 20 is trisected vertically and horizontally and divided into a total of nine sectors. Pure water is dropped in an amount of 0.8 to 1.2 μL , for example 1 μL , with the interval of about 2 seconds and the contact angle of pure water of each sector is measured by using a surface analyzer. After that, the average value of measured values of contact angles of respective sectors is calculated as the contact angle of the light shielding film 20 measured by using pure water as a liquid contacting the surface of the light shielding film. After 2 seconds from the dropping of pure water, diiodo-methane of 0.8 to 1.2 μL , for example, diiodo-methane of 1 μL is dropped at a position spaced apart from the position, where pure water has been dropped, to measure the contact angle of diiodo-methane, and the average value of the measured values of contact angles of respective sectors is calculated as the contact angle of the light shielding film 20. The surface energy, the dispersion component value and the polar component value of the surface energy of the light shielding film 20 are calculated from the contact angle of pure water and diiodo-methane measured from the light shielding film 20.

[0070] The surface energy of pure water used in the measurement is 72.8 mN/m. Polar component of the surface energy of the pure water is 51 mN/m. Dispersion component of the surface energy of the pure water is 21.8 mN/m. The surface energy of diiodo-methane used in the measurement is 50.8 mN/m. Polar component of the surface energy of the diiodo-methane is 0 mN/m. The dispersion component of the diiodo-methane is 50.8 mN/m.

[0071] For example, the ratio of the dispersion component of the surface energy of the light shielding film compared to the surface energy of the light shielding film 20 may be measured through MSA (Mobile Surface Analyzer) double type available from KRÜSS corporation.

[0072] The ratio of the dispersion component of the surface energy of the light shielding film 20 compared to the surface energy of the light shielding film 20 may be 0.84 to 0.865. The ratio may be 0.842 or more. The ratio may be 0.85 or more. The ratio may be 0.8605 or less. The ratio may be 0.86 or less. In such a case, dislocation of a resist pattern film from the surface of the light shielding film 20 may be prevented during a patterning process. Furthermore, the cleaning effect by a cleaning solution may be further improved during a cleaning operation.

[0073] The value of dispersion component of the surface energy of the light shielding film may be 37 mN/m to 40 mN/m. The value of dispersion component may be 37.5 mN/m or more. The value of dispersion component may be 39 mN/m or less. The value of dispersion component may be 38.5 mN/m or less. The value of dispersion component may be 38 mN/m or less. In such a case, while the degree of absorption of particles on the surface of the light shielding film 20 is decreased, a resist film can be stably formed on the surface of the light shielding film 20.

[0074] The surface energy of the light shielding film 20 may be 43 to 47 mN/m. The surface energy of the light shielding film 20 may be 43.5 mN/m or more. The surface energy of the light shielding film 20 may be 44 mN/m or more. The surface energy of the light shielding film 20 may be 46 mN/m or less. The surface energy of the light shielding film may be 45.5mN/m or less. In such a case, the repulsive force between an inactivated surface of the light shielding film 20 and a cleaning solution can be regulated, and organic particles can be effectively prevented from being adhered to the surface of the light shielding film 20.

[0075] The value of dividing the contact angle of the light shielding film 20 measured by diiodo-methane by the contact angle of the light shielding film 20 measured by pure water may be 0.58 to 0.604.

[0076] The value of the contact angle of the surface of the light shielding film 20 measured by a polar material and the value of the contact angle of the surface of the light shielding film 20 measured by a nonpolar material are regulated at the same time. Through the above, the cleaning solution can be easily removed from the surface of the light shielding film 20 where the activation effect has disappeared after completion of a cleaning process. Simultaneously, the repulsive force between particles including organic matters and the surface of the light shielding film 20 is increased, and thereby particles can be easily eliminated from the surface of the light shielding film 20.

[0077] The method of measuring the contact angle of the light shielding film measured by pure water is the same as the method of measuring the surface energy of the light shielding film described in the above.

[0078] The value of dividing the contact angle of the light shielding film 20 measured by diiodo-methane by the contact angle of the light shielding film 20 measured by pure water may be 0.58 to 0.604. The value may be 0.585 or more. The value may be 0.59 or more. The value may be 0.6 or less. The value may be 0.595 or less. In such a case, the convenience of cleaning the surface of the light shielding film 20 can be improved.

[0079] Characteristics Related to Surface Roughness of Light shielding film

[0080] The surface of the light shielding film 20 may have an Rsk value of -1 to 0, and an Rku value of 7 or less.

[0081] Before the formation of a resist film on the light shielding film 20, surface treatment may be performed for the light shielding film 20 by using a material such as an adhesion improver. The surface treatment may be performed by a method of applying a material such as an adhesion improver to the surface of the light shielding film 20.

[0082] The present disclosure can control the Rsk value and Rku value on the surface of the light shielding film 20 in addition to controlling the composition of the light shielding film 20, the surface energy thereof, and the conditions of thermal treatment and cooling treatment of the light shielding film 20. Through these, the adhesive force between the light shielding film 20 and a resist film may be improved, and absorption of particles on the surface of the light shielding film 20 can be suppressed.

[0083] In detail, the material such as an adhesive improver can be applied in a relatively even height within the surface of the light shielding film 20, by controlling the skewness on the surface of the light shielding film 20. In addition, it is possible to keep the external particles from being absorbed on the surface of the light shielding film 20 and to be eliminated easily.

[0084] The Rsk value and Rku value of the surface of the light shielding film 20 may be adjusted at the same time. In such a case, it is possible to apply a material such as an adhesion improver on the surface of the light shielding film 20 in a relatively even distribution overall, and the material can be stably maintained on the light shielding film 20 until the formation of a resist film on the light shielding film 20.

[0085] The method of measuring Rsk value and Rku value of the surface of light shielding film 20 is described below.

[0086] The Rsk value and Rku value are measured at an area of 1 μm vertically and horizontally placed on the center of the surface of the light shielding film 20. The Rsk value is measured in non-contact mode by setting the scan speed to be 0.5 Hz in the area using two-dimensional roughness meter. For example, the Rsk value and Rku value may be measured by using XE-150 model available from PARK SYSTEM equipped with PPP-NCHR, which is Cantilever model available from PARK SYSTEM, as a probe.

[0087] The surface of the light shielding film 20 may have an Rsk value of -1 to 0. The Rsk value may be -0.9 or more. The Rsk value may be -0.85 or more. The Rsk value may be -

0.8 or more. The Rsk value may be -0.7 or more. The Rsk value may be -0.1 or less. The Rsk value may be -0.15 or less. The Rsk value may be -0.2 or less.

[0088] The Rku value of the surface of the light shielding film 20 may be 7 or less. The Rku value may be 6 or less. The Rku value may be 5 or less. The Rku value may be 2 or more.

[0089] In such a case, the improvement effect in the adhesive force between the light shielding film 20 and the resist film caused by a material such as an adhesion improver can be further increased, and particles remaining on the surface of the light shielding film 20 can be easily removed.

[0090] Layer Structure and Composition of Light shielding film

[0091] FIG. 2 is a conceptual view for illustrating a blank mask according to another embodiment of the present disclosure. With reference to FIG. 2, the embodiment is described.

[0092] The light shielding film 20 may include a first light shielding layer 21 and a second light shielding layer 22 disposed on the first light shielding layer 21.

[0093] The second light shielding layer 22 may include a transition metal and at least one selected from the group consisting of oxygen and nitrogen. The second light shielding layer 22 may include the transition metal in an amount of 50 to 80 at%. The second light shielding layer 22 may include the transition metal in an amount of 55 to 75 at%. The second light shielding layer 22 may include the transition metal in an amount of 60 to 70 at%.

[0094] The amount of an element corresponding to oxygen or nitrogen in the second light shielding layer 22 may be 10 to 35 at%. The element corresponding to oxygen or nitrogen in the second light shielding layer 22 may be 15 to 25 at%.

[0095] The second light shielding layer 22 may include nitrogen in an amount of 5 to 20 at%. The second light shielding layer 22 may include nitrogen in an amount of 7 to 13 at%.

[0096] In such a case, a laminate including the light shielding film 20 and a phase shift film 30 can help block an exposure light substantially.

[0097] The first light shielding layer 21 may include a transition metal, oxygen, and nitrogen. The second light shielding layer 22 may include the transition metal in an amount of 30 to 60 at%. The first light shielding layer 21 may include the transition metal in an amount of 35 to 55 at%. The first light shielding layer 21 may include the transition metal in an amount of 40 to 50 at%.

[0098] The sum of the oxygen amount and nitrogen amount of the first light shielding layer 21 may be 40 to 70 at%. The sum of the oxygen amount and nitrogen amount of the first light shielding layer 21 may be 45 to 65 at%. The sum of the oxygen amount and nitrogen amount of the first light shielding layer 21 may be 50 to 60 at%.

[0099] The first light shielding layer 21 may include oxygen in an amount of 20 to 40 at%. The first light shielding layer 21 may include oxygen in an amount of 23 to 33 at%. The first light shielding layer 22 may include oxygen in an amount of 25 to 30 at%.

[0100] The first light shielding layer 21 may include nitrogen in an amount of 5 to 20 at%. The first light shielding layer 21 may include nitrogen in an amount of 7 to 17 at%. The first light shielding layer may include nitrogen in an amount of 10 to 15 at%.

[0101] In such a case, the first light shielding layer can help the light shielding film 20 to have excellent characteristics in extinction.

[0102] The transition metal may include at least one selected from the group consisting of Cr, Ta, Ti and Hf. The transition metal may be Cr.

[0103] The first light shielding layer 21 may have a film thickness of 250 to 650 Å. The first light shielding layer 21 may have a film thickness of 350 to 600 Å. The first light shielding layer 21 may have a film thickness of 400 to 550 Å. In such a case, the first light shielding layer can help the light shielding film to block an exposure light effectively.

[0104] The second light shielding layer 22 may have a film thickness of 30 to 200 Å. The second light shielding layer 22 may have a film thickness of 30 to 100 Å. The second light shielding layer 22 may have a film thickness of 40 to 80 Å. In such a case, the second light shielding layer 22 can improve the characteristics in extinction of the light shielding film 20 and can help control the side shape of the light shielding pattern film more accurately, which is formed when the light shielding film 20 is patterned.

[0105] The ratio of the film thickness of the second light shielding layer 22 to the film thickness of the first light shielding layer 22 may be 0.05 to 0.3. The film thickness ratio may be 0.07 to 0.25. The film thickness ratio may be 0.1 to 0.2. In such a case, the light shielding film 20 may have sufficient characteristics in extinction and a side surface profile of the light shielding pattern film, which is formed when the light shielding film 20 is patterned, can be close to perpendicular.

[0106] The amount of the transition metal of the second light shielding layer 22 may be greater than the amount of the transition metal of the first light shielding layer 21.

[0107] The second light shielding layer 22 may have greater amount of the transition metal compared to the first light shielding layer 21, in order to control the reflectivity of the light shielding film within a predetermined range for a defect test, and the like. In such a case, depending on thermal treatment condition of the light shielding film 20, the transition metal included in the second light shielding layer 22 may go through recovery, recrystallization, and the growth of a grain. When the growth of a grain is not controlled, the surface of the light shielding film 20 may form a deformed outline compared to the surface before the thermal treatment due to transition metal particles grown excessively. This may influence the surface energy and roughness characteristics of the light shielding film 20 and degrade the adhesive force between the light shielding film 20 and the resist film, thus deteriorate convenience in cleaning the light shielding film 20.

[0108] The embodiment controls the surface energy and roughness characteristics of the light shielding film 20 and the process conditions in thermal treatment and cooling treatment to be within a predetermined range, while the amount of the transition metal of the second light shielding layer 22 is greater than the amount of the transition metal of the first light shielding layer 21. Through these, the embodiment can improve the adhesive force between the light shielding film 20 and the resist film and the convenience in cleaning of the light shielding film 20. In addition, the light shielding film 20 can have desired optical properties and etching characteristics.

[0109] Optical Properties of Light shielding film

[0110] The light shielding film 20 may have a transmittance of 1 % or more with respect to a light with the wavelength of 193 nm. The light shielding film 20 may have a transmittance of 1.3 % or more with respect to a light with the wavelength of 193 nm. The light shielding film 20 may have a transmittance of 1.4 % or more with respect to a light with the wavelength of 193 nm. The light shielding film 20 may have a transmittance of 2 % or less with respect to a light with the wavelength of 193 nm.

[0111] The light shielding film 20 may have an optical density of 1.8 or more with respect to a light with the wavelength of 193 nm. The light shielding film 20 may have an optical density of 1.9 or more with respect to a light with the wavelength of 193 nm. The light shielding film 20 may have an optical density of 3 or less with respect to a light with the wavelength of 193 nm.

[0112] In such a case, a thin film comprising the light shielding film 20 can effectively suppress the transmission of an exposure light.

[0113] Other Films

[0114] FIG.3 is a conceptual view for illustrating a blank mask according to another embodiment of the present disclosure. With reference to the FIG.3, a blank mask of an embodiment is described.

[0115] A blank mask 100 according to another embodiment of the present disclosure includes a light transmitting substrate 0, a phase shift film 30 disposed on the light transmitting substrate 10 and a light shielding film 20 disposed on the phase shift film 30.

[0116] The phase shift film 30 includes a transition metal and silicon.

[0117] The light shielding film 20 may includes a transition metal and at least any one between oxygen and nitrogen.

[0118] The light shielding film 20 may have a contact angle of 40 ° to 45 ° measured by diiodo-methane.

[0119] The surface of the light shielding film 20 may have an Rsk value of -1 to 0, and an Rku value of 7 or less.

[0120] The phase shift film 30 may be disposed between the light transmitting substrate 10 and the light shielding film 20. The phase shift film 30 is a thin film for attenuating an exposure light transmitting the phase shift film and regulating the phase difference of the light to substantially suppress the refraction generated at the edge of a pattern.

[0121] The phase shift film 30 may have a phase difference of 170 to 190 ° with respect to a light with a wavelength of 193 nm. The phase shift film 30 may have a phase difference of 175 to 185 ° with respect to the light with the wavelength of 193 nm. The phase shift film 30 may have a transmittance of 3 to 10 % with respect to the light with the wavelength of 193 nm. The phase shift film 30 may have a transmittance of 4 to 8 % with respect to the light with the wavelength of 193 nm. In such a case, the resolution of a photomask including the phase shift film 30 may be improved.

[0122] The phase shift film 30 may include a transition metal and silicon. The phase shift film 30 may include a transition metal, silicon, oxygen, and nitrogen. The transition metal may be molybdenum.

[0123] The description of the properties and composition of the light transmitting substrate 10 and the light shielding film 20 is overlapped with the above description and thus omitted.

[0124] A hard mask (not shown) may be disposed on the light shielding film 20. The hard mask may function as an etching mask film when the light shielding film 20 is etched. The hard mask may include silicon, nitrogen, and oxygen.

[0125] Photomask

[0126] FIG.4 is a conceptual view for illustrating the photomask according to another embodiment of the present disclosure. With reference to the FIG.4, the photomask of the embodiment is described.

[0127] The photomask 200 according to another embodiment of the present disclosure includes a light transmitting substrate 10 and a light shielding pattern film 25 disposed on the light transmitting substrate 10.

[0128] The light shielding pattern film 25 includes a transition metal and at least one selected from the group consisting of oxygen and nitrogen.

[0129] An upper surface of the light shielding pattern film 25 has a contact angle of 40 ° to 45 ° measured by diiodo-methane.

[0130] The upper surface of the light shielding pattern film 25 has an Rsk value of -1 to 0, and the upper surface of the light shielding pattern film 25 has an Rku value of 7 or less.

[0131] The light shielding pattern film 25 may be formed by patterning the light shielding film 20 of the blank mask 100 described above.

[0132] The method of measuring the value of a contact angle of the upper surface of the light shielding pattern film 25 measured by diiodo-methane is the same as the method of measuring the value of a contact angle of the light shielding film 20 measured by diiodo-methane in a blank mask 100, except for the measuring target, which is the upper surface of the light shielding pattern film 25.

[0133] When the value of a contact angle is measured by diiodo-methane, diiodo-methane is dropped onto the upper surface of the light shielding pattern film 25 such that the whole area of the bottom surface of a drop of the diiodo-methane meets the upper surface of the light shielding pattern film 25 completely.

[0134] When the value of a contact angle of the light shielding pattern film 25 is measured by diiodo-methane, if the upper surface of the light shielding pattern film 25 is not located at the center of each sector of the upper surface of the light shielding pattern film 25, the contact angle is measured in an area located around the center.

[0135] The method of measuring Rsk value and Rku value from the upper surface of the light shielding pattern film 25 is the same as the method of measuring Rsk value and Rku value of the surface of the light shielding film 20 from the blank mask. However, when the upper surface of the light shielding pattern film 25 is not placed in an area of 1 μm vertically and horizontally located at the center of the surface of the photomask 200, the values are measured on the upper surface of the light shielding pattern film 25 around the area.

[0136] The description of the properties, the composition, and the structure of the light shielding pattern film 25 is overlapped with the description of the light shielding film 20 of the blank mask and thus omitted.

[0137] Manufacturing Method of Light shielding film

[0138] The manufacturing method of the blank mask according to one embodiment of the present disclosure may include disposing a light transmitting substrate and a sputtering target in a sputtering chamber.

[0139] The manufacturing method of the blank mask according to one embodiment of the present disclosure may include a film formation operation of injecting an atmosphere gas into the sputtering chamber and supplying an electric power to the sputtering target to form a light shielding film on the transparent substrate.

[0140] The film formation operation may include a first light shielding layer formation operation of forming a first light shielding layer on the transparent substrate; and a second light shielding layer formation operation of forming a second light shielding layer on the first light shielding layer.

[0141] The manufacturing method of the blank mask according to one embodiment of the present disclosure may include a thermal treatment operation of thermally treating the light shielding film formed on the transparent substrate for 5 to 30 minutes in an atmosphere at 150 $^{\circ}\text{C}$ to 330 $^{\circ}\text{C}$.

[0142] The manufacturing method of the blank mask according to one embodiment of the present disclosure may include a cooling operation of cooling the light shielding film after performing the thermal treatment operation,

[0143] The manufacturing method of the blank mask according to one embodiment of the present disclosure may include a stabilization operation of stabilizing the blank mask after performing the cooling operation in an atmosphere at 10 $^{\circ}\text{C}$ to 60 $^{\circ}\text{C}$.

[0144] In the preparation, a target may be selected considering the composition of the light shielding film. One target containing a transition metal may be used as the sputtering target. Two or more targets including one target containing a transition metal may be used as the sputtering target. The target containing a transition metal may include the transition metal in an amount of 90 at% or more. The target containing a transition metal may include the transition metal in an amount of 95 at% or more. The target containing a transition metal may include the transition metal of 99 at%.

[0145] The transition metal may include at least one selected from the group consisting of Cr, Ta, Ti, and Hf. The transition metal may include Cr.

[0146] The description of the transparent substrate disposed in the sputtering chamber is overlapped with the above description and thus omitted.

[0147] In preparation, a magnet may be arranged at the sputtering chamber. The magnet may be arranged at a side opposite to one side where sputtering occurs from a sputtering target.

[0148] In the light shielding film formation operation, the conditions for formation of respective layers may be applied differently when the respective layers included in a light shielding film. Particularly, in consideration of the characteristics in surface energy, surface roughness, extinction and etching of a light shielding film, respective process conditions such as the composition of an atmosphere gas, an electric power supplied to a sputtering target, and a film formation time may be applied to be different for the respective layers.

[0149] The atmospheric gas may include an inert gas, a reactive gas, and a sputtering gas. The inert gas is a gas not including an element constituting the formed film. The reactive gas is a gas including an element constituting the formed film. The sputtering gas is a gas ionizing in a plasma atmosphere to collide with the sputtering target.

[0150] The inert gas may include helium.

[0151] The reactive gas may include a gas including a nitrogen element. The gas including the nitrogen element may be for example, N₂, NO, NO₂, N₂O, N₂O₃, N₂O₄, N₂O₅, or the like. The reactive gas may include a gas including an oxygen element. The gas including the oxygen element may be O₂, CO₂, or the like. The reactive gas may include a gas including a nitrogen element and a gas including an oxygen element. The reactive gas may include a gas including both of nitrogen element and oxygen element. The gas including both of

nitrogen element and oxygen element may be for example, NO, NO₂, N₂O, N₂O₃, N₂O₄, N₂O₅, or the like.

[0152] The sputtering gas may be Ar gas.

[0153] A power source for supplying an electric power to a sputtering target may be DC power source, or RF power source.

[0154] In the first light shielding layer formation process, the electric power supplied to a sputtering target may be 1.5 kW to 2.5 kW. In the first light shielding layer formation process, the electric power supplied to a sputtering target may be 1.6 kW to 2 kW.

[0155] In the first light shielding layer formation process, the ratio of the flow rate of the reactive gas to the flow rate of the inert gas of an atmospheric gas may be 1.5 to 3. The flow rate ratio may be 1.8 to 2.7. The flow rate ratio may be 2 to 2.5.

[0156] The ratio of the oxygen amount to the nitrogen amount included in the reactive gas may be 1.5 to 4. The ratio of the oxygen amount to the nitrogen amount included in the reactive gas may be 2 to 3. The ratio of the oxygen amount to the nitrogen amount included in the reactive gas may be 2.2 to 2.7.

[0157] In such a case, the first light shielding layer may help the light shielding film to have sufficient extinction characteristics. The etching characteristics of the first light shielding layer may be controlled to help the side surface profile of the light shielding film pattern to have a shape close to be perpendicular to the light transmitting substrate after being patterned.

[0158] The formation time of the first light shielding layer may be 200 seconds to 300 seconds. The formation time of the first light shielding layer may be 210 seconds to 240 seconds. In such a case, the first light shielding layer can help the light shielding film to have sufficient extinction characteristics.

[0159] In the second light shielding layer formation process, the electric power supplied to a sputtering target may be applied to be 1 kW to 2 kW. In the second light shielding layer formation process, the electric power supplied to a sputtering target may be applied to be 1.2 kW to 1.7 kW.

[0160] In the second light shielding layer formation process, the ratio of the flow rate of the reactive gas to the flow rate of the inert gas of an atmospheric gas may be 0.3 to 0.8. The ratio may be 0.4 to 0.6.

[0161] In the second light shielding layer formation process, the ratio of the oxygen amount to the nitrogen amount included in the reactive gas may be 0.3 or less. The ratio of the oxygen amount to the nitrogen amount included in the reactive gas may be 0.1 or less. The ratio of the oxygen amount to the nitrogen amount included in the reactive gas may be 0.001 or more.

[0162] In such a case, an affinity of the light shielding film with respect to a nonpolar solution can be controlled within a preferred range, and the light shielding film may have stable extinction characteristics.

[0163] The formation time of the second light shielding layer may be 10 seconds to 30 seconds. The formation time of the second light shielding layer may be 15 seconds to 25 seconds. In such a case, the second light shielding layer may help suppressing the transmission of an exposure light.

[0164] In the thermal treatment operation, the light shielding film after completion of the film formation operation may be thermally treated. In detail, the substrate after the formation of the light shielding film is disposed in a thermal treatment chamber, and subsequently the thermal treatment may be performed.

[0165] Through the thermal treatment of the light shielding film, the stress formed in the light shielding film can be decreased, and density of the light shielding film can be further increased. When thermal treatment is applied to the light shielding film, recovery and recrystallization of the transition metal included in the light shielding film may occur, and the stress formed in the light shielding film can be effectively decreased. However, in the thermal treatment operation, when the process conditions such as temperature and time for thermal treatment are not controlled, excessive grain growth may occur in the light shielding film, and due to the grain growth not controlled in the size, the surface profile of the light shielding film may be considerably deformed compared to the state before the thermal treatment. This in turn may influence the surface energy and roughness characteristics of the light shielding film.

[0166] The embodiment may control the time and temperature for thermal treatment in the thermal treatment operation, and may control the cooling speed, the cooling time, the atmosphere during cooling, and the like in the cooling operation to be described below. Therefore, the embodiment can effectively decrease the internal stress formed in the light shielding film, and simultaneously, the surface of the light shielding film may have predetermined characteristics in the surface energy and roughness.

[0167] The thermal treatment operation may be performed at 150 °C to 330 °C. The thermal treatment operation may be performed at 180 °C to 300 °C.

[0168] The thermal treatment operation may be performed for 5 minutes to 30 minutes. The thermal treatment operation may be performed for 10 minutes to 20 minutes.

[0169] In such a case, the internal stress formed in the light shielding film can be effectively removed, and it can help suppressing excessive growth of a transition metal grain caused from thermal treatment.

[0170] In the cooling operation, the light shielding film after completion of the thermal treatment can be cooled. At a substrate surface side of a blank mask after completion of the thermal treatment operation, a cooling plate having a predetermined cooling temperature may be disposed. In the cooling operation, the cooling speed of a blank mask can be controlled by adjusting the gap between the blank mask and the cooling plate and applying a process condition such as applying an atmosphere gas.

[0171] For the blank mask, the cooling operation may be applied within 2 minutes after completion of the thermal treatment operation. In such a case, the growth of a transition metal grain due to residual heat within the light shielding film can be effectively suppressed.

[0172] Pins having a regulated length are set to respective vertexes of the cooling plate, and a blank mask may be arranged on the pins to have a substrate facing the cooling plate, thereby controlling the cooling speed of the blank mask.

[0173] In addition to the cooling method by the cooling plate, an inert gas may be injected to atmosphere, where the cooling operation proceeds, to cool the blank mask. In such a case, the residual heat in the side of the light shielding surface of the blank mask, whose cooling efficiency is slightly degraded, can be further effectively removed.

[0174] The inert gas may be for example, helium.

[0175] In the cooling operation, the cooling temperature applied to the cooling plate may be 10 to 30 °C. The cooling temperature may be 15 to 25 °C.

[0176] In the cooling operation, the gap between the blank mask and the cooling plate may be 0.01 to 30 mm. The gap may be 0.05 to 5 mm. The gap may be 0.1 to 2 mm.

[0177] In the cooling operation, the cooling speed of the blank mask may be 10 to 80 °C/min. The cooling speed may be 20 to 75 °C/min. The cooling speed may be 40 to 70 °C/min.

[0178] In such a case, the growth of the transition metal grain after completion of thermal treatment may be suppressed and it can help the surface of the light shielding film to have predetermined characteristics in the surface energy and roughness within the preferred ranges of embodiments.

[0179] In the stabilization operation, the blank mask after passing through the cooling operation can be stabilized. Through this, damage of the blank mask due to rapid variations in the temperature can be prevented.

[0180] The method of stabilizing a blank mask after passing through the cooling operation may be various. As one example, the blank mask after passing through the cooling operation is separated from the cooling plate, and after that, may be left for a certain time in an atmosphere at a room temperature. As another example, the blank mask after passing through the cooling operation is separated from the cooling plate, and after that, may be stabilized for 10 minutes to 60 minutes in an atmosphere at a temperature of 15 °C to 30 °C. At this time, the blank mask may be rotated at a speed of 20 rpm to 50 rpm. As another example, a gas, which does not react with the blank mask, may be injected in a flow rate of 5 L/min to 10 L/min for 1 minute to 5 minutes. At this time, the gas may have a temperature of 20 °C to 40 °C.

[0181] Manufacturing Method of Semiconductor Element

[0182] The manufacturing method of the semiconductor element according to another embodiment of the present disclosure includes: preparing a light source, a photomask, and a semiconductor wafer, where a resist film have been applied; an exposure operation of selectively transmitting the light incident from the light source through the photomask on the semiconductor wafer to be transferred; and a development operation of developing a pattern on the semiconductor wafer.

[0183] The photomask includes a transparent substrate and a light shielding pattern film disposed on the transparent substrate.

[0184] The light shielding pattern film includes a transition metal and at least one selected from the group consisting of oxygen and nitrogen.

[0185] An upper surface of the light shielding pattern film has a contact angle of 40 ° to 45 ° measured by diiodo-methane.

[0186] The upper surface of the light shielding pattern film has an Rsk value of -1 to 0.

[0187] The upper surface of the light shielding pattern film has an Rku value of 7 or less.

[0188] In the preparation, the light source is a device, which can generate an exposure light with a short wavelength. The exposure light may be a light with a wavelength of 200 nm or less. The exposure light may be an ArF light with a wavelength of 193 nm.

[0189] A lens may be additionally arranged between the photomask and the semiconductor wafer. The lens has a function of miniaturizing the circuit pattern shape of the photomask and transferring miniaturized circuit on the semiconductor wafer. Any lens conventionally applicable to an exposure process of ArF semiconductor wafer may be applied without limitation. For example, the lens may be a lens consisting of calcium fluoride (CaF_2).

[0190] In the exposure operation, the exposure light may be selectively transmitted on the semiconductor wafer through the photomask. In such a case, chemical denaturation may occur in a portion, where the exposure light is incident within a resist film.

[0191] In the development operation, the semiconductor wafer after completion of the exposure operation is treated with a developing solution for developing a pattern on the semiconductor wafer. When the applied resist film is a positive resist, a portion, where an exposure light is incident within the resist film, may be dissolved by a developing solution. When the applied resist film is a negative resist, a portion, where an exposure light is not incident within the resist film, may be dissolved by a developing solution. The resist film is formed into a resist pattern by the treatment with the developing solution. A pattern may be formed on the semiconductor wafer by taking the resist pattern as a mask.

[0192] The description of a photomask is overlapped with the above description and thus omitted.

[0193] Hereinafter, the further detailed description of specific example embodiments will be made.

[0194] Manufacture Example: Formation of Light shielding film

[0195] Example 1: A light transmitting substrate made from quartz in a size of 6-inched width, 6-inched length, and 0.25-inched thickness was disposed in a chamber of DC sputtering apparatus. A chrome target was arranged in the chamber to form a T/S distance of 255 mm, and the angle of 25 degrees between the substrate and the target.

[0196] Thereafter, the atmospheric gas, in which Ar of 21 volume%, N_2 of 11 volume%, CO_2 of 32 volume%, and He of 36 volume% had been mixed, was introduced into the chamber, the electric power of 1.85 kW was supplied to a sputtering target, and thereby a sputtering process was performed for 250 seconds to form a first light shielding layer.

[0197] After the formation of the first light shielding layer, the atmospheric gas, in which Ar of 57 volume% and N₂ of 43 volume% had been mixed, was introduced into the chamber, the electric power supplied to the sputtering target was applied to be 1.5 kW, and a sputtering process was performed for 25 seconds to manufacture a blank mask sample, in which the second light shielding layer had been formed.

[0198] The sample after the formation of the second light shielding layer was disposed in the chamber for thermal treatment, and thermal treatment was performed for 15 minutes at an atmospheric temperature of 200 °C.

[0199] A cooling plate, whose cooling temperature was applied to be 23 °C, was installed in the substrate side of the sample after passing through the thermal treatment. The gap between the substrate and the cooling plate of the sample was adjusted to have a cooling speed of 36 °C/min measured at the surface of the light shielding film of the sample, and a cooling operation was performed for 5 minutes.

[0200] After completion of the cooling treatment, the sample was stabilized for 15 minutes by keeping it in the atmosphere at a temperature of 20 °C to 25 °C.

[0201] Example 2: A blank mask sample was manufactured under the same condition as Example 1. However, the sample was thermally treated at 250 °C after the formation of the light shielding film, cooling treatment was performed for 7 minutes, and the cooled sample was stabilized for 20 minutes.

[0202] Example 3: A blank mask sample was manufactured under the same condition as Example 1. However, the sample was thermally treated at 250 °C after the formation of the light shielding film, the cooling speed measured at the surface of the light shielding film of the sample was applied to be 30 °C/min, and thereby cooling treatment was performed for 8 minutes.

[0203] Example 4: A blank mask sample was manufactured under the same condition as Example 1. However, the sample was thermally treated at 300 °C after the formation of the light shielding film, cooling treatment of the sample treated with heat was performed for 8 minutes, and the cooled sample was stabilized for 30 minutes.

[0204] Example 5: A blank mask sample was manufactured under the same condition as Example 1. However, the sample was thermally treated at 300 °C, a helium gas was injected to the sample in the flow rate of 300 sccm during cooling treatment, thereby having a cooling

speed of 56 °C/min measured at the surface of the light shielding film of the sample, and the cooled sample was stabilized for 45 minutes.

[0205] Comparative Example 1: A blank mask sample was manufactured under the same condition as Example 1. However, thermal treatment, cooling treatment, and stabilization were not performed.

[0206] Comparative Example 2: A blank mask sample was manufactured under the same condition as Example 1. However, the sample was thermally treated at 250 °C after the formation of the light shielding film 20, and cooling treatment of the sample was performed by natural cooling in the atmosphere without using a cooling plate. During the natural cooling, the atmospheric temperature of 23 °C, the cooling time of 120 minutes, and the cooling speed of 2 °C/min measured at the surface of the light shielding film of the sample were applied. After the cooling treatment, stabilization was not performed.

[0207] Comparative Example 3: A blank mask sample was manufactured under the same condition as Example 1. However, the sample was thermally treated at 300 °C after the formation of the light shielding film, and a helium gas was injected to the sample in the flow rate of 300 sccm during cooling treatment, thereby having a cooling speed of 56 °C/min. Stabilization was not performed for the cooled sample.

[0208] The descriptions of conditions for thermal treatment, cooling treatment, and stabilization of each Example or Comparative Example were shown in Table 1 below.

[0209] Evaluation Example: Measurement of Characteristics Related to Surface Energy of Light shielding film

[0210] The surface of the light shielding film of the sample of each Example or Comparative Example was trisected vertically and horizontally and divided into a total of nine sectors. Pure water of 0.8 to 1.2 µL, for example, 1 µL was dropped to the center of each sector with an interval of about 2 seconds, and the contact angle of pure water of each sector was measured by a surface analyzer. The average value of the measured values of contact angles of respective sectors was calculated as the contact angle of the light shielding film measured with pure water. After pure water was dropped, diiodo-methane of 0.8 to 1.2 µL, for example, 1 µL was dropped to the spot spaced apart from the spot where pure water was dropped, and the contact angle of diiodo-methane of each sector was measured by a surface analyzer. The average value of measured values of contact angles of respective sectors was calculated as the contact angle of the light shielding film measured with diiodo-methane. The surface

energy, the polar component of the surface energy, and dispersion component were calculated from the contact angle values of the light shielding film measured and calculated by pure water and diiodo-methane.

[0211] The surface energy of the pure water used in the measurement is 72.8 mN/m, the polar component of the surface energy is 51 mN/m, and the dispersion component is 21.8 mN/m. The surface energy of the diiodo-methane used in the measurement is 50.8 mN/m, the polar component of the surface energy is 0 mN/m, and the dispersion component is 50.8 mN/m.

[0212] The surface analyzer was MSA (Mobile Surface Analyzer) double type model available from KRÜSS corporation.

[0213] The measured values of respective Examples and Comparative Examples were described in Table 2 below.

[0214] Evaluation Example: Measurement of Surface Roughness Characteristics of Light shielding film

[0215] The Rsk and Rku values of the surface of the light shielding film of each Example or Comparative Example were measured in accordance with ISO_4287.

[0216] In detail, XE-150 model available from PARK SYSTEM applied with PPP_NCHR, which was Cantilever model available from PARK SYSTEM as a probe in the area of 1 μm vertically and horizontally of the center of the light shielding film, was used to measure Rsk value and Rku value in non-contact mode at a scan speed of 0.5 Hz.

[0217] The measured results of respective Examples and Comparative Examples were described in Table 3.

[0218] Evaluation Example: Evaluation of Resist Film Coating

[0219] A resist film was applied on the light shielding film of each Example or Comparative Example by injecting a resist solution of XFP255 model available from FUJI corporation in a spin coating method. Subsequently, the applied resist film was dried for 620 seconds at 140 °C to form a resist film in the thickness of 1300 Å.

[0220] Thereafter, the surface, where the resist film had been applied of each Example or Comparative Example, was divided into seven areas vertically and horizontally. In the respective areas, the thickness of a resist film was measured by using a MG Pro model test available from NANOVIEW. When the value of subtracting the minimum from the maximum

within the thickness values of the resist film measured from each area was less than 130 Å, it was evaluated as Pass, and when the value was 130 Å or more, it was evaluated as Fail.

[0221] The evaluated results of respective Examples and Comparative Examples were described in Table 3 below.

[0222] Evaluation Example: Evaluation of Cleaning Effect of Light shielding film

[0223] The sample of each Example or Comparative Example kept in SMIF (Standard Mechanical InterFace) was opened to be left allowing the sample surface to be polluted. An area of 146 mm vertically and horizontally within the surface of the light shielding film of the left sample was inspected by M6641S tester available from LASERTEC corporation, and the number of particles was measured. The wavelength of a testing light used in the inspection for particles was 532 nm.

[0224] Thereafter, the sample surface, where pollution had been ascertained, was cleaned.

[0225] The cleaning was performed as follows. The surface of the light shielding film of the sample was activated by irradiation of a light with a wavelength of 172 nm for 120 seconds. After the activation, a carbonated water was injected to the sample surface for 1 minute and 30 seconds in the flow rate of 1500 ml/min, thereby performing rinsing. After the rinsing, while the sample was rotated at 80 rpm, SC-1 solution in the flow rate of 800 ml/min and hydrogen water in the flow rate of 600 ml/min were injected at the same time for 8 minutes and 30 seconds to perform cleaning. The SC-1 solution was applied by a solution including NH_4OH of 0.1 volume%, H_2O_2 of 0.08 volume%, and H_2O of 99.82 volume%. After the cleaning, carbonated water was injected to the sample surface for 1 minute and 30 seconds in the flow rate of 1500 ml/min to perform rinsing.

[0226] Thereafter, the number of particles was inspected from the surface of the light shielding film of the sample after completion of cleaning by using the same method as the method of inspecting particles of the sample before being cleaned. When all particles were removed from the surface of the light shielding film after the cleaning, the measuring result was evaluated as O, when particles of 70 % or more were removed, it was evaluated as Δ, and when particles less than 70 % were removed, it was evaluated as X.

[0227] The measured results of respective Examples and Comparative Examples were described in Table 3 below.

[0228] Evaluation Example: Evaluation of Additional Particle Measurement within Light shielding film

[0229] The sample of each Example or Comparative Example kept in SMIF (Standard Mechanical InterFace) was opened and loaded in the internal space of an inspector of M6641S model available from LASERTEC corporation and the number of particles was measured in an area of 146 mm vertically and horizontally within the surface of the light shielding film. The wavelength of the testing light used in the particle inspection was 532 nm.

[0230] Thereafter, cleaning was performed to the sample surface. In detail, the surface of the light shielding film of the sample was irradiated for 120 seconds by a light with a wavelength of 172 nm to be activated. After the activation, carbonated water was injected in the flow rate of 1500 ml/min for 1 minute and 30 seconds, thereby performing rinsing. After the rinsing, while the sample was rotated at 80 rpm, SC-1 solution in the flow rate of 800 ml/min and hydrogen water in the flow rate of 600 ml/min were injected to the surface of the light shielding film at the same time for 8 minutes and 30 seconds, thereby performing cleaning. The SC-1 solution was applied by a solution including NH_4OH of 0.1 volume%, H_2O_2 of 0.08 volume%, and H_2O of 99.82 volume%. After the cleaning, carbonated water was injected to the sample surface in the flow rate of 1500 ml/min for 1 minute and 30 seconds, thereby performing rinsing.

[0231] Thereafter, the number of particles present on the surface of the light shielding film of the sample after being cleaned was inspected by the same method as the method of inspecting particles of the sample before being cleaned. Compared to the light shielding film before being cleaned, when a newly additional particle was not detected, it was evaluated as X, and when a newly additional particle was detected, it was evaluated as Δ .

[0232] The evaluation results of respective Examples and Comparative Examples were described in Table 3 below.

[0233] [Table 1]

	Temperature for Thermal Treatment (°C)	Time for Thermal Treatment (Minute)	Whether Cooling Plate Is Used	The Flow rate of Helium Gas (sccm)	Temperature of Cooling Plate (°C)	Cooling Time (Minute)	Cooling Speed (°C/minute)	Temperature for Stabilization (°C)	Stabilization Time (Minute)

Example 1	200	15	O	-	23	5	36	20 to 25	15
Example 2	250	15	O	-	23	7	36	20 to 25	20
Example 3	250	15	O	-	23	8	30	20 to 25	15
Example 4	300	15	O	-	23	8	36	20 to 25	30
Example 5	300	15	O	300	23	5	56	20 to 25	45
Comparative Example 1	-	-	-	-	-	-	-	-	-
Comparative Example 2	250	15	X	-	23 (Atmosphere Temperature)	120	2	-	-
Comparative Example 3	300	15	O	300	23	5	56	-	-

[0234] [Table 2]

	$\theta_1(^{\circ})^{(1)}$	$\theta_2(^{\circ})^{(2)}$	θ_2/θ_1	Surface Energy of Light shielding film (mN/m)	Polar component of the surface energy of Light shielding film (mN/m)	Dispersion component of the surface energy of Light shielding film (mN/m)	The Ratio of Dispersion component of the surface energy Compared to Surface Energy
Example 1	71.58	42.91	0.599	45.25	7.13	38.12	0.842
Example 2	72.71	43.56	0.599	44.5	6.73	37.78	0.849

Example 3	73.11	43.75	0.598	44.25	6.58	37.68	0.852
Example 4	74.25	43.9	0.591	43.71	6.11	37.6	0.860
Example 5	74.46	44.95	0.604	43.21	6.17	37.04	0.857
Comparative Example 1	68.31	39.45	0.578	48.02	8.13	39.89	0.831
Comparative Example 2	68.95	39.03	0.566	47.87	7.77	40.09	0.837
Comparative Example 3	75.15	45.43	0.605	42.73	5.95	36.78	0.861

1) θ_1 is the contact angle of the surface of the light shielding film measured by pure water.

2) θ_2 is the contact angle of the surface of the light shielding film measured by diiodomethane.

[0235] [Table 3]

	Rsk	Rku	Cleaning Effect	Resist Coating	Additional Particle Evaluation
Example 1	-0.885	4.125	○	P	X
Example 2	-0.651	3.795	○	P	X
Example 3	-0.714	3.923	○	P	X
Example 4	-0.399	2.972	○	P	X
Example 5	-0.204	2.845	○	P	X
Comparative Example 1	-1.316	9.245	△	F	△

Comparative Example 2	-1.154	7.352	△	F	△
Comparative Example 3	-1.168	5.054	X	F	X

[0236] All the cases of Examples, in which the contact angle of the surface of the light shielding film measured by diiodo-methane, the Rsk and Rku values, and the like were controlled within the range predetermined in embodiments, were evaluated as P for the cleaning effect. However, Comparative Examples 1 and 2 were evaluated as △, and the case of Comparative Example 3 was evaluated as X.

[0237] For evaluation of resist film coating, all Examples were evaluated as P. However, all Comparative Examples were evaluated as F.

[0238] For evaluation of cleaning effect, Examples were evaluated as O. However, Comparative Examples were evaluated as △ or X.

[0239] For evaluating whether an additional particle was present, Examples did not show an additional particle. However, Comparative Examples 1 and 2 were evaluated as △.

[0240] While this disclosure includes specific examples, it will be apparent after an understanding of the disclosure of this application that various changes in form and details may be made in these examples without departing from the spirit and scope of the claims and their equivalents. The examples described herein are to be considered in a descriptive sense only, and not for purposes of limitation. Descriptions of features or aspects in each example are to be considered as being applicable to similar features or aspects in other examples. Suitable results may be achieved if the described techniques are performed in a different order, and/or if components in a described system, architecture, device, or circuit are combined in a different manner, and/or replaced or supplemented by other components or their equivalents. Therefore, the scope of the disclosure is defined not by the detailed description, but by the claims and their equivalents, and all variations within the scope of the claims and their equivalents are to be construed as being included in the disclosure.

WHAT IS CLAIMED IS:

1. A blank mask comprising a transparent substrate and a light shielding film disposed on the transparent substrate,

wherein the light shielding film comprises a transition metal and at least one selected from the group consisting of oxygen and nitrogen, and

wherein a surface of the light shielding film has a first contact angle of 40° to 45° measured by using diiodo-methane as a first liquid contacting the surface of the light shielding film.

2. The blank mask of claim 1, wherein the surface of the light shielding film has an Rsk value, which is a skewness value, of -1 to 0.

3. The blank mask of claim 1, wherein the surface of the light shielding film has an Rku value, which is kurtosis value, of 7 or less.

4. The blank mask of claim 1, wherein a ratio of a dispersion component of a surface energy of the surface of the light shielding film to the surface energy of the surface of the light shielding film is 0.84 to 0.865.

5. The blank mask of claim 4, wherein the dispersion component of the surface energy of the surface of the light shielding film is 37 mN/m to 40 mN/m.

6. The blank mask of claim 4, wherein the light shielding film has the surface energy of 43 mN/m to 47 mN/m.

7. The blank mask of claim 1, wherein the first contact angle divided by a second contact angle of the light shielding film measured by using pure water as a second liquid contacting the surface of the light shielding film is 0.58 to 0.604.

8. The blank mask of claim 1, wherein the surface of the light shielding film has an Rku value of 2 or more.

9. The blank mask of claim 1, wherein the light shielding film comprises a first light shielding layer and a second light shielding layer disposed on the first light shielding layer.

10. The blank mask of claim 9, wherein an amount of the transition metal in the second light shielding layer is greater than an amount of the transition metal in the first light shielding layer.

11. The blank mask of claim 1, wherein the transition metal further comprises at least one selected from the group consisting of Cr, Ta, Ti, and Hf.

12. A photomask comprising a transparent substrate and a light shielding pattern film disposed on the transparent substrate,

wherein the light shielding pattern film comprises a transition metal and at least one selected from the group consisting of oxygen and nitrogen, and

wherein an upper surface of the light shielding pattern film has a contact angle of 40 ° to 45 ° measured by using diiodo-methane as a liquid contacting the surface of the light shielding film.

13. The photomask of claim 12, wherein the upper surface of the light shielding pattern film has an Rsk value, which is a skewness value, of -1 to 0.

14. The photomask of claim 12, wherein the upper surface of the light shielding pattern film has an Rku value, which is kurtosis value, of 7 or less.

15. A method of manufacturing a semiconductor element comprising:

preparing a light source, a photomask, and a semiconductor wafer, onto which a resist film has been applied;

selectively transmitting a light incident from the light source through the photomask onto the semiconductor wafer; and

developing a pattern on the semiconductor wafer,

wherein the photomask comprises a transparent substrate and a light shielding pattern film disposed on the transparent substrate,

wherein the light shielding pattern film comprises a transition metal and at least one selected from the group consisting of oxygen and nitrogen, and

wherein an upper surface of the light shielding pattern film has a contact angle of 40° to 45° measured by using diiodo-methane as a liquid contacting the surface of the light shielding film.

16. The method of claim 15, wherein the upper surface of the light shielding pattern film has an R_{sk} value, which is a skewness value, of -1 to 0.

17. The method of claim 15, wherein the upper surface of the light shielding pattern film has an R_{ku} value, which is kurtosis value, of 7 or less.