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updated as appropriate

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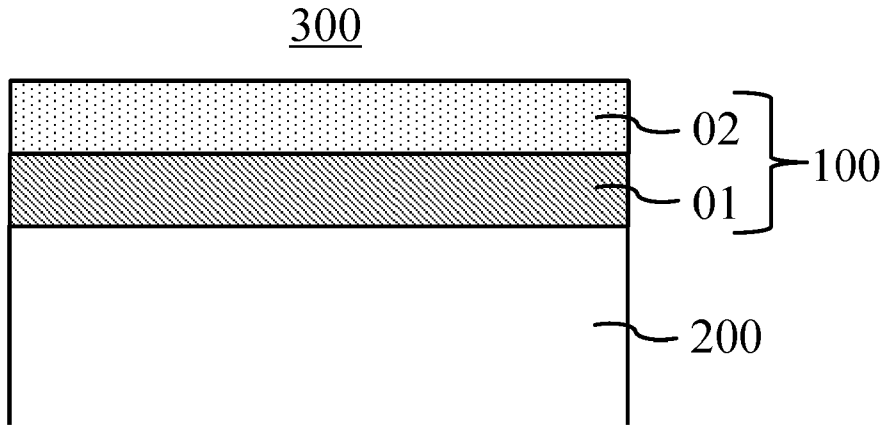


FIG. 1

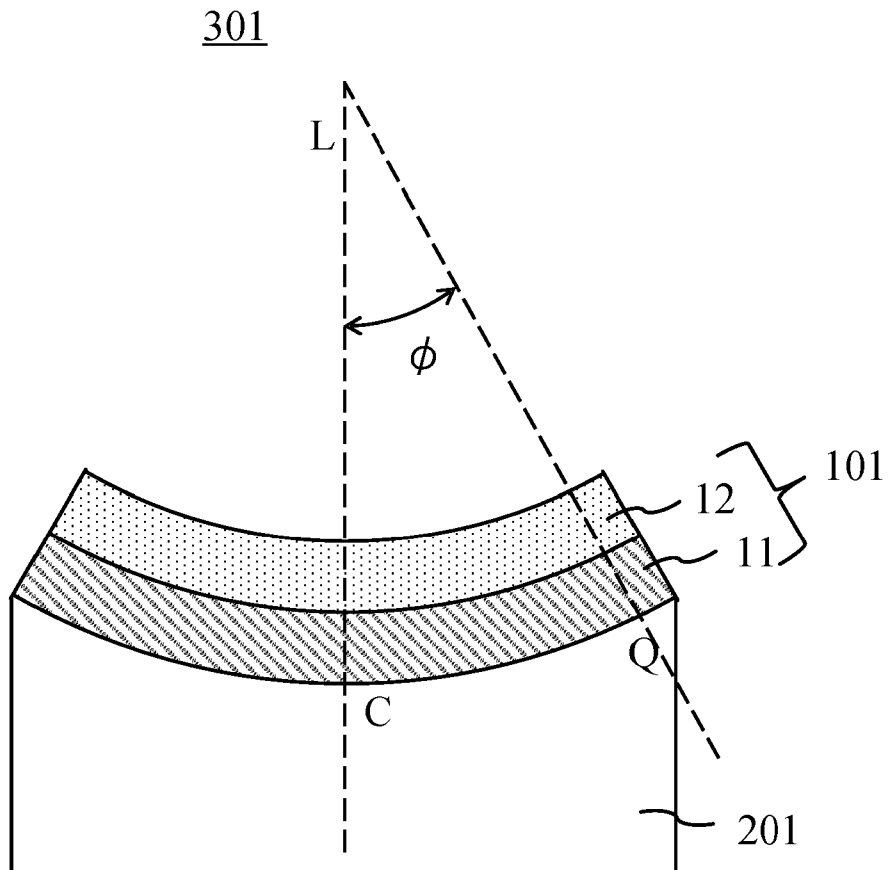


FIG. 2

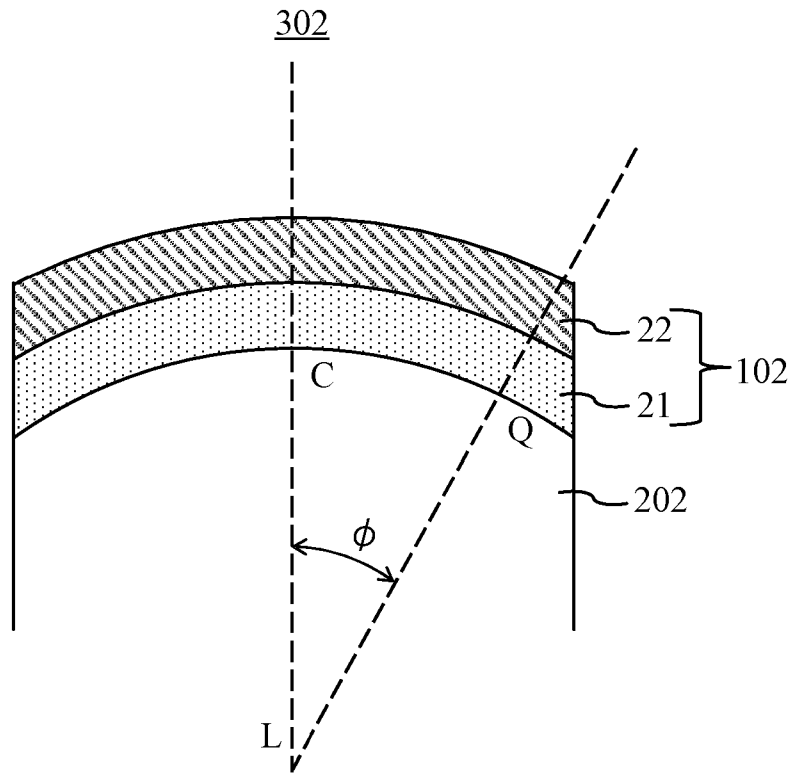


FIG. 3

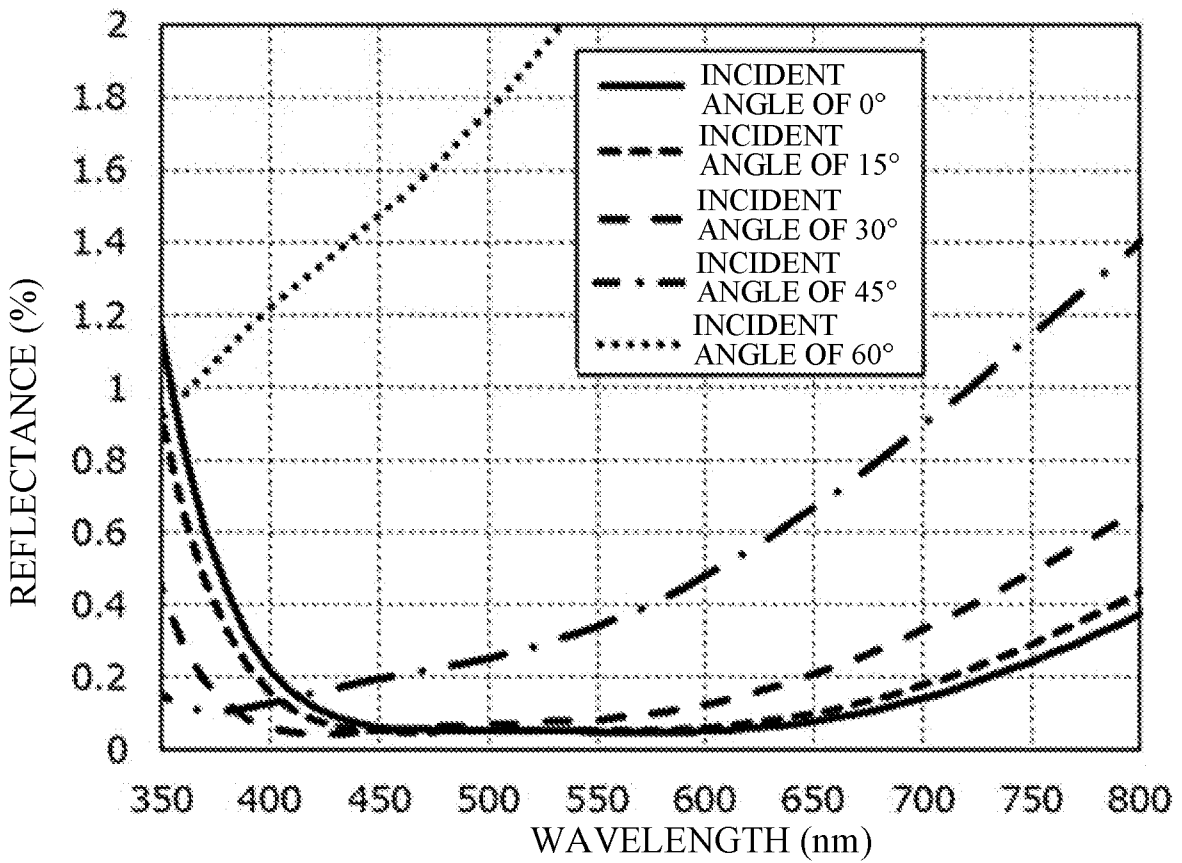


FIG. 4

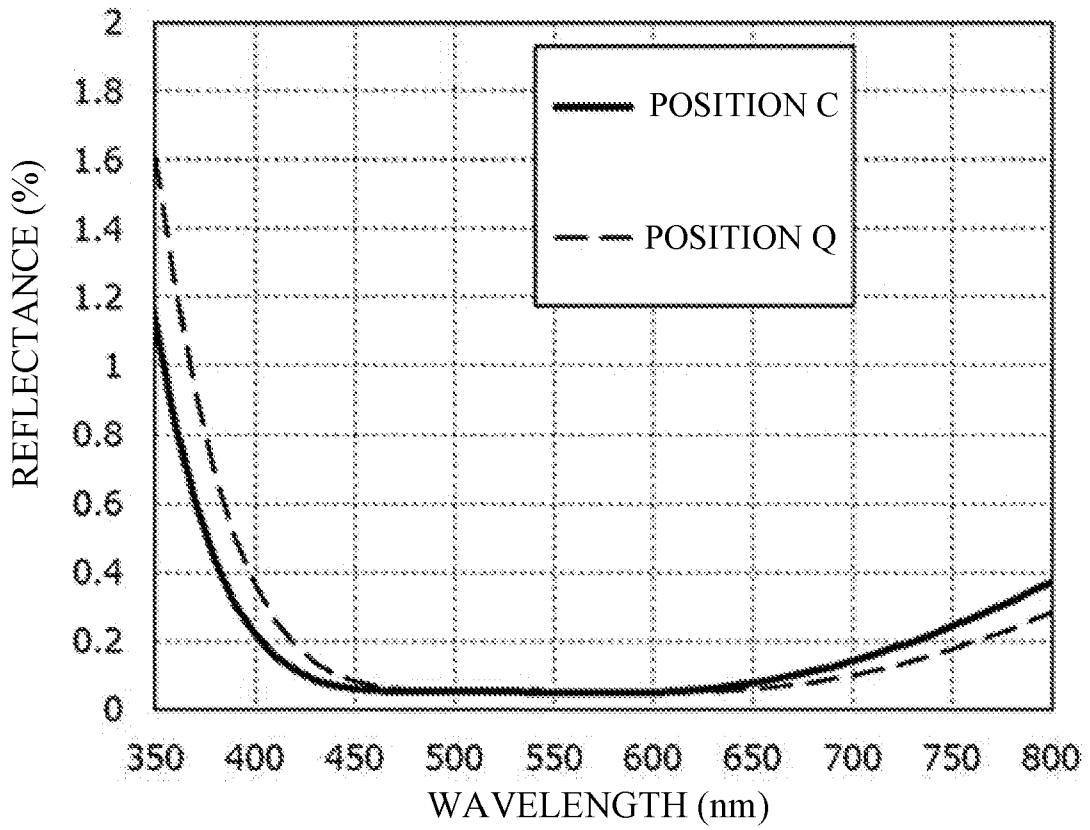


FIG. 5

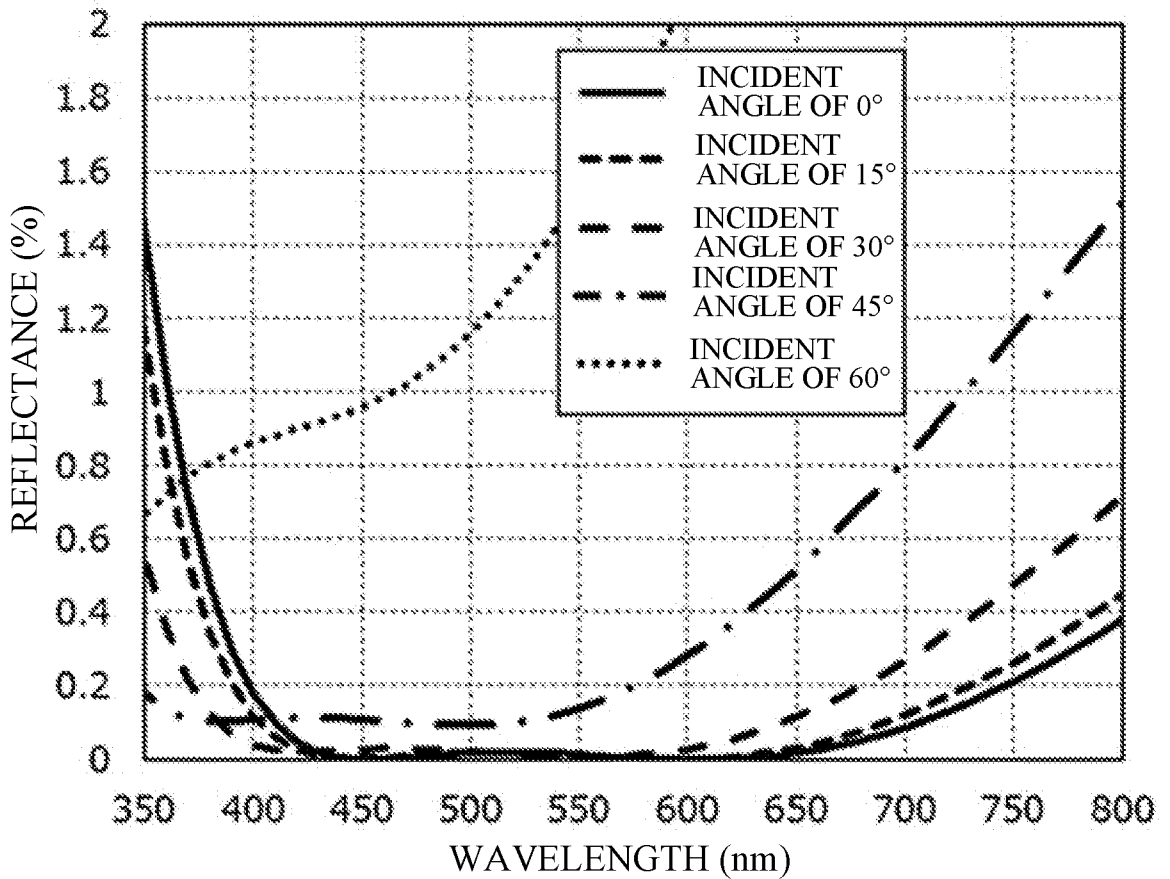


FIG. 6

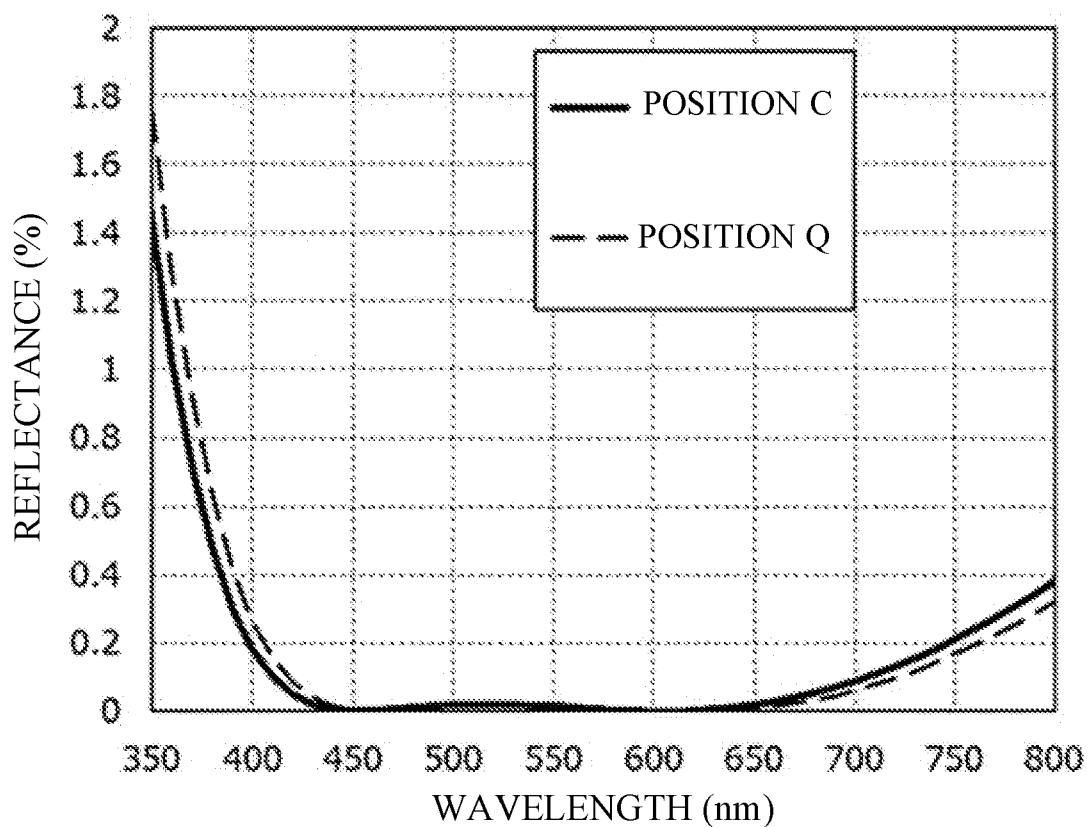


FIG. 7

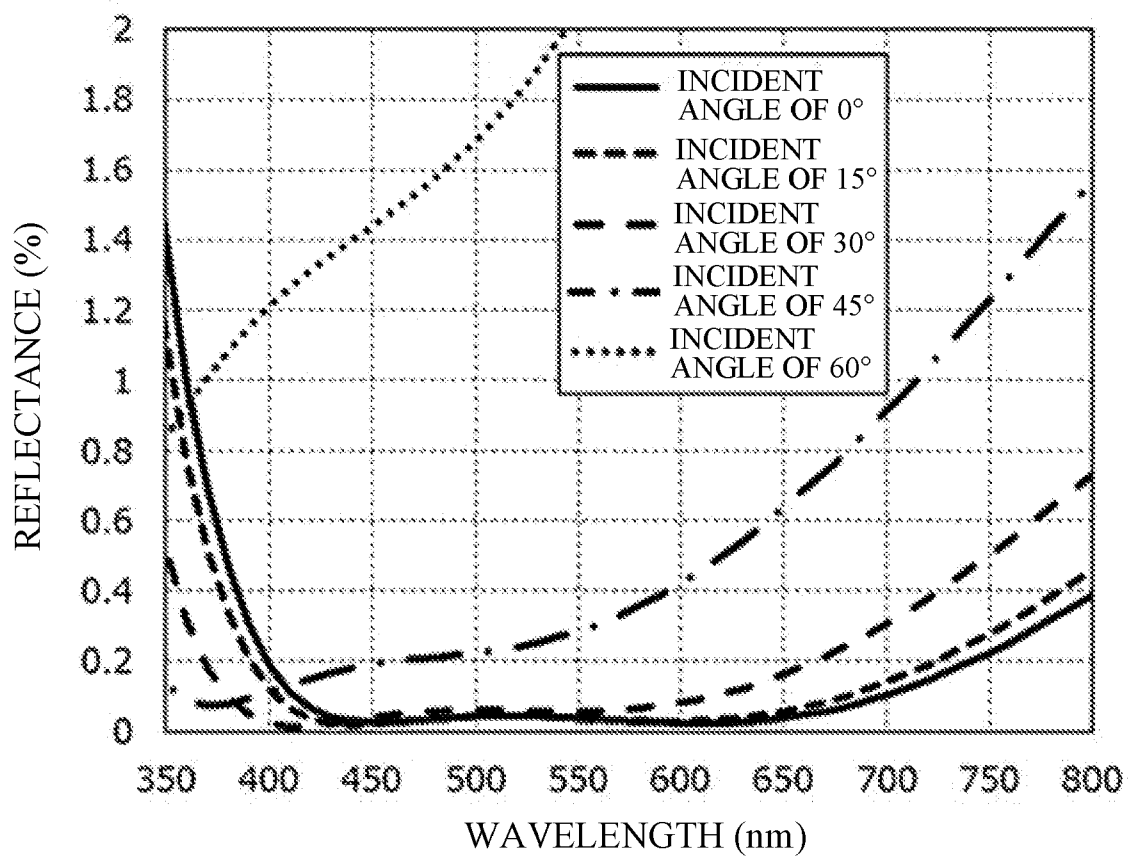


FIG. 8

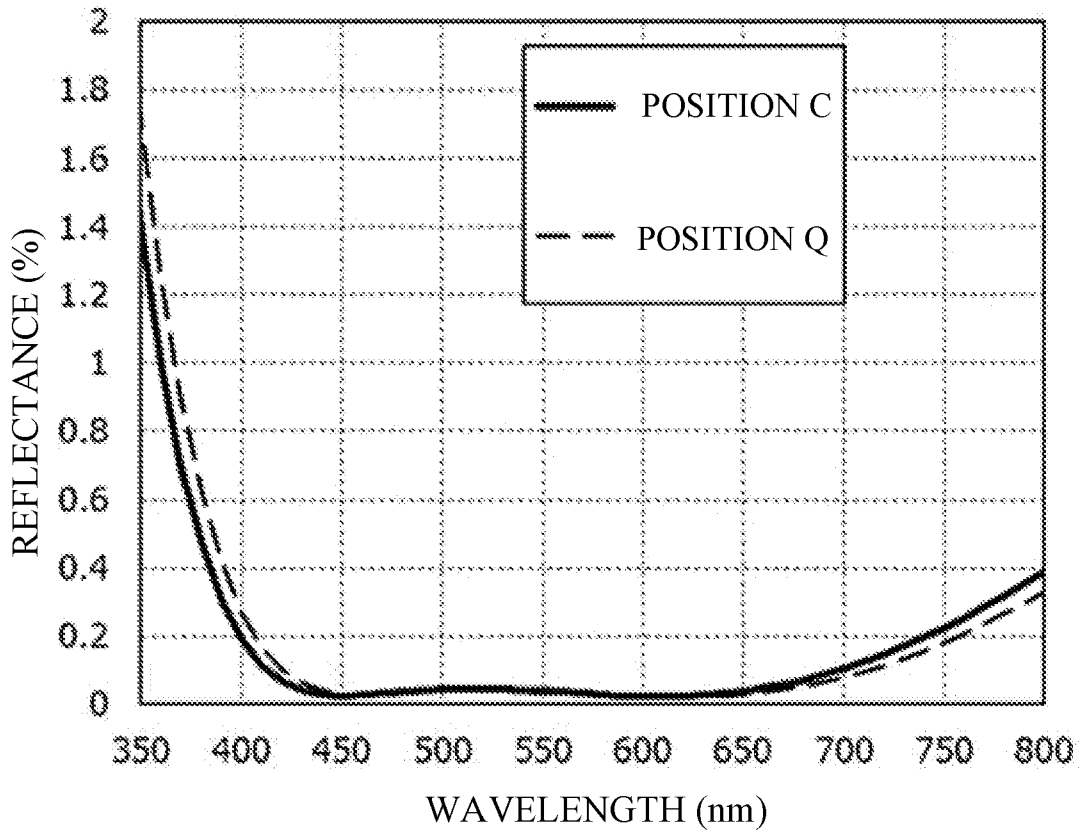


FIG. 9

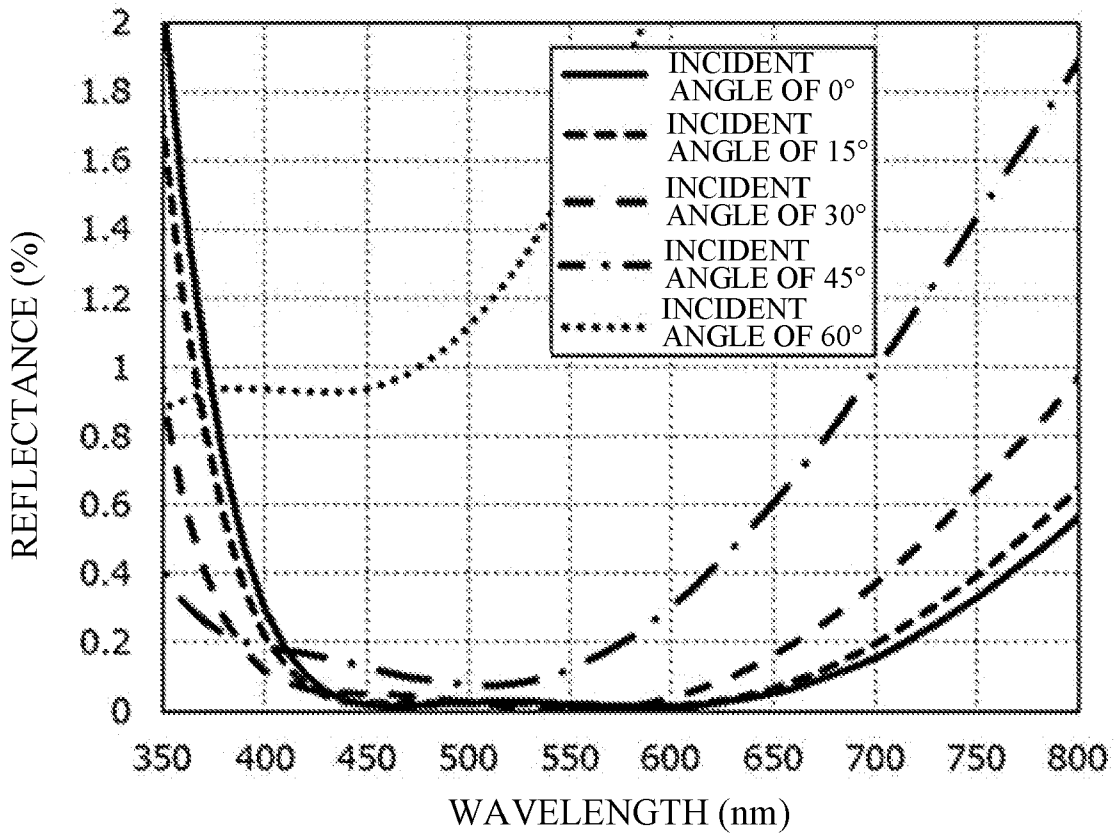


FIG. 10

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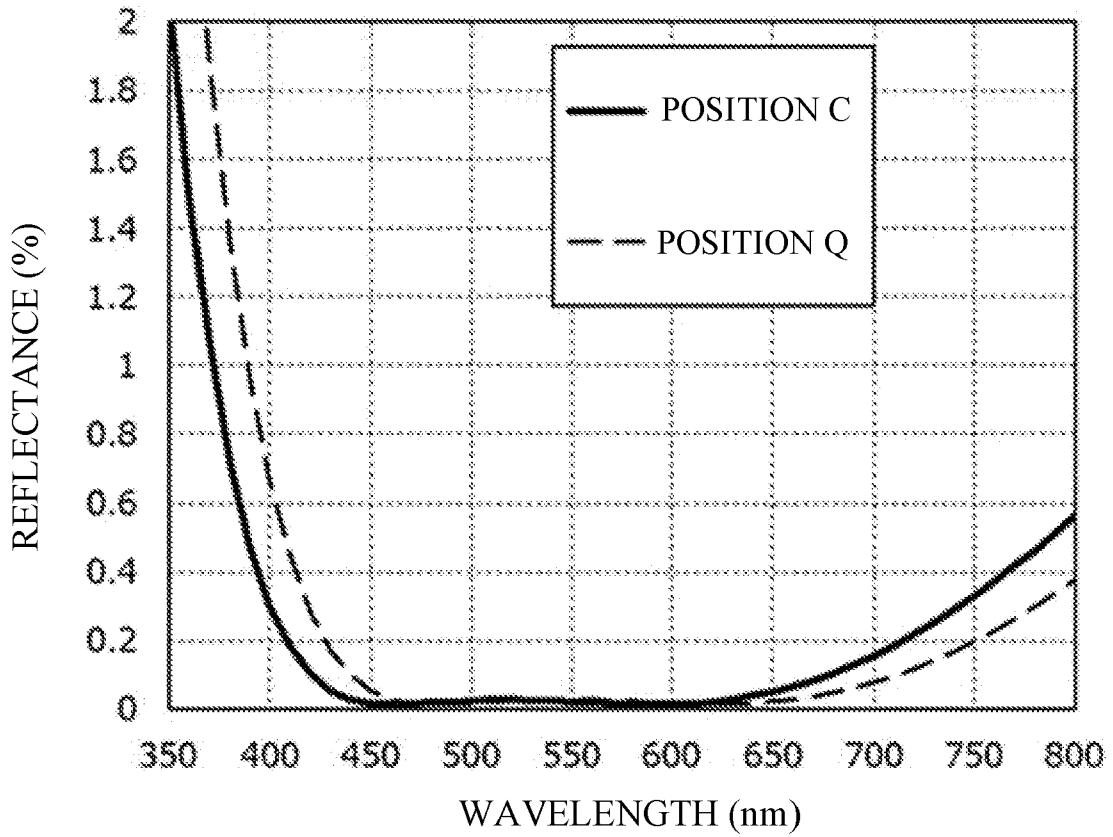


FIG. 11

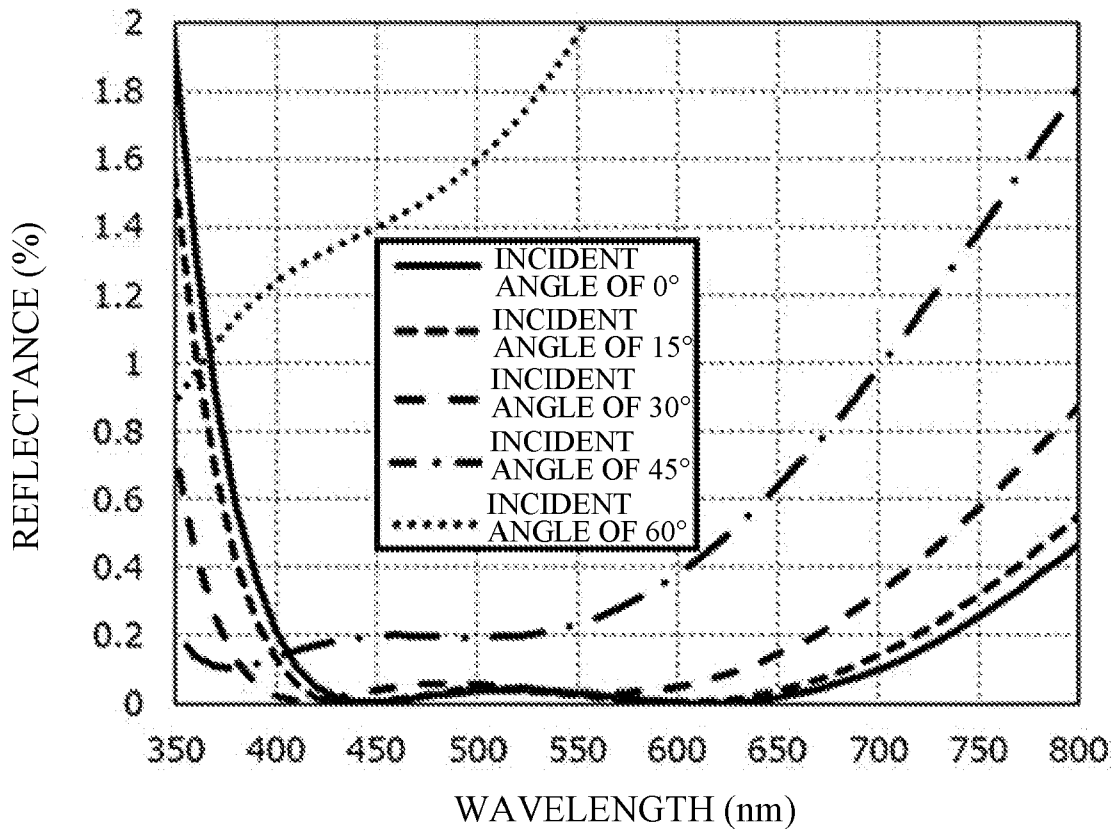


FIG. 12

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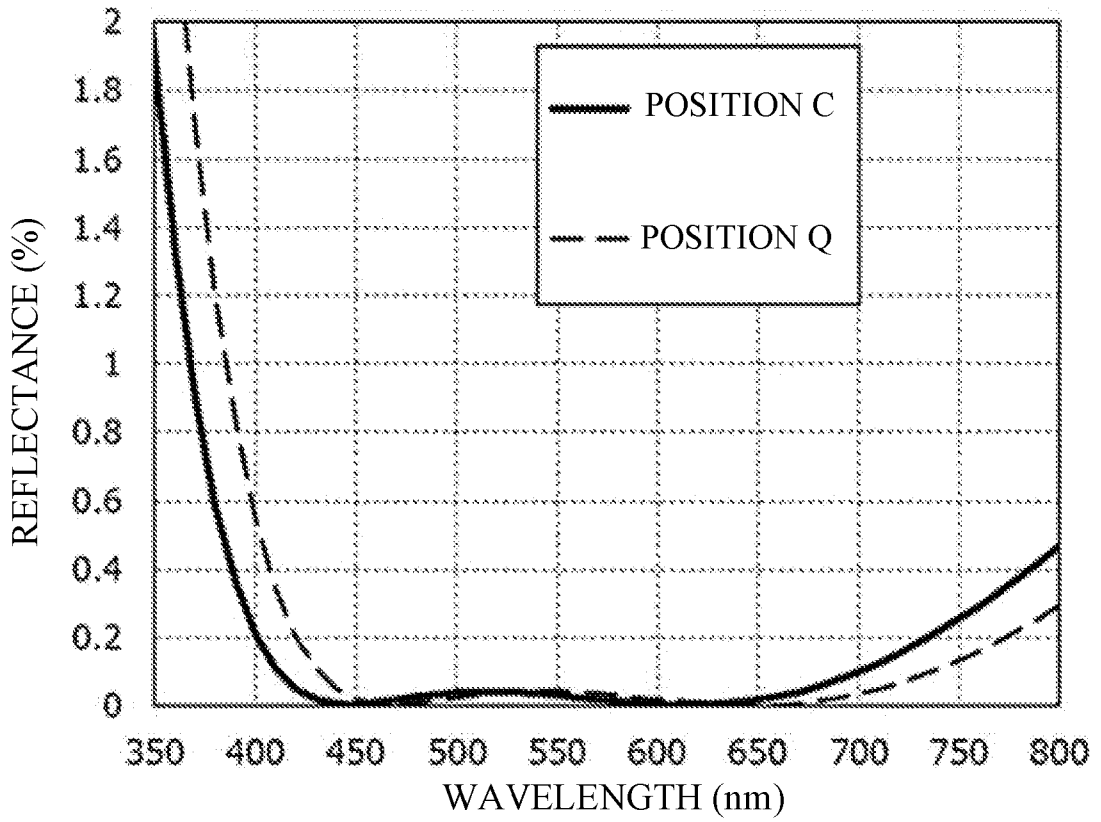


FIG. 13

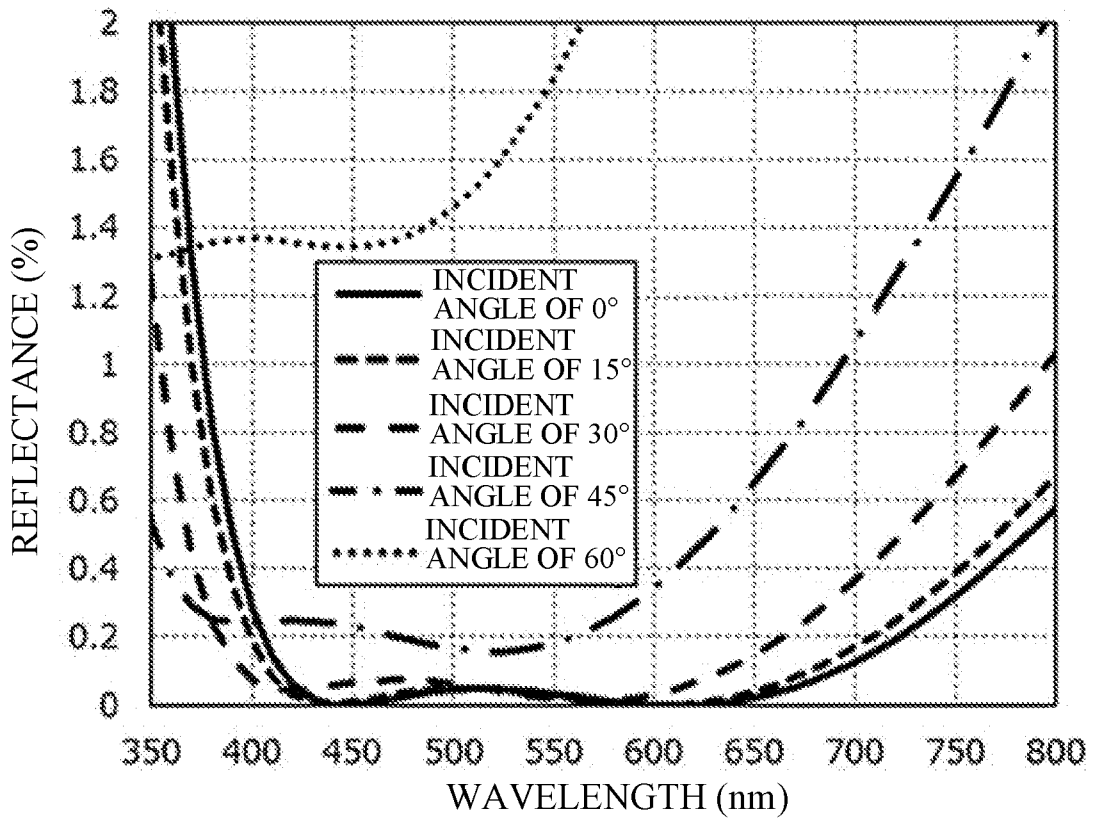


FIG. 14

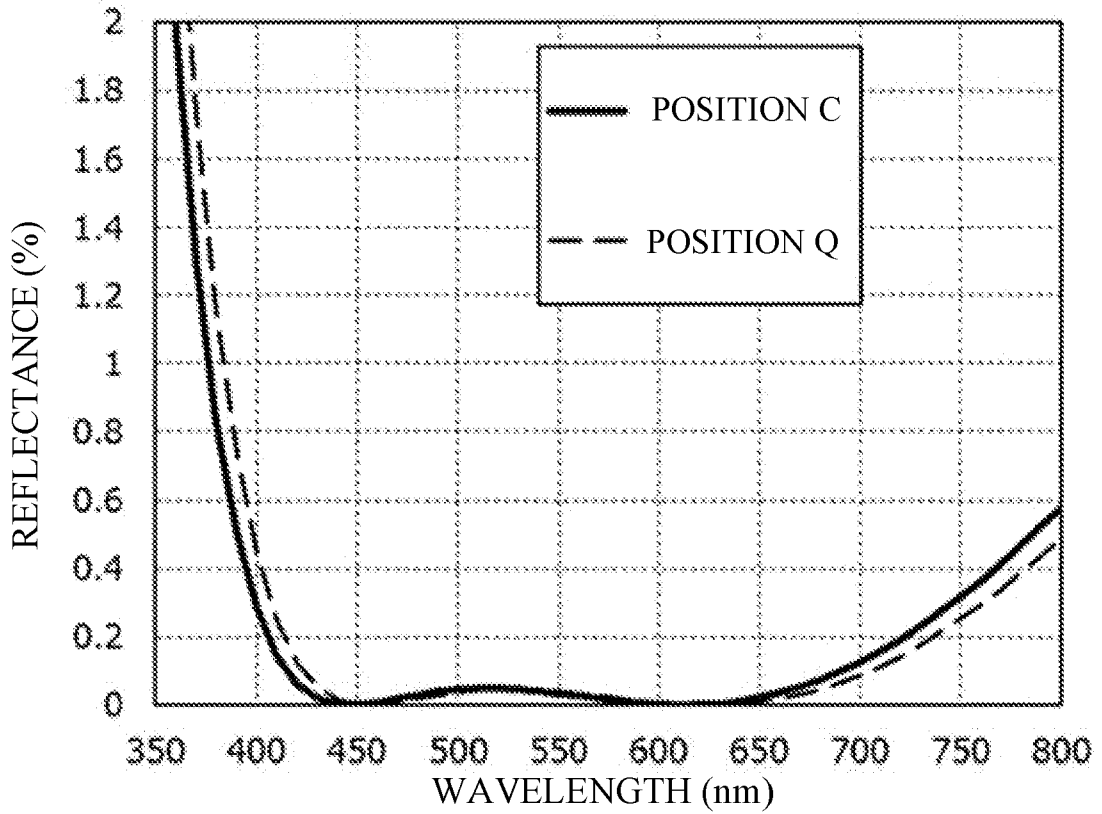


FIG. 15

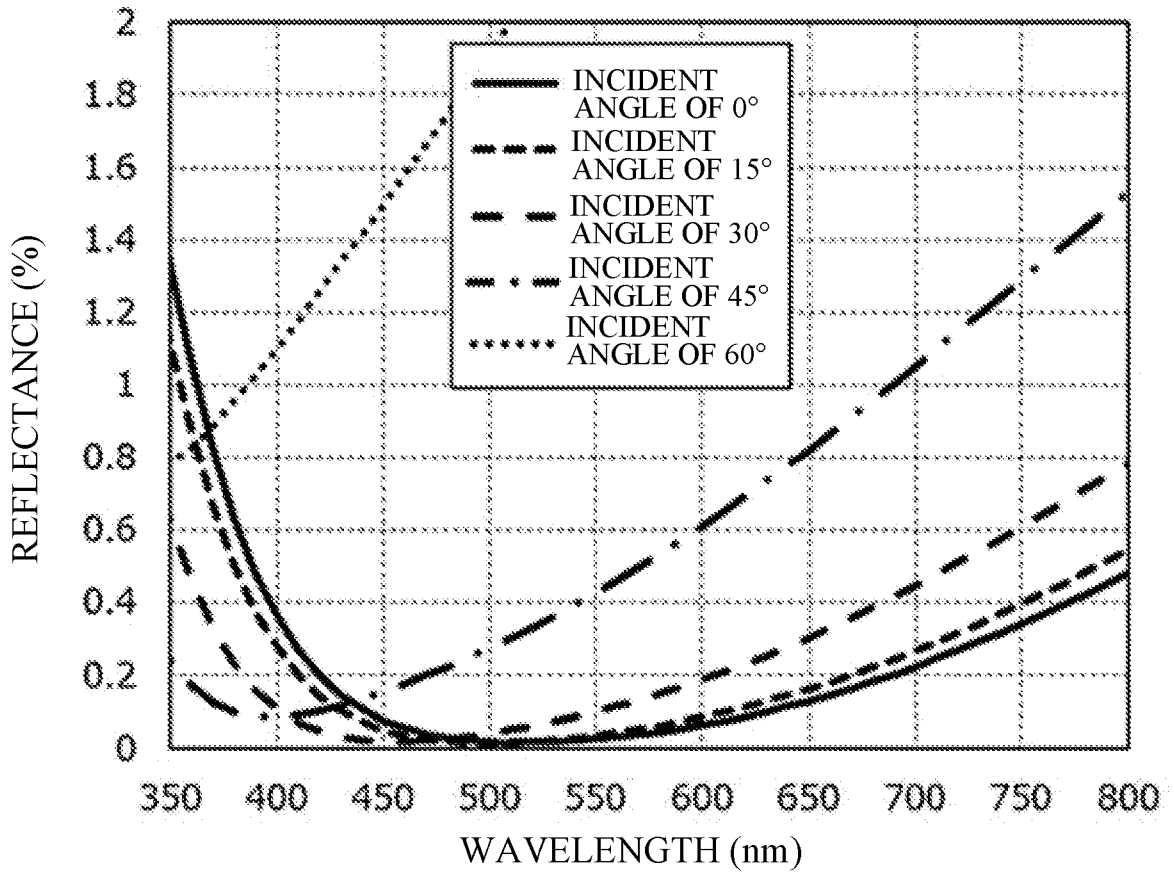


FIG. 16

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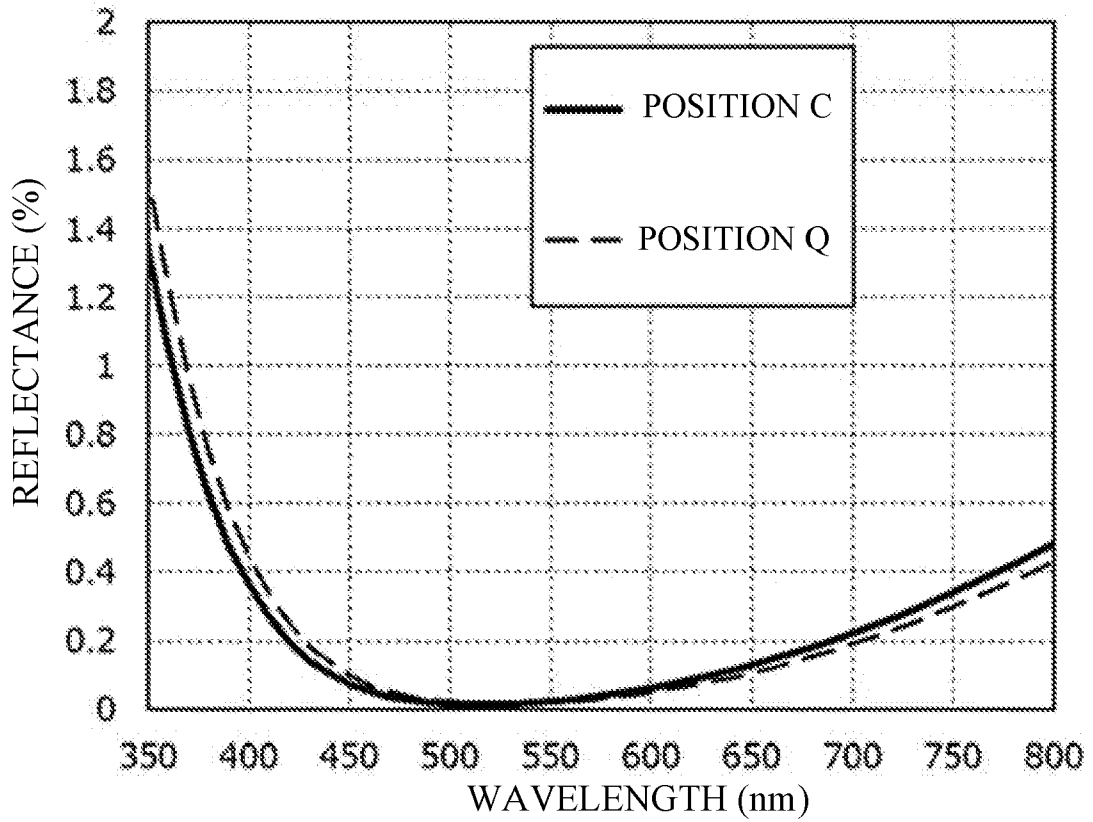


FIG. 17

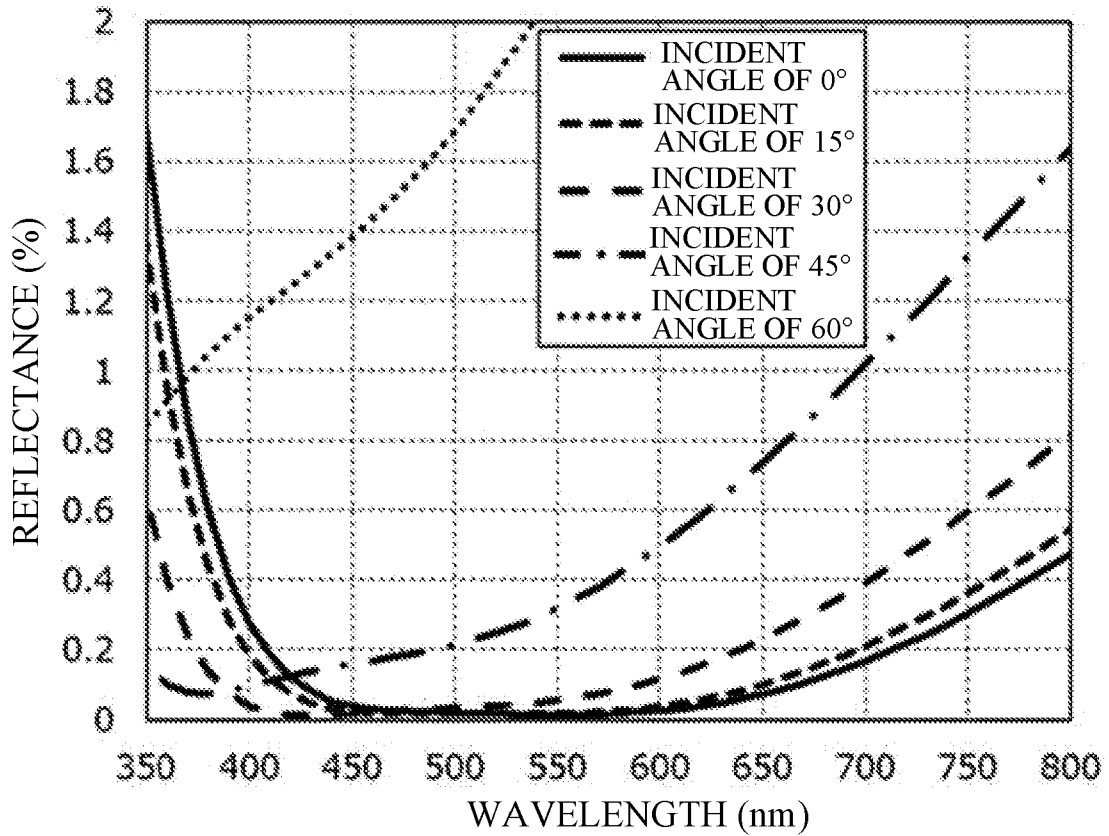


FIG. 18

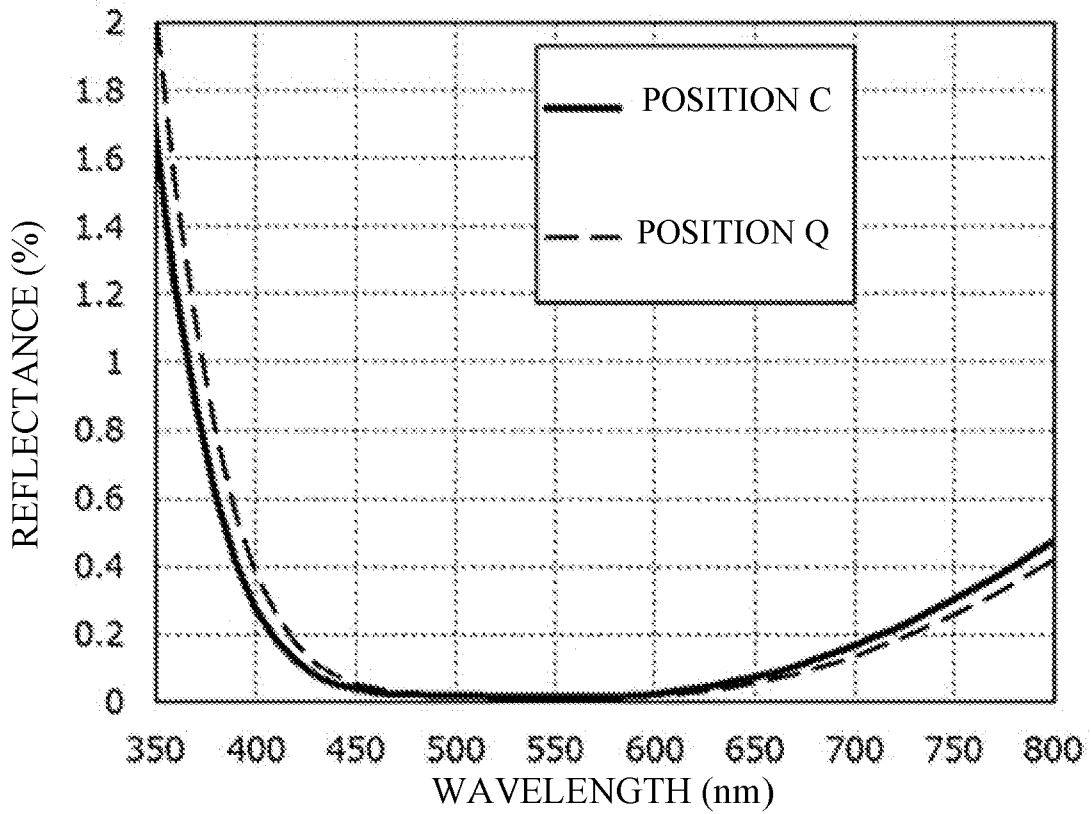


FIG. 19

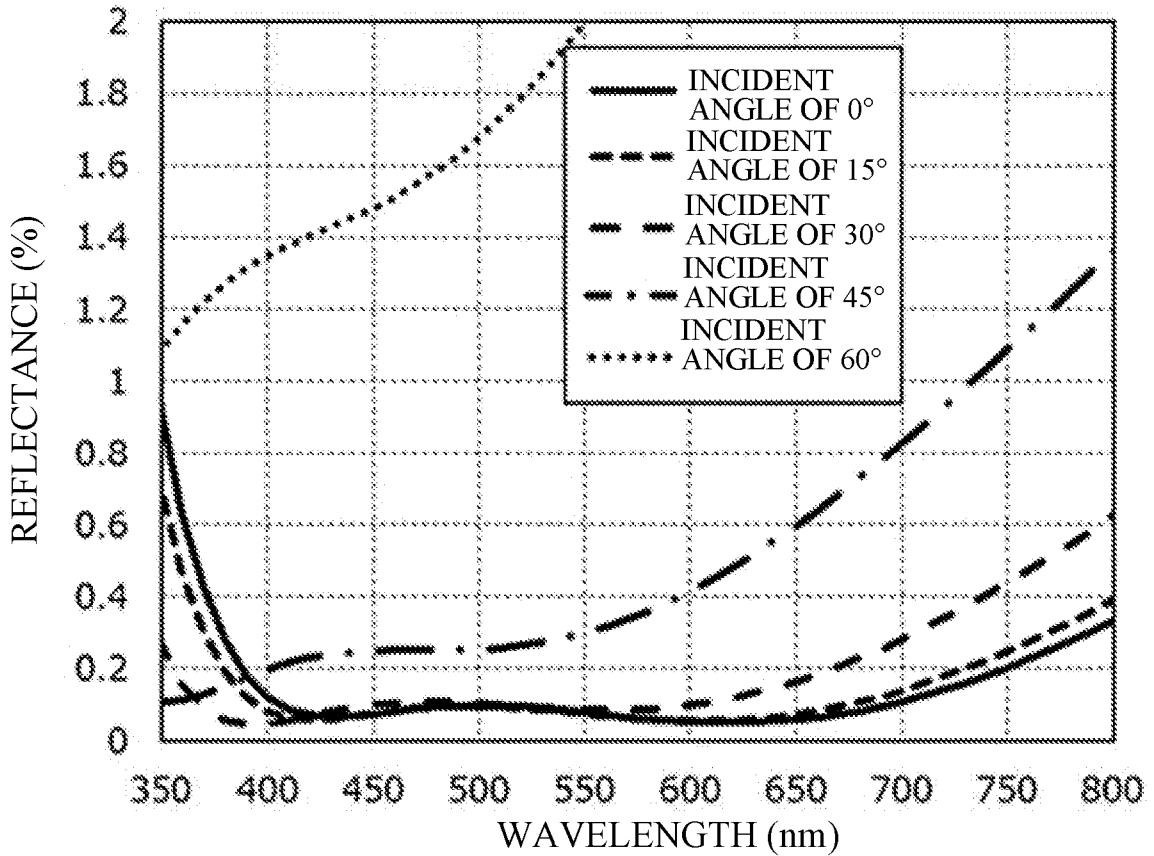


FIG. 20

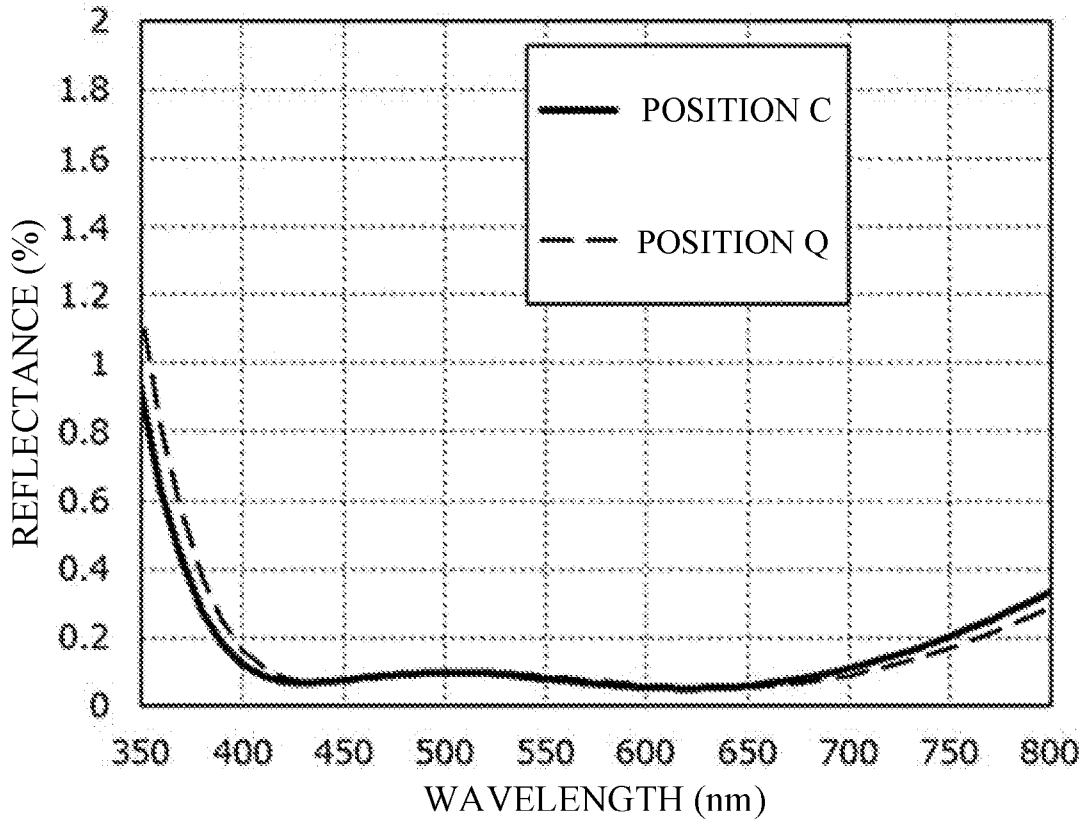


FIG. 21

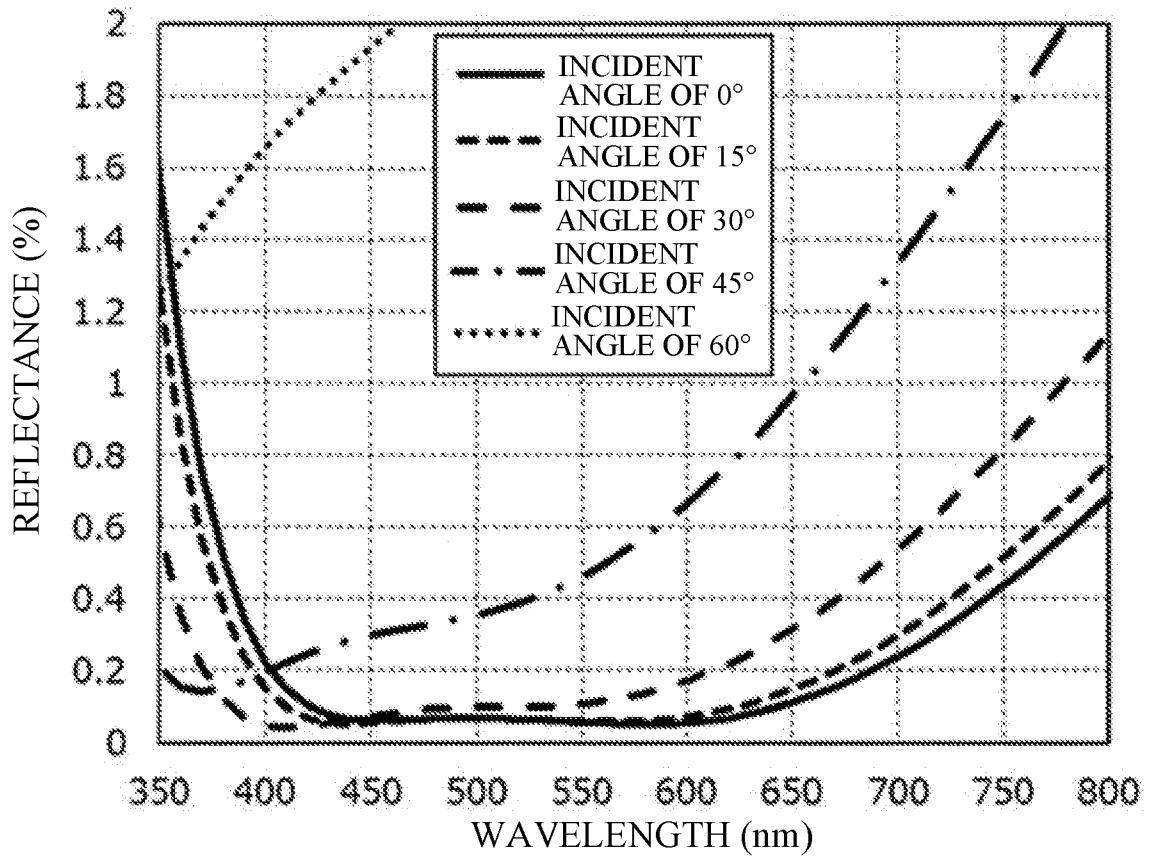


FIG. 22

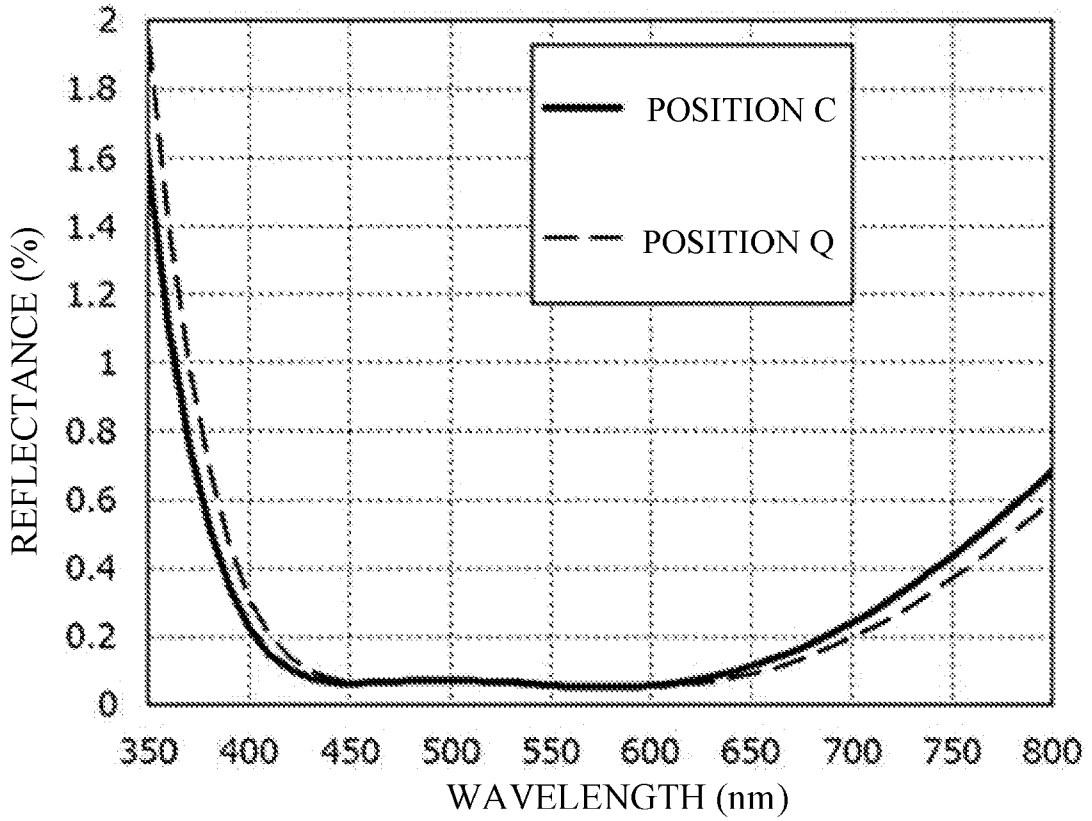


FIG. 23

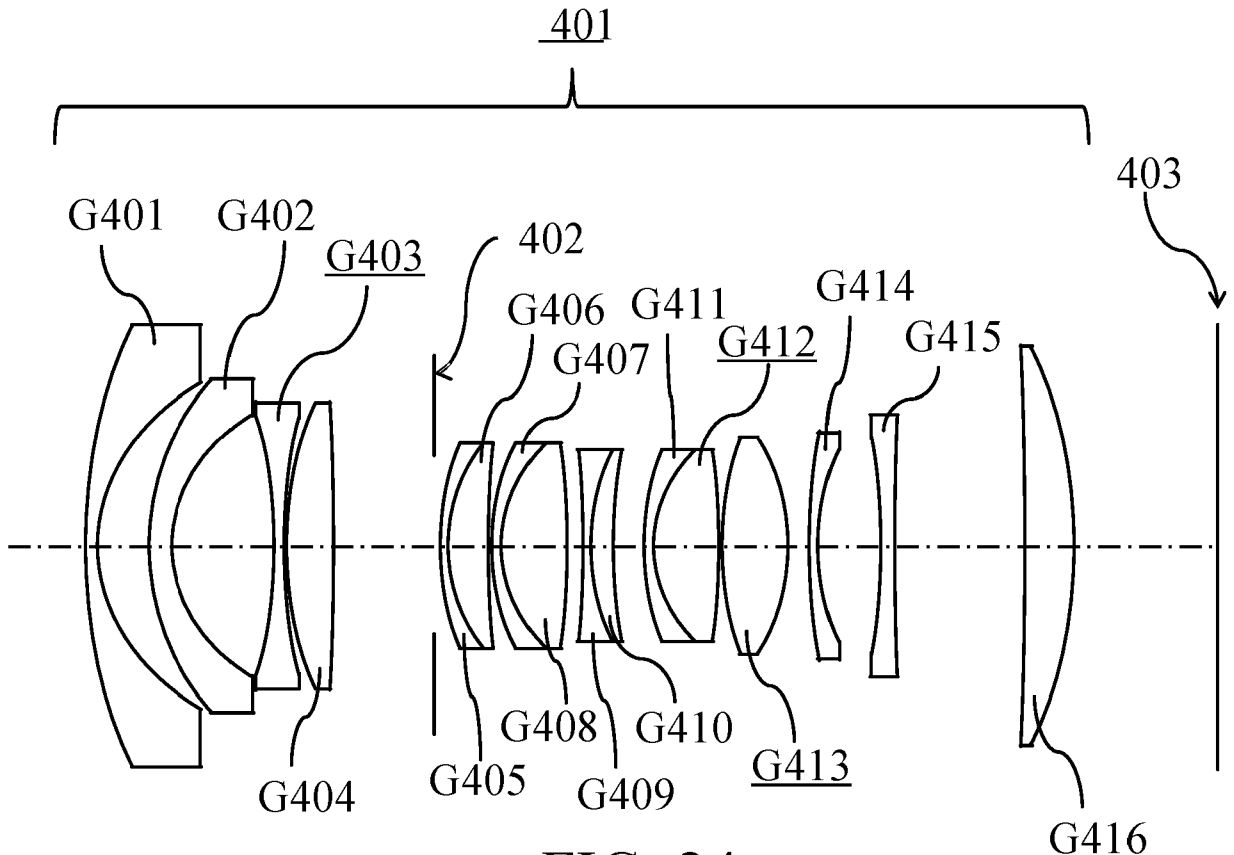


FIG. 24

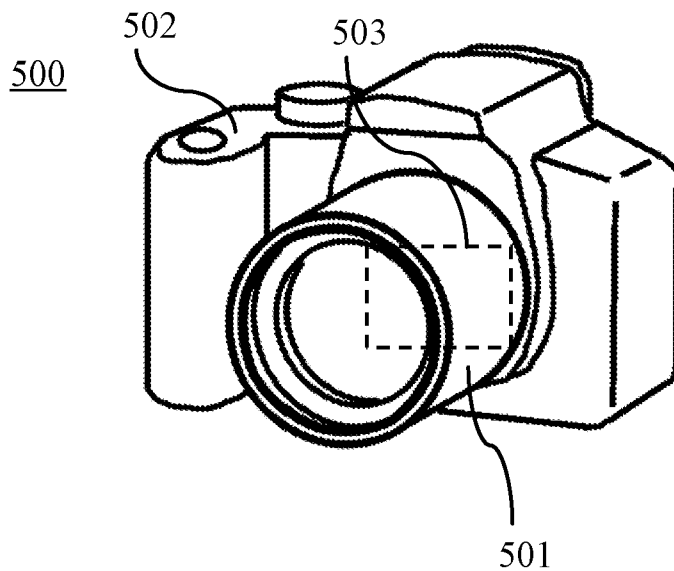


FIG. 25

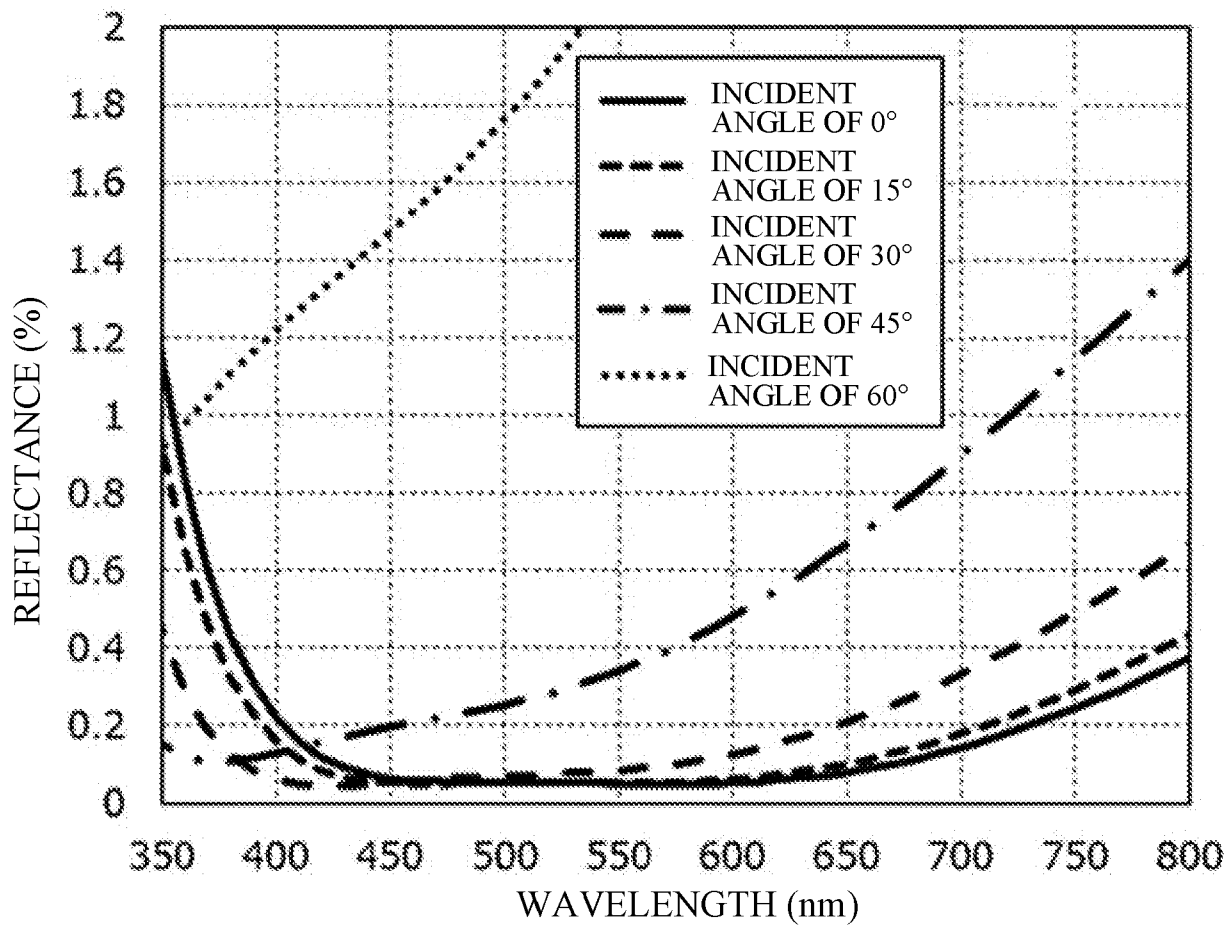


FIG. 26

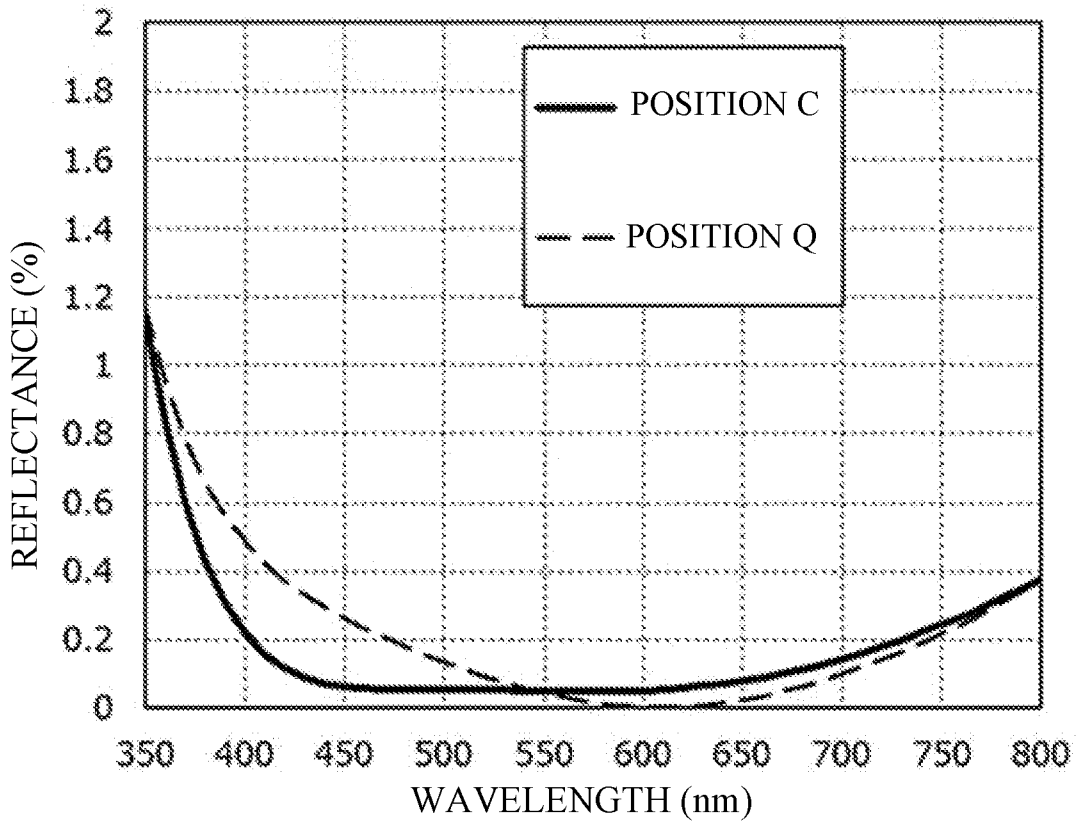


FIG. 27

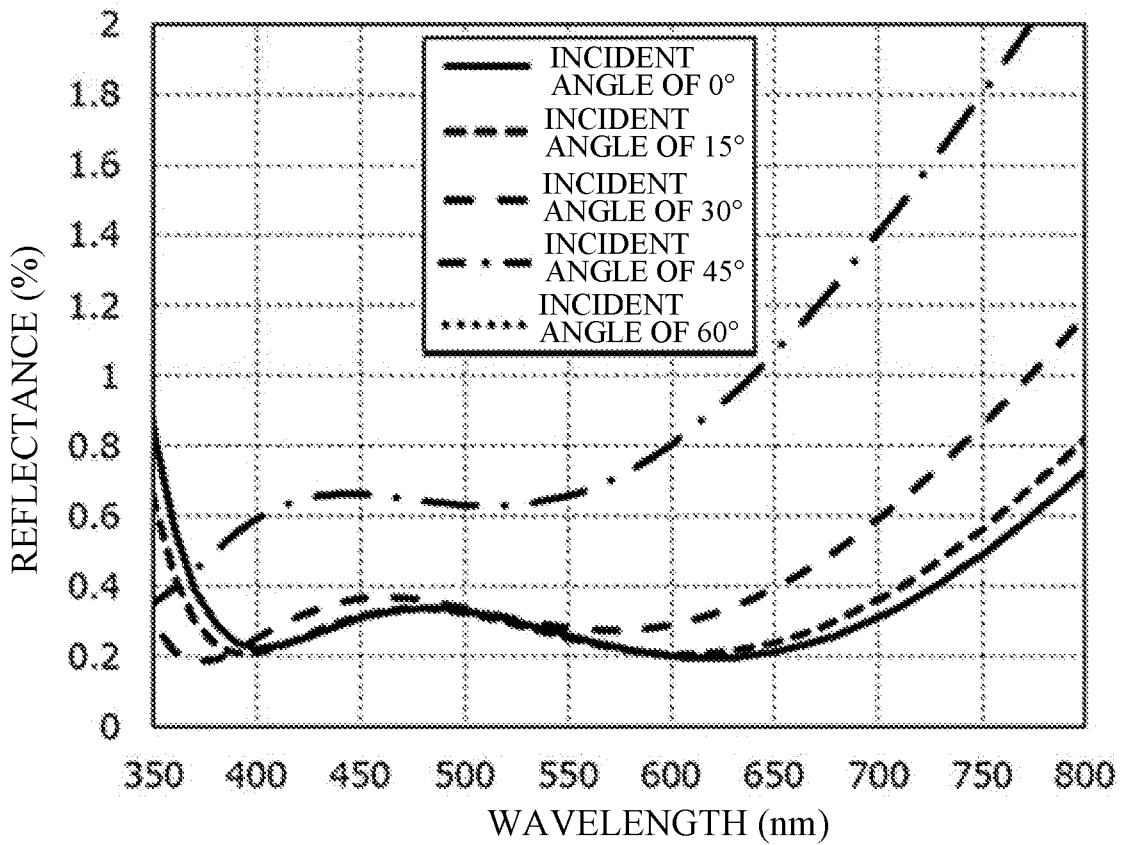


FIG. 28

OPTICAL ELEMENT, OPTICAL SYSTEM, IMAGE PICKUP APPARATUS,
AND OPTICAL APPARATUS

BACKGROUND

5 Technical Field

[0001] One of the aspects of the embodiments relates to an optical element, an optical system, an image pickup apparatus, and an optical apparatus.

Description of Related Art

10 [0002] Dielectric multilayers (antireflection films) with an antireflection function are often formed on the surface of an optical element such as a lens and a filter in an optical system to prevent a flare and a ghost caused by unnecessary reflections of light.

[0003] High-performance antireflective performance can be obtained if a material with a low refractive index is used for the outermost layer. An inorganic material such as a silica and a magnesium fluoride, and an organic material such as a silicon resin and an amorphous fluoro resin are known to be used as the material with the low refractive index. These materials can lower the refractive index by forming voids in the layers.

20 [0004] Japanese Patent Laid-Open No. 2009-162989 discloses a two-layer antireflection film formed on a substrate with a refractive index of 1.70 to 1.95, consisting of a first layer that is mainly alumina and a second layer that is silica aerogel with a refractive index of 1.27.

[0005] However, the antireflection film disclosed in Japanese Patent Laid-Open No. 25 2009-162989 is formed by vapor deposition of the first layer consisting mainly of alumina. For this reason, in a large-open angle lens (wide-angle lens), there is a problem of film unevenness in the lens surface and insufficient antireflection performance over the entire lens surface. Furthermore, since the refractive index

of the top layer is about 1.27, the antireflection performance is not sufficient when the refractive index of the substrate is 1.70 or less.

SUMMARY

5 [0006] The present invention in its first aspect provides an optical element as specified in claims 1 to 16.

[0007] The present invention in its second aspect provides an optical system as specified in claim 17.

10 [0008] The present invention in its third aspect provides an image pickup apparatus as specified in claim 18.

[0009] The present invention in its fourth aspect provides an optical apparatus as specified in claim 19.

[0010] Further features of the disclosure will become apparent from the following description of embodiments with reference to the attached drawings. Each of the
15 embodiments of the present invention described below can be implemented solely or as a combination of a plurality of the embodiments. Also, features from different embodiments can be combined where necessary or where the combination of elements or features from individual embodiments in a single embodiment is beneficial.

20

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] FIG. 1 is a schematic diagram illustrating one embodiment of an optical element.

25 [0012] FIG. 2 illustrates a schematic cross-sectional view of optical elements of Examples 1, 4, 5, 7, 9, 10, and Comparative Examples 1 and 2.

[0013] FIG. 3 illustrates a schematic cross-sectional view of optical elements of Examples 2, 3, 6, and 8.

[0014] FIG. 4 shows reflectance characteristics at incident angles of 0, 15, 30, 45,

and 60 degrees at position C in Example 1.

[0015] FIG. 5 shows reflectance characteristics at an incident angle of 0 degrees at positions C and Q in Example 1.

[0016] FIG. 6 shows reflectance characteristics at incident angles of 0, 15, 30, 45,
5 and 60 degrees at position C in Example 2.

[0017] FIG. 7 shows reflectance characteristics at an incident angle of 0 degrees at positions C and Q in Example 2.

[0018] FIG. 8 shows reflectance characteristics at incident angles of 0, 15, 30, 45,
and 60 degrees at position C in Example 3.

10 [0019] FIG. 9 shows reflectance characteristics at an incident angle of 0 degrees at positions C and Q in Example 3.

[0020] FIG. 10 shows reflectance characteristics at incident angles of 0, 15, 30, 45,
and 60 degrees at position C in Example 4.

[0021] FIG. 11 shows reflectance characteristics at an incident angle of 0 degrees
15 at positions C and Q in Example 4.

[0022] FIG. 12 shows reflectance characteristics at incident angles of 0, 15, 30, 45,
and 60 degrees at position C in Example 5.

[0023] FIG. 13 shows reflectance characteristics at an incident angle of 0 degrees
at positions C and Q in Example 5.

20 [0024] FIG. 14 shows reflectance characteristics at incident angles of 0, 15, 30, 45,
and 60 degrees at position C in Example 6.

[0025] FIG. 15 shows reflectance characteristics at an incident angle of 0 degrees
at positions C and Q in Example 6.

[0026] FIG. 16 shows reflectance characteristics at incident angles of 0, 15, 30, 45,
25 and 60 degrees at position C in Example 7.

[0027] FIG. 17 shows reflectance characteristics at an incident angle of 0 degrees
at positions C and Q in Example 7.

[0028] FIG. 18 shows reflectance characteristics at incident angles of 0, 15, 30, 45,

and 60 degrees at position C in Example 8.

[0029] FIG. 19 shows reflectance characteristics at an incident angle of 0 degrees at positions C and Q in Example 8.

[0030] FIG. 20 shows reflectance characteristics at incident angles of 0, 15, 30, 45,
5 and 60 degrees at position C in Example 9.

[0031] FIG. 21 shows reflectance characteristics at an incident angle of 0 degrees at positions C and Q in Example 9.

[0032] FIG. 22 shows reflectance characteristics at incident angles of 0, 15, 30, 45,
and 60 degrees at position C in Example 10.

10 [0033] FIG. 23 shows reflectance characteristics at an incident angle of 0 degrees at positions C and Q in Example 10.

[0034] FIG. 24 illustrates a cross-sectional view of an optical system in Example 11.

[0035] FIG. 25 illustrates an external perspective view of an image pickup
15 apparatus in Example 12.

[0036] FIG. 26 shows reflectance characteristics at incident angles of 0, 15, 30, 45,
and 60 degrees at position C in Comparative Example 1.

[0037] FIG. 27 shows reflectance characteristics at an incident angle of 0 degrees at positions C and Q in Comparative Example 1.

20 [0038] FIG. 28 shows reflectance characteristics at incident angles of 0, 15, 30, 45,
and 60 degrees at position C in Comparative Example 2.

DESCRIPTION OF THE EMBODIMENTS

[0039] Referring now to the accompanying drawings, a detailed description will be
25 given of embodiments according to the disclosure. Corresponding elements in
respective figures will be designated by the same reference numerals, and a
duplicate description thereof will be omitted.

[0040] FIG. 1 is a schematic diagram illustrating one embodiment of an optical

element 300 of the present disclosure. The optical element 300 has a transparent substrate (base or base material) 200 and an antireflection film 100 that is a two-layer film. The antireflection film 100 consists of a first thin film layer (first layer) 01 and a second thin film layer (second layer) 02, formed in order from the transparent substrate 200 to the air side. In other words, the first thin film layer 01 is formed on the transparent substrate 200 and the second thin film layer 02 is formed on the first thin film layer 01.

[0041] The first thin film layer 01 and the second thin film layer 02 are each made of a material containing an organic compound. An "organic compound" is a compound that contains carbon, excluding compounds with simple structures such as carbon monoxide and carbon dioxide.

[0042] Let the reference wavelength λ be 550 nm and n_s be the refractive index of the transparent substrate 200 at a wavelength of 550 nm. Let n_1 be the refractive index of the first thin film layer 01 at a wavelength of 550 nm and n_2 be the refractive index of the second thin film layer 02 at a wavelength of 550 nm. Let d_1 (nm) be the physical film thickness of the first thin film layer 01 and d_2 (nm) be the physical film thickness of the second thin film layer 02. The optical element 300 satisfies the following inequalities (1) through (5).

$$1.30 \leq n_1 \leq 1.70 \quad (1)$$

$$1.10 \leq n_2 \leq 1.26 \quad (2)$$

$$-0.2 \leq (n_s - 1) - 2(n_1 - n_2) \leq 0.2 \quad (3)$$

$$100 \leq n_1 d_1 \leq 155 \quad (4)$$

$$100 \leq n_2 d_2 \leq 155 \quad (5)$$

[0043] Inequality (1) defines the refractive index n_1 of the first thin film layer 01 at the wavelength of 550 nm. In a case where the value becomes lower than the lower limit of inequality (1), the refractive index n_1 of the first thin film layer 01 becomes too low relative to the refractive index of the second thin film layer 02 formed on it, and sufficient anti-reflection performance cannot be obtained. On

the other hand, in case where the value becomes higher than the upper limit of inequality (1), it becomes difficult to fabricate the first thin-film layer 01, which is made of a material containing an organic compound, with a commonly used material.

5 **[0044]** Inequality (2) defines the refractive index n_2 of the second thin film layer 02 at the wavelength of 550 nm. In a case where the value becomes lower than the lower limit of inequality (2), it becomes difficult to fabricate the second thin film layer 02, which is made of a material containing an organic compound, with a commonly used material. On the other hand, in a case where the value becomes
10 higher than the upper limit of inequality (2), a high-performance antireflection film 100 cannot be obtained in the two-layer configuration of the first thin film layer 01 and the second thin film layer 02.

[0045] Inequality (3) defines the reflectance of the optical element 300. In a case where the value becomes lower than the lower limit of inequality (3) or higher than
15 the upper limit of inequality (3), the reflectance becomes too high and sufficient antireflection performance cannot be obtained.

[0046] Inequality (4) defines the optical film thickness of the first thin film layer 01. In a case where the value becomes lower than the lower limit of inequality (4) or higher than the upper limit of inequality (4), the optical film thickness of the first
20 thin film layer 01 does not become about $\lambda/4$, and sufficient anti-reflection performance cannot be obtained.

[0047] Inequality (5) defines the optical film thickness of the second thin film layer 02. In a case where the value becomes lower than the lower limit of inequality (5) or higher than the upper limit of inequality (5), the optical film thickness of the
25 second thin film layer 02 does not become about $\lambda/4$, and sufficient anti-reflection performance cannot be obtained.

[0048] The numerical ranges of inequalities (1) to (5) are more preferably the ranges of inequalities (1a) to (5a) below.

$$1.40 \leq n_1 \leq 1.68 \quad (1a)$$

$$1.11 \leq n_2 \leq 1.25 \quad (2a)$$

$$-0.15 \leq (n_s - 1) - 2(n_1 - n_2) \leq 0.15 \quad (3a)$$

$$105 \leq n_1 d_1 \leq 150 \quad (4a)$$

5

$$105 \leq n_2 d_2 \leq 150 \quad (5a)$$

[0049] Further, the numerical ranges of inequalities (1) to (5) are more preferably the ranges of inequalities (1b) to (5b) below.

$$1.42 \leq n_1 \leq 1.65 \quad (1b)$$

$$1.12 \leq n_2 \leq 1.24 \quad (2b)$$

10

$$-0.12 \leq (n_s - 1) - 2(n_1 - n_2) \leq 0.12 \quad (3b)$$

$$110 \leq n_1 d_1 \leq 145 \quad (4b)$$

$$110 \leq n_2 d_2 \leq 145 \quad (5b)$$

[0050] It is further preferred that the upper limit of inequality (2b) be 1.22.

[0051] In the optical element 300, the refractive index n_s of the transparent substrate 200 preferably satisfies inequality (6) below.

15

$$1.50 \leq n_s \leq 2.10 \quad (6)$$

[0052] Inequality (6) defines the refractive index n_s of the transparent substrate 200 at the wavelength of 550 nm. In a case where the value becomes lower than the lower limit of inequality (6), the refractive index n_s of the transparent substrate 200 becomes too low relative to the refractive indices of the first and second thin film layers 01 and 02 formed on it, which is undesirable because sufficient antireflection performance cannot be obtained. On the other hand, in a case where the value becomes higher than the upper limit of inequality (6), it becomes difficult to fabricate the transparent substrate 200 with a commonly used material, which is

20

25

undesirable.

[0053] The numerical range of inequality (6) is more preferably the range of inequality (6a) below.

$$1.52 \leq n_s \leq 2.00 \quad (6a)$$

[0054] Further, the numerical range of inequality (6) is more preferably the range of inequality (6b) below.

$$1.53 \leq n_s \leq 1.95 \quad (6b)$$

[0055] FIG. 2 illustrates a schematic cross-sectional view of optical elements 301 of Examples 1, 4, 5, 7, 9, 10, and Comparative Examples 1 and 2. FIG. 3 illustrates a schematic cross-sectional view of optical elements 302 of Examples 2, 3, 6, and 8.

[0056] In the optical element 301, the surface of the transparent substrate 201 on which the antireflection film 101 is formed is concave in shape. In the optical element 302, the surface of the transparent substrate 202 on which the antireflection film 102 is formed is convex in shape. Hereinafter, the concave shape shown in FIG. 2 will be used for explanation, but the same applies to the convex shape shown in FIG. 3.

[0057] In the optical element 301, an optical surface forming the antireflection film 101 has a rotationally symmetrical axis, i.e., the optical surface forming the antireflection film 101 has a rotationally symmetrical shape. In FIG. 2, position C is the rotation center of the lens surface of the transparent substrate 201 provided with the antireflection film 101. In other words, position C is the intersection position where the rotationally symmetrical axis of the lens surface of the transparent substrate 201 (hereinafter referred to as optical axis L) and the lens surface of the transparent substrate 201 intersect. On the other hand, position Q is the most distant position from position C within the optically effective area on the lens surface of the transparent substrate 201. Let φ be the angle between the optical axis L and the normal at arbitrary point on the lens surface of the transparent substrate 201 (hereinafter referred to as the half-open angle). The angle between the optical axis L and the normal at position Q (half-open angle φ at position Q) is the maximum value of the half-open angle φ in the optically effective area. The half-open angle φ at position Q is the half-open angle at the maximum effective

diameter of the lens surface of the transparent substrate 201. When position C of the intersection of the lens surface of the transparent substrate 201 and the optical axis L is the optical axis center, the optical axis center has the half-open angle of 0 degrees, which is a reference of the lens surface of the transparent substrate 201.

5 The antireflection film 101 consists of the first thin film layer 11 and the second thin film layer 12, formed in order from the transparent substrate 201.

[0058] Let $d1c$ (nm) be the physical film thickness of the first thin film layer 11 at position C and $d2c$ (nm) be the physical film thickness of the second thin film layer 12 at position C. Let $d1q$ (nm) be the physical film thickness of the first thin film
10 layer 11 at position Q and $d2q$ (nm) be the physical film thickness of the second thin film layer 12 at position Q. The optical element 301 preferably satisfies inequalities (7) and (8) below.

$$1.0 < d1q/d1c \leq 1.3 \quad (7)$$

$$1.0 < d2q/d2c \leq 1.3 \quad (8)$$

15 **[0059]** Inequality (7) defines the ratio of the physical film thickness $d1q$ of the first thin film layer 11 at position Q to the physical film thickness $d1c$ of the first thin film layer 11 at position C, and defines the film thickness distribution between the center and the periphery of the first thin film layer 11. As described below, the first thin film layer 11 is prepared by spin-coating to prevent unevenness in film
20 thickness, but it is physically impossible that the value becomes lower than the lower limit of inequality (7). In a case where the value becomes higher than the upper limit of inequality (7), the difference in film thickness distribution between the center and the periphery of the first thin film layer 11 becomes larger, resulting in a larger variation in reflectance characteristics between the center and the
25 periphery, which is undesirable.

[0060] Inequality (8) defines the ratio of the physical film thickness $d2q$ of the second thin film layer 12 at position Q to the physical film thickness $d2c$ of the second thin film layer 12 at position C, and defines the film thickness distribution

between the center and the periphery of the second thin film layer 12. As described below, the second thin film layer 12 is prepared by spin-coating to prevent unevenness in film thickness, but it is physically impossible that the value becomes lower than the lower limit of inequality (8). In a case where the value becomes higher than the upper limit of inequality (8), the difference in film thickness distribution between the center and the periphery of the second thin film layer 12 becomes larger, resulting in a larger variation in reflectance characteristics between the center and the periphery, which is undesirable.

[0061] The numerical ranges of inequalities (7) to (8) are more preferably the ranges of inequalities (7a) to (8a) below.

$$1.01 \leq d1q/d1c \leq 1.25 \quad (7a)$$

$$1.01 \leq d2q/d2c \leq 1.25 \quad (8a)$$

[0062] Further, the numerical ranges of inequalities (7) to (8) are more preferably the ranges of inequalities (7b) to (8b) below.

$$1.015 \leq d1q/d1c \leq 1.200 \quad (7b)$$

$$1.015 \leq d2q/d2c \leq 1.200 \quad (8b)$$

[0063] In each of the first thin film layer 11 and the second thin film layer 12 that constitute the antireflection film 101, preferably, the film thickness at position C, which is the optical axis center, is the smallest and the film thickness increases as a distance from the optical axis center increases.

[0064] Furthermore, the half-open angle ϕ (degrees) at position Q preferably satisfies inequality (9) below.

$$25 \leq \phi < 90 \quad (9)$$

[0065] Inequality (9) defines the half-open angle ϕ at position Q. In a case where the value become lower than the lower limit of inequality (9), the half-open angle ϕ at position Q is too small, and when the optical element 301 is used as a lens, the power to refract off-axis light beam among light beams passing through the lens becomes weak. This results in a decrease in peripheral light amount, which is

undesirable. It is physically impossible that the value becomes higher than the upper limit of inequality (9).

[0066] The numerical range of inequality (9) is more preferably the range of inequality (9a) below.

5
$$27 \leq \phi < 70 \quad (9a)$$

[0067] Further, the numerical range of inequality (9) is more preferably the range of inequality (9b) below.

$$29 \leq \phi < 45 \quad (9b)$$

[0068] The second thin film layer 12 preferably contains voids. By containing
10 voids or air with refractive index of 1.0 in the second thin film layer 12, the refractive index of the second thin film layer 12 can be reduced to the range of inequality (2). In a case where the refractive index of the second thin film layer 12 is less than 1.10, the film strength becomes weak because of the large proportion of voids in the layer. In a case where the refractive index of the second thin film
15 layer 12 is larger than 1.26, the sufficient antireflection performance cannot be obtained.

[0069] The surface of the second thin film layer 12 may be provided with an antifouling layer containing a fluororesin, if necessary. Examples of the antifouling layer include a fluoropolymer layer, a fluorosilane monolayer, a
20 titanium oxide particle layer, and the like.

[0070] The second thin film layer 12 preferably contains at least one of solid particles, chain particles, or hollow particles, and it is even more desirable to contain hollow particles with internal vacancies. The vacancies may be either monoporous or porous, and can be selected as appropriate. The material of solid
25 particles, chain particles, or hollow particles preferably is of low refractive index, and examples thereof include organic resins such as SiO₂ (silica), MgF₂, fluorine, silicon, etc. SiO₂ is more desirable in that it is easier to manufacture particles. The average particle diameter of hollow particles preferably is 15 nm or more and

100 nm or less, more preferably 15 nm or more and 80 nm or less. In a case where the average particle diameter of hollow particles is less than 15 nm, it is difficult to stably produce core particles. In a case where the average particle diameter is larger than 100 nm, the size of the voids between particles becomes larger, which
5 tends to generate large voids and scattering associated with the size of the particles, which is undesirable.

[0071] The first thin film layer 11 is preferably made of a material containing polyimide resin, which is a "polymer compound containing imide (-CO-NR-CO-) bonds". The first thin film layer 11 is preferably made of a material containing an
10 acrylic resin, which is "a polymer of acrylate or methacrylate." The first thin film layer 11 is preferably made of a material containing an epoxy resin, which is "a cured resin obtained by cross-linking an epoxy group having oxacyclopropane (oxirane), which is a three-membered ring ether, in its structural formula". Alternatively, the first thin film layer 11 is preferably made of a material containing
15 solid particles, particularly solid silica particles, bound by a binder such as a siloxane bond.

[0072] As a method for forming the first thin film layer 11 and the second thin film layer 12, a wet film forming method in which a coating solution containing a film material is applied and dried or baked is preferable. The wet film forming method
20 can coat large areas at low cost. In particular, the spin coating method is preferable because the in-plane film thickness distribution can be suppressed by performing the coating while rotating the rotating shaft of a coating surface. In a dry film forming method such as vapor deposition method and sputtering method, a film is formed in such a positional relationship that an evaporation source faces the central
25 portion of a lens. In a case of a large-open angle lens, since the incident angle of vapor-deposited material to the lens surface becomes large at the peripheral portion, the film thickness is smaller than at the central portion. This causes film unevenness in the lens surface, resulting in uneven antireflection performance. In

order to prevent uneven film deposition, it is necessary to set up masks and control the position and rotational motion of the substrate, which requires extensive equipment and is undesirable.

[0073] The organic solvent that can be used in the coating solution is not particularly limited to the extent that it does not impair coating properties or performance, and any known solvent can be used. Examples includes the following: monohydric alcohols such as methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methylpropanol, 1-pentanol, 2-pentanol, cyclopentanol, 2-methylbutanol, 3-methylbutanol, 1 -hexanol, 2-hexanol, 3-hexanol, 4-methyl-2-pentanol, 2-methyl-1-pentanol, 2-ethylbutanol, 2,4-dimethyl-3-pentanol, 3-ethylbutanol, 1-heptanol, 2-heptanol, 1-octanol, and 2-octanol; dihydric or higher alcohols such as ethylene glycol and triethylene glycol; ether alcohols such as methoxyethanol, ethoxyethanol, propoxyethanol, isopropoxyethanol, butoxyethanol, 1-methoxy-2-propanol, 1-ethoxy-2-propanol, and 1-propoxy-2-propanol; ethers such as dimethoxyethane, diglyme, tetrahydrofuran, dioxane, diisopropyl ether, dibutyl ether, and cyclopentyl methyl ether; esters such as ethyl formate, ethyl acetate, n-butyl acetate, methyl lactate, ethyl lactate, ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, ethylene glycol monobutyl ether acetate, and propylene glycol monomethyl ether acetate; various aliphatic or alicyclic hydrocarbons such as n-hexane, n-octane, cyclohexane, cyclopentane, and cyclooctane; various aromatic hydrocarbons such as toluene, xylene, and ethylbenzene; various ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclopentanone, and cyclohexanone; various chlorinated hydrocarbons such as chloroform, methylene chloride, carbon tetrachloride, and tetrachloroethane; and aprotic polar solvents such as N-methylpyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide, and ethylene carbonate. Two or more of these solvents can be mixed and used.

[0074] In a case of using solid particles, chain particles, or hollow particles for the

second thin film layer 12 and solid particles for the first thin film layer 11, the particles preferably are bound together by a binder to improve strength. It is desirable to use siloxane bonds as a binder. This is especially suitable when silica particles with many hydroxyl groups on the surfaces are used.

5 [0075] Since the first film thin layer 11 and the second thin film layer 12 are made of materials that can be formed by the wet film forming method, the materials themselves or the binders contain organic compounds. Furthermore, since the antireflection film 101 is not baked at high temperature during a drying process after a coating process, it is possible to use plastics or other materials that are prone
10 to thermal deformation for the transparent substrate 201.

[0076] Specific examples 1 through 10 are given below. However, these are only examples, and this disclosure is not limited to the scope of Examples 1-10.

In the optical element 300, in the wavelength range of 450 nm to 650 nm, the reflectance of the antireflection film at position C is 0.5% or less at an incident
15 angle of 0 degrees and 1.0% or less at an incident angle of 30 degrees.

EXAMPLE 1

[0077] FIG. 2 is a schematic cross-sectional view of the optical element 301 according to Example 1. The optical element 301 in this example is an optical
20 element with the antireflection film 101 formed on the transparent substrate 201. The transparent substrate 201 is made of S-TIL26 (manufactured by OHARA) with a refractive index of 1.57 (wavelength 550 nm). The lens surface of the transparent substrate 201, on which the antireflection film 101 is formed, is concave in shape. The half-open angle ϕ at position Q on the maximum effective diameter
25 of the lens surface of the transparent substrate 201 is 40 degrees. As layer materials, the first thin film layer 11 consists mainly of solid silica, and the second thin film layer 12 consists mainly of hollow silica. Table 1 shows the details of the film composition of the optical element 301 in this example. The refractive

index and film thickness of each material satisfy inequalities (1) through (9).

[0078] The method of forming the antireflection film 101 in this example is as follows.

5 (Hollow particle coating solution 1)

[0079] While 1-ethoxy-2-propanol (hereinafter referred to as 1E2P) was added to 580 g of an isopropyl alcohol dispersion liquid of hollow silica particles (manufactured by JGC Catalysts and Chemicals, Suluria 4110, average particle diameter: approx. 60 nm, shell thickness: approx. 12 nm, solid concentration: 20.5 mass%), the isopropyl alcohol dispersion liquid was distilled off by heating. The isopropyl alcohol dispersion liquid was distilled off to a solid concentration of 19.5 mass% to prepare 610 g of 1E2P solvent-substituted solution of hollow silica particles (hereinafter referred to as solvent-substituted solution 1). To the resulting solvent-substituted solution 1, an organic acid containing fluorine
10 (manufactured by Tokyo Chemical Industry, trifluoroacetic acid, fluorine number 3) was added so that a component ratio of the hollow silica particles to the organic acid containing fluorine was 100/1 to obtain a hollow particle dispersion liquid 1.

[0080] In a separate vessel, 3.6 g of phosphinic acid diluted to 0.1% concentration with pure water, 11.4 g of 1-propoxy-2-propanol, and 4.5 g of methyl polysilicate
20 (manufactured by Colcoat, methyl silicate 53A) were slowly added, and stirred at room temperature for 120 minutes. A silica sol with a solid concentration of 12.0 mass% (hereafter referred to as silica sol 1) was prepared.

[0081] After diluting the hollow particle dispersion liquid 1 with ethyl lactate to a solid concentration of 4.5 mass%, the silica sol 1 was added so that a component
25 ratio of the hollow silica particles to the silica sol was 100/12. The hollow particle coating solution 1 containing hollow silica particles was obtained by mixing and stirring at room temperature for 2 hours.

(Intermediate layer coating solution 1)

[0082] The intermediate layer coating solution 1 was prepared by adding 300 g of 1-methoxy-2-propanol and 5 g of silica sol 1 to 25 g of silica particle dispersion liquid PL-1 (manufactured by Fusco Chemical).

5 **[0083]** The intermediate layer coating solution 1 and the hollow particle coating solution 1 are used to form the antireflection film 101.

0.2 ml of the intermediate layer coating solution 1 was dropped onto the lens surface of the transparent substrate 201 and spin coated at 4000 rpm for 20 seconds. Next, 0.2 ml of the hollow particle coating solution 1 was continuously dropped onto the
10 lens surface of the transparent substrate 201 and spin coated at 4000 rpm for 20 seconds. Then, drying was performed in a clean room at a room temperature of 23°C for at least 24 hours.

[0084] FIG. 4 shows reflectance characteristics of the antireflection film 101 at incident angles of 0, 15, 30, 45, and 60 degrees at position C. The reflectance is
15 less than or equal to 0.2% at an incident angle of 0 degrees and within wavelengths from 420 nm to 680 nm, indicating very good reflectance properties. FIG. 5 shows reflectance characteristics at an incident angle of 0 degrees at positions C and Q. Table 1 shows that although the film thickness of each thin film layer at position Q is 4% thicker than at position C, the reflectance characteristics are almost the same
20 at positions C and Q, confirming that the reflectance characteristics are good.

TABLE 1

			REFRA- CTIVE INDEX	PHYSICAL FILM THICKNESS (nm)	
				POSITION C	POSITION Q
ANTI- REFLECTION FILM 101	SECOND THIN FILM LAYER 12	HOLLOW SILICA	1.19	106.9	111.2
	FIRST THIN FILM LAYER 11	SOLID SILICA	1.45	85.4	88.9
TRANSPARENT SUBSTRATE 201		S-TIL26	1.57	—	—

EXAMPLE 2

[0085] FIG. 3 is a schematic cross-sectional view of the optical element 302 according to Example 2. The optical element 302 in this example is an optical element with the antireflection film 102 formed on the transparent substrate 202. The transparent substrate 202 is made of S-LAL12 (manufactured by OHARA) with a refractive index of 1.68 (wavelength 550 nm). The lens surface of the transparent substrate 202, on which the antireflection film 102 is formed, is convex in shape. The half-open angle ϕ at position Q on the maximum effective diameter of the lens surface of the transparent substrate 202 is 30 degrees. As layer materials, the first thin film layer 21 consists mainly of solid silica, and the second thin film layer 22 consists mainly of hollow silica. Table 2 shows the details of the film composition of the optical element 302 in this example. The refractive index and film thickness of each material satisfy inequalities (1) through (9).

[0086] The method of forming the antireflection film 102 in this example is as follows.

(Hollow particle coating solution 2)

[0087] The preparation method for the hollow particle dispersion liquid 1 and the

silica sol 1 is the same as for the hollow particle coating solution 1. After diluting the hollow particle dispersion liquid 1 with ethyl lactate to a solid concentration of 4.5 mass%, silica sol 1 was added so that a component ratio of the hollow silica particles to the silica sol was 100/9. The hollow particle coating solution 2
5 containing hollow silica particles was obtained by mixing and stirring at room temperature for 2 hours.

[0088] The intermediate layer coating solution 1 and the hollow particle coating solution 2 are used to form the antireflection film 102.

[0089] 0.2 ml of the intermediate layer coating solution 1 was dropped onto the lens
10 surface of the transparent substrate 202 and spin coated at 4000 rpm for 20 seconds. Next, 0.2 ml of the hollow particle coating solution 2 was continuously dropped onto the lens surface of the transparent substrate 202 and spin coated at 4000 rpm for 20 seconds. Then, drying was performed in a clean room at a room temperature of 23°C for at least 24 hours.

[0090] FIG. 6 shows reflectance characteristics of the antireflection film 102 at
15 incident angles of 0, 15, 30, 45, and 60 degrees at position C. The reflectance is less than or equal to 0.2% at an incident angle of 0 degrees and within wavelengths from 420 nm to 680 nm, indicating very good reflectance properties. FIG. 7 shows reflectance characteristics at an incident angle of 0 degrees at positions C and Q.
20 Table 2 shows that although the film thickness of each thin film layer at position Q is 2% thicker than at position C, the reflectance characteristics are almost the same at positions C and Q, confirming that the reflectance characteristics are good.

TABLE 2

			REFRA- CTIVE INDEX	PHYSICAL FILM THICKNESS (nm)	
				POSITION C	POSITION Q
ANTI- REFLECTION FILM 102	SECOND THIN FILM LAYER 22	HOLLOW SILICA	1.14	111.3	113.5
	FIRST THIN FILM LAYER 21	SOLID SILICA	1.45	87.6	89.3
TRANSPARENT SUBSTRATE 202		S-LAL12	1.68	---	---

EXAMPLE 3

[0091] FIG. 3 is a schematic cross-sectional view of the optical element 302 according to Example 3. The optical element 302 in this example is an optical element with the antireflection film 102 formed on the transparent substrate 202. The transparent substrate 202 is made of S-LAL12 (manufactured by OHARA) with a refractive index of 1.68 (wavelength 550 nm). The lens surface of the transparent substrate 202, on which the antireflection film 102 is formed, is convex in shape. The half-open angle ϕ at position Q on the maximum effective diameter of the lens surface of the transparent substrate 202 is 30 degrees. As layer materials, the first thin film layer 21 consists mainly of acrylic resin, and the second thin film layer 22 consists mainly of hollow silica. Table 3 shows the details of the film composition of the optical element 302 in this example. The refractive index and film thickness of each material satisfy inequalities (1) through (9).

[0092] The method of forming the antireflection film 102 in this example is as follows.

(Intermediate layer coating solution 2)

[0093] 6.1 g of N-cyclohexylmaleimide (hereinafter referred to as CHMI), 4.0 g of 2,2,2-trifluoroethyl methacrylate (product name M-3F: manufactured by Kyoeisha

Chemical), 0.45 g of 3-(methacryloyloxy) propyltrimethoxysilane (product name LS-3380: manufactured by Shin-Etsu Chemical), and 0.08 g of 2,2'-azobis (isobutyronitrile) (hereafter referred to as AIBN) were stirred and dissolved in 24.8 g of toluene. This solution was repeatedly degassed and replaced with nitrogen
5 while chilled in ice water, and then stirred at 60-70°C for 7 hours with nitrogen flow. The polymerization solution was slowly fed into strongly stirred methanol, and the precipitated polymer was filtered off and washed several times in methanol with stirring. The filtrated and collected polymers were vacuum dried at 80-90°C. 8.3 g (81% yield) of a white powdery maleimide copolymer with a maleimide
10 copolymerization ratio of 0.57 was obtained. The solution of maleimide copolymer 1 was prepared by dissolving 2.2 g of the powder of the maleimide copolymer 1 in 97.8 g of cyclopentanone/cyclohexanone mixed solvent to make the intermediate layer coating solution 2.

[0094] The intermediate layer coating solution 2 and the hollow particle coating
15 solution 1 are used to form the antireflection film 102.

[0095] 0.2 ml of the intermediate layer coating solution 2 was dropped onto the lens surface of the transparent substrate 202 and spin coated at 4000 rpm for 20 seconds. Next, 0.2 ml of the hollow particle coating solution 1 was continuously dropped onto the lens surface of the transparent substrate 202 and spin coated at 4000 rpm
20 for 20 seconds. Then, drying was performed in a clean room at a room temperature of 23°C for at least 24 hours.

[0096] FIG. 8 shows reflectance characteristics of the antireflection film 102 at incident angles of 0, 15, 30, 45, and 60 degrees at position C. The reflectance is less than or equal to 0.2% at an incident angle of 0 degrees and within wavelengths
25 from 420 nm to 680 nm, indicating very good reflectance properties. FIG. 9 shows reflectance characteristics at an incident angle of 0 degrees at positions C and Q. Table 3 shows that although the film thickness of each thin film layer at position Q is 2% thicker than at position C, the reflectance characteristics are almost the same

at positions C and Q, confirming that the reflectance characteristics are good.

TABLE 3

			REFRA- CTIVE INDEX	PHYSICAL FILM THICKNESS (nm)	
				POSITION C	POSITION Q
ANTI- REFLECTION FILM 102	SECOND THIN FILM LAYER 22	HOLLOW SILICA	1.19	106.9	109.0
	FIRST THIN FILM LAYER 21	ACRYLIC RESIN	1.50	83.6	85.2
TRANSPARENT SUBSTRATE 202		S-LAL12	1.68	—	—

5

EXAMPLE 4

[0097] FIG. 2 is a schematic cross-sectional view of the optical element 301 according to Example 4. The optical element 301 in this example is an optical element with the antireflection film 101 formed on the transparent substrate 201.

10 The transparent substrate 201 is made of S-LAH53 (manufactured by OHARA) with a refractive index of 1.81 (wavelength 550 nm). The lens surface of the transparent substrate 201, on which the antireflection film 101 is formed, is concave in shape. The half-open angle ϕ at position Q on the maximum effective diameter of the lens surface of the transparent substrate 201 is 45 degrees. As layer
15 materials, the first thin film layer 11 consists mainly of acrylic resin, and the second thin film layer 12 consists mainly of hollow silica. Table 4 shows the details of the film composition of the optical element 301 in this example. The refractive index and film thickness of each material satisfy inequalities (1) through (9).

[0098] The method of forming the antireflection film 101 in this example is as
20 follows.

[0099] The intermediate layer coating solution 2 and the hollow particle coating

solution 2 are used to form the antireflection film 101.

[0100] 0.2 ml of the intermediate layer coating solution 2 was dropped onto the lens surface of the transparent substrate 201 and spin coated at 4000 rpm for 20 seconds. Next, 0.2 ml of the hollow particle coating solution 2 was continuously dropped

5 onto the lens surface of the transparent substrate 201 and spin coated at 4000 rpm for 20 seconds. Then, drying was performed in a clean room at a room temperature of 23°C for at least 24 hours.

[0101] FIG. 10 shows reflectance characteristics of the antireflection film 101 at incident angles of 0, 15, 30, 45, and 60 degrees at position C. The reflectance is

10 less than or equal to 0.2% at an incident angle of 0 degrees and within wavelengths from 420 nm to 680 nm, indicating very good reflectance properties. FIG. 11 shows reflectance characteristics at an incident angle of 0 degrees at positions C and Q. Table 4 shows that although the film thickness of each thin film layer at position Q is 5% thicker than at position C, the reflectance characteristics are almost

15 the same at positions C and Q, confirming that the reflectance characteristics are good.

TABLE 4

			REFRA- CTIVE INDEX	PHYSICAL FILM THICKNESS (nm)	
				POSITION C	POSITION Q
ANTI- REFLECTION FILM 101	SECOND THIN FILM LAYER 12	HOLLOW SILICA	1.14	112.2	117.8
	FIRST THIN FILM LAYER 11	ACRYLIC RESIN	1.50	85.0	89.2
TRANSPARENT SUBSTRATE 201		S-LAH53	1.81	—	—

20

EXAMPLE 5

[0102] FIG. 2 is a schematic cross-sectional view of the optical element 301 according to Example 5. The optical element 301 in this example is an optical element with the antireflection film 101 formed on the transparent substrate 201. The transparent substrate 201 is made of S-LAH53 (manufactured by OHARA) with a refractive index of 1.81 (wavelength 550 nm). The lens surface of the transparent substrate 201, on which the antireflection film 101 is formed, is concave in shape. The half-open angle ϕ at position Q on the maximum effective diameter of the lens surface of the transparent substrate 201 is 45 degrees. As layer materials, the first thin film layer 11 consists mainly of epoxy resin, and the second thin film layer 12 consists mainly of hollow silica. Table 5 shows the details of the film composition of the optical element 301 in this example. The refractive index and film thickness of each material satisfy inequalities (1) through (9).

[0103] The method of forming the antireflection film 101 in this example is as follows.

(Intermediate layer coating solution 3)

[0104] The intermediate layer coating solution 3 was prepared by adding 500 g of 1-methoxy-2-propanol to 25 g of epoxy resin jER828 (manufactured by Mitsubishi Chemical).

[0105] The intermediate layer coating solution 3 and the hollow particle coating solution 1 are used to form the antireflection film 101.

[0106] 0.2 ml of the intermediate layer coating solution 3 was dropped onto the lens surface of the transparent substrate 201 and spin coated at 4000 rpm for 20 seconds. Next, 0.2 ml of the hollow particle coating solution 1 was continuously dropped onto the lens surface of the transparent substrate 201 and spin coated at 4000 rpm for 20 seconds. Then, drying was performed in a clean room at a room temperature of 23°C for at least 24 hours.

[0107] FIG. 12 shows reflectance characteristics of the antireflection film 101 at

incident angles of 0, 15, 30, 45, and 60 degrees at position C. The reflectance is less than or equal to 0.2% at an incident angle of 0 degrees and within wavelengths from 420 nm to 680 nm, indicating very good reflectance properties. FIG. 13 shows reflectance characteristics at an incident angle of 0 degrees at positions C and Q. Table 5 shows that although the film thickness of each thin film layer at position Q is 5% thicker than at position C, the reflectance characteristics are almost the same at positions C and Q, confirming that the reflectance characteristics are good.

10 TABLE 5

			REFRA- CTIVE INDEX	PHYSICAL FILM THICKNESS (nm)	
				POSITION C	POSITION Q
ANTI- REFLECTION FILM 101	SECOND THIN FILM LAYER 12	HOLLOW SILICA	1.19	107.7	113.1
	FIRST THIN FILM LAYER 11	EPOXY RESIN	1.56	81.4	85.5
TRANSPARENT SUBSTRATE 201		S-LAH53	1.81	—	—

EXAMPLE 6

[0108] FIG. 3 is a schematic cross-sectional view of the optical element 302 according to Example 6. The optical element 302 in this example is an optical element with the antireflection film 102 formed on the transparent substrate 202. The transparent substrate 202 is made of S-NPH2 (manufactured by OHARA) with a refractive index of 1.92 (wavelength 550 nm). The lens surface of the transparent substrate 202, on which the antireflection film 102 is formed, is convex in shape. The half-open angle ϕ at position Q on the maximum effective diameter of the lens surface of the transparent substrate 202 is 30 degrees. As layer

materials, the first thin film layer 21 consists mainly of polyimide resin, and the second thin film layer 22 consists mainly of hollow silica. Table 6 shows the details of the film composition of the optical element 302 in this example. The refractive index and film thickness of each material satisfy inequalities (1) through
5 (9).

[0109] The method of forming the antireflection film 102 in this example is as follows.

(Intermediate layer coating solution 4)

10 **[0110]** To 200 g of 4,4'-methylenebis (aminocyclohexane) (hereinafter referred to as DADCM, manufactured by Tokyo Chemical Industry), hexane was gradually added under reflux to completely dissolve the product. After heating was stopped and the product was left at room temperature for several days, the precipitate was filtered off and dried under reduced pressure. 58 g of purified DADCM in white
15 solid form was obtained.

[0111] Three types of diamines, alicyclic diamine DADCM, aromatic diamine 4,4'-bis (4-aminophenoxy) biphenyl (product name BODA, manufactured by Wakayama Seika Kogyo), and siloxane-containing diamine 1,3-bis (3-aminopropyl) tetramethyldisiloxane (product name PAM-E, manufactured by Shin-
20 Etsu Chemical) were dissolved in N,N-dimethylacetamide (hereinafter referred to as DMAc) so that the total volume is 12 mmol.

[0112] About 12 mmol of acid dianhydride was added while this diamine solution was being cooled in water. The acid dianhydride was 4-(2,5-dioxotetrahydrofuran-3-yl)-1,2,3,4-tetrahydronaphthalene 1,2-
25 dicarboxylic anhydride (product name TDA-100, manufactured by New Japan Chemical) or 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclo 3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride (product name B-4400, manufactured by DIC). The amount of DMAc was adjusted so that the total mass of diamine and

acid dianhydride was 20% by weight.

[0113] This solution was stirred at room temperature for 15 hours for polymerization reaction. After further dilution with DMAc to 8% by weight, 7.4 ml of pyridine and 3.8 ml of acetic anhydride were added and the solution was stirred at room temperature for 1 hour. The mixture was further stirred for 4 hours while heated to 60 to 70°C in an oil bath. The polymerization solution was put into methanol, and after removing the polymer that had re-precipitated in the methanol, the polymer was washed several times in the methanol. After drying at 60°C for 24 hours, a white to pale yellow powdery polyimide was obtained.

10 [0114] The resulting polyimide was dissolved in cyclohexanone to a solid concentration of 2.5 mass% to make the intermediate layer coating solution 4.

[0115] The intermediate layer coating solution 4 and the hollow particle coating solution 1 are used to form the antireflection film 102.

15 [0116] 0.2 ml of the intermediate layer coating solution 4 was dropped onto the lens surface of the transparent substrate 202 and spin coated at 4000 rpm for 20 seconds. Next, 0.2 ml of the hollow particle coating solution 1 was continuously dropped onto the lens surface of the transparent substrate 202 and spin coated at 4000 rpm for 20 seconds. Then, drying was performed in a clean room at a room temperature of 23°C for at least 24 hours.

20 [0117] FIG. 14 shows reflectance characteristics of the antireflection film 102 at incident angles of 0, 15, 30, 45, and 60 degrees at position C. The reflectance is less than or equal to 0.2% at an incident angle of 0 degrees and within wavelengths from 420 nm to 680 nm, indicating very good reflectance properties. FIG. 15 shows reflectance characteristics at an incident angle of 0 degrees at positions C and Q. Table 6 shows that although the film thickness of each thin film layer at position Q is 2% thicker than at position C, the reflectance characteristics are almost the same at positions C and Q, confirming that the reflectance characteristics are good.

25

TABLE 6

			REFRA- CTIVE INDEX	PHYSICAL FILM THICKNESS (nm)	
				POSITION C	POSITION Q
ANTI- REFLECTION FILM 102	SECOND THIN FILM LAYER 22	HOLLOW SILICA	1.19	109.7	111.9
	FIRST THIN FILM LAYER 21	POLYIMIDE RESIN	1.62	79.5	81.1
TRANSPARENT SUBSTRATE 202		S-NPH2	1.92	—	—

5 EXAMPLE 7

[0118] FIG. 2 is a schematic cross-sectional view of the optical element 301 according to Example 7. The optical element 301 in this example is an optical element with the antireflection film 101 formed on the transparent substrate 201. The transparent substrate 201 is made of ZEONEX K22R (manufactured by Nippon
10 Zeon) with a refractive index of 1.54 (wavelength 550 nm). The lens surface of the transparent substrate 201, on which the antireflection film 101 is formed, is concave in shape. The half-open angle ϕ at position Q on the maximum effective diameter of the lens surface of the transparent substrate 201 is 30 degrees. As layer materials, the first thin film layer 11 consists mainly of solid silica, and the
15 second thin film layer 12 consists mainly of hollow silica. Table 7 shows the details of the film composition of the optical element 301 in this example. The refractive index and film thickness of each material satisfy inequalities (1) through (9).

[0119] The method of forming the antireflection film 101 in this example is as
20 follows.

[0120] The intermediate layer coating solution 1 and the hollow particle coating

solution 1 are used to form the antireflection film 101.

[0121] 0.2 ml of the intermediate layer coating solution 1 was dropped onto the lens surface of the transparent substrate 201 and spin coated at 4000 rpm for 20 seconds. Next, 0.2 ml of the hollow particle coating solution 1 was continuously dropped

5 onto the lens surface of the transparent substrate 201 and spin coated at 4000 rpm for 20 seconds. Then, drying was performed in a clean room at a room temperature of 23°C for at least 24 hours.

[0122] FIG. 16 shows reflectance characteristics of the antireflection film 101 at incident angles of 0, 15, 30, 45, and 60 degrees at position C. The reflectance is

10 less than or equal to 0.2% at an incident angle of 0 degrees and within wavelengths from 420 nm to 680 nm, indicating very good reflectance properties. FIG. 17 shows reflectance characteristics at an incident angle of 0 degrees at positions C and Q. Table 7 shows that although the film thickness of each thin film layer at position Q is 2% thicker than at position C, the reflectance characteristics are almost

15 the same at positions C and Q, confirming that the reflectance characteristics are good.

TABLE 7

			REFRA- CTIVE INDEX	PHYSICAL FILM THICKNESS (nm)	
				POSITION C	POSITION Q
ANTI- REFLECTION FILM 101	SECOND THIN FILM LAYER 12	HOLLOW SILICA	1.19	107.2	109.3
	FIRST THIN FILM LAYER 11	SOLID SILICA	1.45	85.5	87.2
TRANSPARENT SUBSTRATE 201		K22R	1.54	—	—

20

EXAMPLE 8

[0123] FIG. 3 is a schematic cross-sectional view of the optical element 302 according to Example 8. The optical element 302 in this example is an optical element with the antireflection film 102 formed on the transparent substrate 202. The transparent substrate 202 is made of OKP-1 (manufactured by Osaka Gas
5 Chemical) with a refractive index of 1.65 (wavelength 550 nm). The lens surface of the transparent substrate 202, on which the antireflection film 102 is formed, is convex in shape. The half-open angle ϕ at position Q on the maximum effective diameter of the lens surface of the transparent substrate 202 is 35 degrees. As layer materials, the first thin film layer 21 consists mainly of acrylic resin, and the
10 second thin film layer 22 consists mainly of hollow silica. Table 8 shows the details of the film composition of the optical element 302 in this example. The refractive index and film thickness of each material satisfy inequalities (1) through (9).

[0124] The method of forming the antireflection film 102 in this example is as
15 follows.

[0125] The intermediate layer coating solution 2 and the hollow particle coating solution 1 are used to form the antireflection film 102.

[0126] 0.2 ml of the intermediate layer coating solution 2 was dropped onto the lens surface of the transparent substrate 202 and spin coated at 4000 rpm for 20 seconds.
20 Next, 0.2 ml of the hollow particle coating solution 1 was continuously dropped onto the lens surface of the transparent substrate 202 and spin coated at 4000 rpm for 20 seconds. Then, drying was performed in a clean room at a room temperature of 23°C for at least 24 hours.

[0127] FIG. 18 shows reflectance characteristics of the antireflection film 102 at
25 incident angles of 0, 15, 30, 45, and 60 degrees at position C. The reflectance is less than or equal to 0.2% at an incident angle of 0 degrees and within wavelengths from 420 nm to 680 nm, indicating very good reflectance properties. FIG. 19 shows reflectance characteristics at an incident angle of 0 degrees at positions C

and Q. Table 8 shows that although the film thickness of each thin film layer at position Q is 3% thicker than at position C, the reflectance characteristics are almost the same at positions C and Q, confirming that the reflectance characteristics are good.

5

TABLE 8

			REFRA- CTIVE INDEX	PHYSICAL FILM THICKNESS (nm)	
				POSITION C	POSITION Q
ANTI- REFLECTION FILM 102	SECOND THIN FILM LAYER 22	HOLLOW SILICA	1.19	109.3	111.5
	FIRST THIN FILM LAYER 21	ACRYLIC RESIN	1.50	85.2	86.9
TRANSPARENT SUBSTRATE 202		OKP-1	1.65	—	—

EXAMPLE 9

10 [0128] FIG. 2 is a schematic cross-sectional view of the optical element 301 according to Example 9. The optical element 301 in this example is an optical element with the antireflection film 101 formed on the transparent substrate 201. An optical element called a replica element is used, in which the transparent substrate 201 is formed on the surface of a glass substrate (not shown in the figure)

15 that serves as a base material. The transparent substrate 201 is made of LPQ-1500 (manufactured by Mitsubishi Gas Chemical) with a refractive index of 1.59 (wavelength 550 nm). The lens surface of the transparent substrate 201, on which the antireflection film 101 is formed, is concave in shape. The half-open angle ϕ at position Q on the maximum effective diameter of the lens surface of the

20 transparent substrate 201 is 30 degrees. As layer materials, the first thin film layer 11 consists mainly of solid silica, and the second thin film layer 12 consists mainly

of hollow silica. Table 9 shows the details of the film composition of the optical element 301 in this example. The refractive index and film thickness of each material satisfy inequalities (1) through (9).

[0129] The method of forming the antireflection film 101 in this example is as follows.

[0130] The intermediate layer coating solution 1 and the hollow particle coating solution 1 are used to form the antireflection film 101.

[0131] 0.2 ml of the intermediate layer coating solution 1 was dropped onto the lens surface of the transparent substrate 201 and spin coated at 4000 rpm for 20 seconds.

10 Next, 0.2 ml of the hollow particle coating solution 1 was continuously dropped onto the lens surface of the transparent substrate 201 and spin coated at 4000 rpm for 20 seconds. Then, drying was performed in a clean room at a room temperature of 23°C for at least 24 hours.

[0132] FIG. 20 shows reflectance characteristics of the antireflection film 101 at 15 incident angles of 0, 15, 30, 45, and 60 degrees at position C. The reflectance is less than or equal to 0.2% at an incident angle of 0 degrees and within wavelengths from 420 nm to 680 nm, indicating very good reflectance properties. FIG. 21 shows reflectance characteristics at an incident angle of 0 degrees at positions C and Q. Table 9 shows that although the film thickness of each thin film layer at 20 position Q is 2% thicker than at position C, the reflectance characteristics are almost the same at positions C and Q, confirming that the reflectance characteristics are good.

TABLE 9

			REFRA- CTIVE INDEX	PHYSICAL FILM THICKNESS (nm)	
				POSITION C	POSITION Q
ANTI- REFLECTION FILM 101	SECOND THIN FILM LAYER 12	HOLLOW SILICA	1.19	106.3	108.4
	FIRST THIN FILM LAYER 11	SOLID SILICA	1.45	85.0	86.7
TRANSPARENT SUBSTRATE 201		LPQ- 1500	1.59	—	—

EXAMPLE 10

[0133] FIG. 2 is a schematic cross-sectional view of the optical element 301 according to Example 10. The optical element 301 in this example is an optical element with the antireflection film 101 formed on the transparent substrate 201. The transparent substrate 201 is made of S-LAH53 (manufactured by OHARA) with a refractive index of 1.81 (wavelength 550 nm). The lens surface of the transparent substrate 201, on which the antireflection film 101 is formed, is concave in shape. The half-open angle ϕ at position Q on the maximum effective diameter of the lens surface of the transparent substrate 201 is 30 degrees. As layer materials, the first thin film layer 11 consists mainly of polyimide resin, and the second thin film layer 12 consists mainly of chain silica. Table 10 shows the details of the film composition of the optical element 301 in this example. The refractive index and film thickness of each material satisfy inequalities (1) through (9).

[0134] The method of forming the antireflection film 101 in this example is as follows.

20 (Chain particle coating solution 3)

[0135] The solvent 2-propanol in the 2-propanol (IPA) dispersion liquid of chain silica particles (manufactured by Nissan Chemical, IPA-ST-UP, average particle diameter: 12 nm, solid concentration: 15 mass%) was replaced by 1-propoxy-2-propanol (manufactured by Sigma) using an evaporator to make the 1-propoxy-2-propanol dispersion liquid (solid concentration 17 wt%). This was the dispersion liquid 2. Next, 18.5 g of tetraethoxysilane (TEOS, manufactured by Tokyo Chemical Industry) and 16.0 g of 0.1 wt% phosphinic acid in 10 equivalents to TEOS as catalyst water were added, and mixed and stirred in a 20°C water bath for 60 minutes to obtain the binder solution 2.

10 [0136] To 251.3 g of the dispersion liquid 2, 33.4 g of the binder solution 2 was added. Then 174.5 g of 1-propoxy-2-propanol and 546.5 g of ethyl lactate were added and stirred for 60 minutes to obtain the chain particle coating solution 3.

[0137] The intermediate layer coating solution 4 and the chain particle coating solution 3 are used to form the antireflection film 101.

15 [0138] 0.2 ml of the intermediate layer coating solution 4 was dropped onto the lens surface of the transparent substrate 201 and spin coated at 4000 rpm for 20 seconds. Next, 0.2 ml of the chain particle coating solution 3 was continuously dropped onto the lens surface of the transparent substrate 201 and spin coated at 4000 rpm for 20 seconds. Then, drying was performed in a clean room at a room temperature of
20 23°C for at least 24 hours.

[0139] FIG. 22 shows reflectance characteristics of the antireflection film 101 at incident angles of 0, 15, 30, 45, and 60 degrees at position C. The reflectance is less than or equal to 0.2% at an incident angle of 0 degrees and within wavelengths from 420 nm to 680 nm, indicating very good reflectance properties. FIG. 23 shows reflectance characteristics at an incident angle of 0 degrees at positions C and Q. Table 10 shows that although the film thickness of each thin film layer at position Q is 2% thicker than at position C, the reflectance characteristics are almost the same at positions C and Q, confirming that the reflectance characteristics are

good.

TABLE 10

			REFRA- CTIVE INDEX	PHYSICAL FILM THICKNESS (nm)	
				POSITION C	POSITION Q
ANTI- REFLECTION FILM 101	SECOND THIN FILM LAYER 12	CHAIN SILICA	1.24	101.7	103.7
	FIRST THIN FILM LAYER 11	POLYIMIDE RESIN	1.62	76.6	78.1
TRANSPARENT SUBSTRATE 201		S-LAH53	1.81	—	—

5

EXAMPLE 11

[0140] Referring to FIG. 24, the optical system 401 according to Example 11 is described. FIG. 24 is a cross-sectional view of the optical system 401 in this example. The optical system 401 has a plurality of optical elements G401-G416.

10 The reference numeral 402 indicates an aperture stop and the reference numeral 403 indicates an imaging plan. The optical elements G401-G411 are lenses, respectively. At least one of the incident surface and the exit surface of each of G401-G411 is provided with the antireflection film according to any one of Examples 1 to 10. That is, the optical system 401 has a plurality of optical
15 elements G401-G416, and the plurality of optical elements G403, G412, and G413 are the optical elements with the antireflection film according to any one of Examples 1 to 10.

[0141] The optical system 400 in this example is not limited to an image pickup optical system used in the image pickup apparatus described below, but can be
20 applied to optical systems for various uses in binoculars, projectors, telescopes, and

other optical apparatuses.

EXAMPLE 12

[0142] Next, with reference to FIG. 25, the image pickup apparatus 500 according to Example 12 is described. FIG. 25 is an external perspective view of the image pickup apparatus (digital camera) 500 in this example.

[0143] The digital camera 500 has a camera body 502 and a lens apparatus 501 that is integrally configured with the camera body 502. However, this example is not limited to this, and the lens apparatus 501 may be a detachable interchangeable lens for the camera body 502, such as for single-lens reflex cameras or mirrorless cameras. The lens apparatus 501 has the optical system 401 according to Example 11. The camera body 502 has an image sensor 503, such as a CMOS sensor or CCD sensor. The image sensor 503 is placed on the imaging plane 403 of the optical system 401.

[0144] Comparative Examples 1 and 2 of this disclosure are described below.

COMPARATIVE EXAMPLE 1

[0145] FIG. 2 is a schematic cross-sectional view of the optical element 301 according to Comparative Example 1. The optical element 301 in this comparative example is an optical element with the antireflection film 101 formed on the transparent substrate 201. The transparent substrate 201 is made of S-TIL26 (manufactured by OHARA) with a refractive index of 1.57 (wavelength 550 nm). The lens surface of the transparent substrate 201, on which the antireflection film 101 is formed, is concave in shape. The half-open angle ϕ at position Q on the maximum effective diameter of the lens surface of the transparent substrate 201 is 40 degrees. As layer materials, the first thin film layer 11 consists of SiO₂ formed by vapor deposition, and the second thin film layer 12 consists mainly of hollow silica. Table 11 shows the details of the film composition of the optical

element 301 in this comparative example. The refractive index and film thickness of each material satisfy inequalities (1) through (6) but do not satisfy inequalities (7) and (8).

5 [0146] The method of forming the antireflection film 101 in this comparative example is as follows.

[0147] The first thin film layer 11 was formed by vapor deposition. The vacuum chamber of the evaporation apparatus was evacuated to a high vacuum region near 2×10^{-3} (Pa). After confirming that the inside of the vacuum chamber had reached a high vacuum state, oxygen was introduced into the vacuum chamber to
10 create a vacuum pressure of about 1×10^{-2} (Pa) for SiO₂ deposition.

[0148] After the film formation of the first thin film layer 11 was completed, 0.2 ml of the hollow particle coating solution 1 was dropped onto the first thin film layer 11 and spin coated at 4000 rpm for 20 seconds. Then, drying was performed in a clean room at a room temperature of 23°C for at least 24 hours.

15 [0149] FIG. 26 shows reflectance characteristics of the antireflection film 101 at incident angles of 0, 15, 30, 45, and 60 degrees at position C. The reflectance is less than or equal to 0.2% at an incident angle of 0 degrees and within wavelengths from 420 nm to 680 nm, indicating very good reflectance properties. However, comparing the reflectance characteristics at incident angle of 0 degrees between
20 position C and position Q in FIG. 27, it can be seen that the reflectance characteristics at position Q are worse than those at position C. According to Table 11, the film thickness at position Q of the second thin film layer 12 is 4% thicker than at position C, but the film thickness at position Q of the first thin film layer 11 is 13% less than at position C. Therefore, it can be said that the
25 reflectance property at position Q has deteriorated.

TABLE 11

			REFRA- CTIVE INDEX	PHYSICAL FILM THICKNESS (nm)	
				POSITION C	POSITION Q
ANTI- REFLECTION FILM 101	SECOND THIN FILM LAYER 12	HOLLOW SILICA	1.19	106.9	111.2
	FIRST THIN FILM LAYER 11	SiO ₂	1.45	85.4	74.0
TRANSPARENT SUBSTRATE 201		S-TIL26	1.57	—	—

COMPARATIVE EXAMPLE 2

[0150] FIG. 2 is a schematic cross-sectional view of the optical element 301 according to Comparative Example 2. The optical element 301 in this comparative example is an optical element with the antireflection film 101 formed on the transparent substrate 201. The transparent substrate 201 is made of S-LAH53 (manufactured by OHARA) with a refractive index of 1.81 (wavelength 550 nm). The lens surface of the transparent substrate 201, on which the antireflection film 101 is formed, is concave in shape. The half-open angle ϕ at position Q on the maximum effective diameter of the lens surface of the transparent substrate 201 is 30 degrees. As layer materials, the first thin film layer 11 consists mainly of polyimide resin, and the second thin film layer 12 consists mainly of chain silica. Table 12 shows the details of the film composition of the optical element 301 in this comparative example. The refractive index of the second thin film layer does not satisfy inequality (2).

[0151] The method of forming the antireflection film 101 in this comparative example is as follows.

20 (Chain particle coating solution 4)

[0152] The preparation of the chain particle dispersion liquid 2 and the binder solution 2 is the same as for the hollow particle coating solution 1.

[0153] To 251.3 g of the chain particle dispersion liquid 2, 78.0 g of the binder solution 2 was added. Then, 174.5 g of 1-propoxy-2-propanol and 510.8 g of ethyl
5 lactate were added and stirred for 60 minutes to obtain the chain particle coating solution 4.

[0154] The intermediate layer coating solution 4 and the chain particle coating solution 4 are used to form the antireflection film 101.

[0155] 0.2 ml of the intermediate layer coating solution 4 was dropped onto the lens
10 surface of the transparent substrate 201 and spin coated at 4000 rpm for 20 seconds. Next, 0.2 ml of the chain particle coating solution 4 was continuously dropped onto the lens surface of the transparent substrate 201 and spin coated at 4000 rpm for 20 seconds. Then, drying was performed in a clean room at a room temperature of 23°C for at least 24 hours.

[0156] FIG. 28 shows reflectance characteristics of the antireflection film 101 at
15 incident angles of 0, 15, 30, 45, and 60 degrees at position C. The reflectance is larger than or equal to 0.2% at an incident angle of 0 degrees and within wavelengths from 420 nm to 680 nm, which means that sufficient antireflection properties have not been achieved.

20

TABLE 12

			REFRA- CTIVE INDEX	PHYSICAL FILM THICKNESS (nm) POSITION C
ANTI- REFLECTION FILM 101	SECOND THIN FILM LAYER 12	CHAIN SILICA	1.28	95.1
	FIRST THIN FILM LAYER 11	POLYIMIDE RESIN	1.62	73.5
TRANSPARENT SUBSTRATE 201		S-LAH53	1.81	—

[0157] While the disclosure has been described with reference to embodiments, it is to be understood that the disclosure is not limited to the disclosed embodiments.

[0158] This disclosure can provide an optical element that enable sufficient

5 reduction of reflectance throughout the entire lens surface.

CLAIMS

1. An optical element comprising:
a substrate; and
5 an antireflection film,
wherein the antireflection film consists of a first layer formed on the
substrate, and a second layer formed on the first layer,
wherein the first layer and the second layer each include an organic
compound, and

10 wherein the following inequalities are satisfied:

$$1.30 \leq n_1 \leq 1.70$$

$$1.10 \leq n_2 \leq 1.26$$

$$-0.2 \leq (n_s - 1) - 2(n_1 - n_2) \leq 0.2$$

$$100 \leq n_1 d_1 \leq 155$$

15 $100 \leq n_2 d_2 \leq 155$

where n_s is a refractive index of the substrate at a wavelength of 550 nm, n_1 is a refractive index of the first layer at a wavelength of 550 nm, n_2 is a refractive index of the second layer at a wavelength of 550 nm, d_1 (nm) is a physical film thickness of the first layer, and d_2 (nm) is a physical film thickness of the second layer.

20

2. The optical element according to claim 1, wherein the following inequality is satisfied:

$$1.12 \leq n_2 \leq 1.22.$$

25

3. The optical element according to claim 1 or 2,
wherein an optical surface forming the antireflection film has a
rotationally symmetrical axis, and

wherein the following inequalities are satisfied:

$$1.0 < d1q/d1c \leq 1.3$$

$$1.0 < d2q/d2c \leq 1.3$$

where $d1c$ (nm) is a physical film thickness of the first layer at an intersection of the optical surface and the rotationally symmetrical axis, $d2c$ (nm) is a physical film thickness of the second layer at an intersection of the optical surface and the rotationally symmetrical axis, $d1q$ (nm) is a physical film thickness of the first layer at a most distant position from the intersection within an optically effective area on the optical surface, and $d2q$ (nm) is a physical film thickness of the second layer at a most distant position from the intersection within an optically effective area on the optical surface.

4. The optical element according to any one of claims 1 to 3, wherein an optical surface forming the antireflection film has a rotationally symmetrical axis, and wherein when an intersection of the optical surface and the rotationally symmetrical axis is an optical axis center and the optical axis center has a half-open angle of 0 degrees, which is a reference of the optical surface, a half-open angle φ (degrees) at a maximum effective diameter of the optical surface satisfies the following inequality:

$$25 \leq \varphi < 90.$$

5. The optical element according to claim 4, wherein in each of the first layer and the second layer, a film thickness is the smallest at the optical axis center and the film thickness increases as a distance from the optical axis center increases.

6. The optical element according to any one of claims 1 to 5, wherein the second layer includes a void.

7. The optical element according to any one of claims 1 to 6, wherein the second layer includes at least one of a solid particle, a chain particle, or a hollow particle.

5

8. The optical element according to claim 7, wherein the second layer includes at least one of a solid particle made of silica, a chain particle made of silica, or a hollow particle made of silica.

10

9. The optical element according to any one of claims 1 to 8, wherein the first layer includes a polyimide resin.

10. The optical element according to any one of claims 1 to 9, wherein the first layer includes an epoxy resin.

15

11. The optical element according to any one of claims 1 to 10, wherein the first layer includes an acrylic resin.

12. The optical element according to any one of claims 1 to 11, wherein the first layer includes a solid particle.

20

13. The optical element according to claim 12, wherein the first layer includes a solid particle made of silica.

25

14. The optical element according to any one of claims 1 to 13, wherein an optical surface forming the antireflection film has a rotationally symmetrical axis, and

wherein in a wavelength range of 450 nm to 650 nm, a reflectance at

an intersection of the optical surface of the antireflection film and the rotationally symmetrical axis is 0.5% or less at an incident angle of 0 degrees and 1.0% or less at an incident angle of 30 degrees.

5 15. The optical element according to any one of claims 1 to 14, wherein a surface of the second layer is provided with an antifouling layer including a fluororesin.

 16. The optical element according to any one of claims 1 to 15, wherein
10 the following inequality is satisfied:

$$1.50 \leq n_s \leq 2.10.$$

 17. An optical system comprising a plurality of optical elements, wherein the plurality of optical elements includes the optical element according to any one
15 of claims 1 to 16.

 18. An image pickup apparatus comprising:
 an optical system including the optical element according to any one
of claims 1 to 16; and
20 an image sensor configured to capture an image of an object via the optical system.

 19. An optical apparatus comprising the optical element according to any one of claims 1 to 16.