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(54) Titre : COMPOSE POUR DEPOT PAR EVAPORATION SOUS VIDE, METHODE POUR FORMER UNE COUCHE
 ANTIREFLET A L'AIDE DE CE COMPOSE, ET ELEMENT OPTIQUE
 (54) Title: COMPOSITION FOR VAPOR DEPOSITION, METHOD FOR FORMING ANTIREFLECTION FILM USING IT,
 AND OPTICAL ELEMENT

(57) **Abrégé/Abstract:**

It is an object of the invention to provide a method for producing an optical element having a multi-layered antireflection film formed on a synthetic resin substrate, in which the antireflection film formed has good heat resistance, and its heat resistance lowers little with time. The method makes it possible to form high-refraction layers within a shorter period of time, not detracting from the good physical properties intrinsic to the layers. At least one high-refraction layer of the multi-layered anti-reflection film contains niobium oxide, zirconium oxide, yttrium oxide, and optionally aluminum oxide.

Abstract

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At least one high-refraction layer of the multi-layered anti-reflection film contains niobium oxide, zirconium oxide, yttrium oxide, and optionally aluminum oxide.

Title of the Invention

COMPOSITION FOR VAPOR DEPOSITION, METHOD FOR FORMING
ANTIREFLECTION FILM USING IT, AND OPTICAL ELEMENT

Detailed Description of the Invention

[0001]

Technical Field of the Invention

The present invention relates to a composition suitable for vapor deposition, to a method for forming an antireflection film using it, and to an optical element.

[0002]

Prior Art

For improving the surface reflection characteristic of an optical element that comprises a synthetic resin, it is well known to form an antireflection film on the surface of the synthetic resin. For example, Japanese Patent Laid-Open No. 116003/1981 discloses an optical element having an antireflection film formed on a substrate of CR-39 (diethylene glycol bisallyl carbonate) resin, in which the antireflection film comprises a basic layer made of SiO_2 having a thickness of 1.5λ , a first layer made of a two-layered equivalent film constructed of a ZrO_2 layer and an SiO_2 layer and having an overall thickness of about 0.25λ , a second layer made of ZrO_2 having a thickness of about 0.50λ and a third layer made of SiO_2 having a thickness of about 0.25λ that are formed in that order on the CR-39 resin substrate.

[0003]

However, when an antireflection film is formed on a resin substrate through vapor deposition, the temperature resistance of the resin substrate could not be made so high like that of glass substrates. Therefore, it cannot be said that, for example, the heat resistance of a layer made of ZrO_2 formed on a resin substrate through vapor deposition is sufficient. In addition, the heat resistance of the ZrO_2 layer is apt to greatly lower with time. Optical elements of which the heat resistance of the antireflection film is not good as a whole and is apt to greatly lower with time are often problematic in their practical use, for example, for lenses for spectacles. This is because plastic frames of spectacles are heated before lenses are fitted thereinto and the heat is conducted to the lenses having been fitted into the frames. An antireflection film of low heat resistance is often cracked owing to the difference in the thermal expansion, etc.

[0004]

To solve the problem of heat resistance, for example, Japanese Patent Laid-Open No. 291502/1990 and USP 5,181,141 disclose an optical element having an antireflection film of which the high-refraction layer is formed from a vapor deposition film containing Ta_2O_5 , ZrO_2 and Y_2O_3 , and discloses a composition for vapor deposition to form a vapor deposition film containing Ta_2O_5 , ZrO_2 and Y_2O_3 .

[0005]

Object of the invention

The composition for vapor deposition disclosed in Japanese Patent Laid-Open No. 291502/1990 and USP 5,181,141 containing Ta₂O₅, ZrO₂ and Y₂O₃, requires a relatively long period of time to form the intended antireflection film, and is therefore unfavorable in point of the working efficiency.

Especially in the field of spectacles, desired are new optical elements for plastic lenses coated with an antireflection film of which the heat resistance is good and does not lower with time.

[0006]

The first object of the invention is to provide an optical element, which comprises a synthetic resin substrate that must be subjected to vapor deposition thereon at low temperatures and which has an antireflection film formed, and in which the heat resistance of the antireflection film is good and lowers little with time.

The second object of the invention is to provide a composition, which is suitable for vapor deposition and capable of forming a high-refraction layer within a shorter period of time not detracting from the physical properties intrinsic to the high-refraction layer, and to provide a method for forming an antireflection film.

[0007]

Summary of the invention

We, the present inventors assiduously studied to attain the objects as above, and, as a result, have found that, when niobium oxide and optionally aluminum oxide are added to the conventional composition for vapor deposition in addition to zirconium oxide and yttrium oxide, and when the resulting composition is used for forming an antireflection film, then a multi-layered antireflection film of good heat resistance can be obtained, and that the vapor deposition film can be formed within a short period of time, leading to the invention.

Specifically, the first aspect of the invention is concerned with a composition, which contains niobium oxide, zirconium oxide, yttrium oxide, and optionally aluminum oxide.

The second aspect of the invention is concerned with a method for forming an antireflection film, which comprises sintering a powdery mixture of niobium oxide, zirconium oxide, yttrium oxide, and optionally aluminum oxide, vaporizing the sintered material to form a vapor of the mixed oxide, and depositing the mixed oxide vapor on a substrate.

The third aspect of the invention is concerned with an optical element having the antireflection film according to the method of the second aspect as above formed on a plastic substrate.

[0008]

Detailed description of the invention

The invention is described in detail hereinunder.

The composition of the invention is prepared by sintering a powdery mixture that contains niobium oxide powder, zirconium oxide powder and yttrium oxide powder, preferably a powdery mixture that contains Nb_2O_5 powder, ZrO_2 powder and Y_2O_3 powder, or a powdery mixture that contains Nb_2O_5 powder, ZrO_2 powder, Y_2O_3 powder and Al_2O_3 powder, and is short in the period of time to form a vapor deposition film and high in the film productivity, as compared with a conventional composition for vapor deposition that is prepared by sintering ZrO_2 alone.

[0009]

The reason why it is intended to mix the three components in the invention is because pellets of niobium oxide alone often cause a problem of splashes when heated with an electronic gun. If splashed, an influence is caused such that fine particles are attached to lens substrates, thereby causing failed products. In addition, the thin film is liable to be colored (absorbed). To improve the tendency that the chemical resistance such as acid resistance and alkali resistance is weak, a plurality of components are mixed.

The addition of zirconium oxide (ZrO_2) is effective for reducing splashes which are often seen in vapor deposition of pellets of niobium oxide alone heated with an electronic gun and which cause the film to peel off and cause adhesion of impurities, and therefore, is favorable for obtaining films for vapor deposition of stable quality.

The addition of yttrium oxide (Y_2O_3) acts to vary the oxide condition of the thin film formed through vapor deposition under heat with an electronic gun, and is therefore effective for preventing the film from coloration (absorption) occurred in the thin films formed through vapor deposition of pellets of niobium oxide alone or of pellets of a mixture of niobium oxide and zirconium oxide.

[0010]

In the invention, the above-mentioned three components that are mixed to form the composition for vapor deposition all exhibit their individual effects, and, in addition, the heat resistance of the antireflection film as formed lowers little with time. This gives rise to an unexpected effect.

For better results, one ideal blend ratio in the composition for vapor deposition is as follows. It is preferred that based on the total amount of the composition for vapor deposition, the amount of niobium oxide (calculated in terms of Nb_2O_5) is from 60 to 90 % by weight, more preferably from 80 to 90 by weight, that of zirconium oxide (calculated in terms of ZrO_2) is from 5 to 20 % by weight, more preferably from 5 to 10 by weight, and that of yttrium oxide (calculated in terms of Y_2O_3) is from 5 to 35 % by weight, more preferably from 5 to 10 by weight. If the amount of Nb_2O_5 and/or the amount of ZrO_2 and/or that of Y_2O_3 are within the preferred ranges, the obtained high-refraction layer will exhibit particularly

beneficial absorption characteristics; an amount of Y_2O_3 above 50% by weight will furthermore lead to an improved acid resistance of the obtained antireflection film .

[0011]

The composition for vapor deposition may furthermore contain aluminum oxide so as to control the refractivity.

In the composition, the amount of aluminum oxide (in terms of Al_2O_3) is preferably from 0.3 to 7.5% by weight, more preferably from 0.3 to 2.0 by weight, of the total of Nb_2O_5 , ZrO_2 and Y_2O_3 . An amount of aluminum oxide above the lower limit of the preferred range will lead to most satisfactory results in controlling the refractivity; an aluminum oxide content of not more than the upper limit of the preferred range will result in a particularly good alkali resistance of the obtained antireflection film. Not interfering with the characteristics of the layer that are induced by Nb_2O_5 , ZrO_2 and Y_2O_3 , aluminum oxide (Al_2O_3) can well control the refractivity of the layer, and an amount within the preferred range will prove to be particularly beneficial in this respect.

The composition for vapor deposition of the invention may further contain any other metal oxides such as tantalum oxide (Ta_2O_5), titanium oxide (TiO_2) and the like not detracting from the above-mentioned effects. The amount of the any other metal oxides preferably does not exceed 30 wt.%, more preferably 10 wt.%, on the basis of the total composition.

[0012]

For the low-refraction layer of the multi-layered antireflection film in the invention, for example, usable is a silicon dioxide (SiO_2) film in view of its heat resistance.

Regarding its layer constitution, the antireflection film includes a two-layered film of $\lambda/4 - \lambda/4$, and a three-layered film of $\lambda/4 - \lambda/4 - \lambda/4$ or $\lambda/4 - \lambda/2 - \lambda/4$. In the context of the present application, λ has a value in the range of from 450 to 550 nm. In practice, a typical value of λ is 500 nm. Not limited thereto, the antireflection film may be any other four-layered or multi-layered film. The first low-refraction layer nearest to the substrate may be any of known two-layered equivalent films, three-layered equivalent films or other composite films.

[0013]

For the synthetic resin substrate used for the optical element of the invention, for example, usable are methyl methacrylate homopolymers, copolymers of methyl methacrylate and one or more other monomers as monomer components, diethylene glycol bisallyl carbonate homopolymers, copolymers of diethylene glycol bisallyl carbonate and one or more other monomers as monomer components, sulfur-containing copolymers, halogen-containing copolymers, polycarbonates, polystyrenes, polyvinyl chlorides, unsaturated polyesters, polyethylene terephthalates, polyurethanes, etc.

[0014]

For forming an antireflection film on a synthetic resin in the invention, it is desirable that a hard coat layer containing an organosilicon polymer is first formed on the synthetic resin surface in a method of dipping, spin coating or the like, and thereafter the antireflection film is formed on the hard coat layer. Typical compositions and coating methods for the hard coat layer are disclosed in EP1041404. For improving the adhesiveness between the synthetic resin substrate and the antireflection film, the scratch resistance, etc., it is desirable to dispose a basic layer between the synthetic resin surface and the antireflection film or between the hard coat layer formed on the synthetic resin substrate and the antireflection film. The basic layer may be, for example, a vapor deposition film of silicon oxide or the like. Suitable basic layers are disclosed in USP5,181,141.

[0015]

In the invention, preferred compositions comprise a three-component composition consisting of niobium oxide, zirconium oxide and yttrium oxide, as well as a four component composition consisting of niobium oxide, zirconium oxide, yttrium oxide and aluminum oxide.

It is desirable that the composition of the invention is formed by mixing a powder of niobium oxide (Nb_2O_5), a powder of zirconium oxide (ZrO_2) and a powder of yttrium oxide (Y_2O_3), optionally,

a powder of aluminum oxide (Al_2O_3), and optionally powders of other metal oxides (these powders mixed may sometimes be hereinafter referred to as powdery mixtures), and pressing the powdery mixture, followed by heating, for example, with electronic beams to thereby deposit its vapor on a substrate. The use of a sintered material in a pellet form prepared by pressing and sintering is more preferred because the vapor deposition time can be reduced. The amount of each oxide in the powdery mixture or in the sintered pellets may be properly varied, depending on the desired properties of the high-refraction layer to be formed.

[0016]

As mentioned hereinabove, the antireflection film in the invention may be formed by sintering the powdery mixture comprising powders of niobium oxide, zirconium oxide, yttrium oxide and, optionally, aluminum oxide and, optionally, other metal oxides, generating a vapor of the mixed oxide, and depositing the generated vapor on a substrate. Preferably, the process of forming the antireflection film is combined with an ion-assisted process. Such ion-assisted processes are described in M. Flindner et al., Society of Vacuum Coaters Albuquerque, NM, USA. p237-241, 1995 as well as from the cited therein.

Combined with an ion-assisted process, the film formation produces various advantages. Concretely, when the high-refraction layer is formed through vapor deposition

assisted by oxygen ions, the absorption of the lenses can be reduced further. When an ion-assisted process using a mixed gas of oxygen and argon is employed, the alkali resistance is improved. Preferably, the mixed gas comprises from 90 to 95 % of oxygen gas and from 5 to 10 % of argon gas. If the amount of the oxygen gas is too small, the films formed may possibly not keep the optical properties. With a suitable amount of argon gas, the film density can be increased.

[0017]

For obtaining the composition for vapor deposition in the invention, the powdery mixture may be pressed in any conventional method. Preferably, for example, it is pressed under a pressure of from 200 kg/cm² to 400 kg/cm² (from 19.6 to 39.2 MPa). The sintering temperature varies depending on the composition of the constituent components, etc., but may be in the range of, for example, from 1000 to 1400°C. The sintering time varies depending on the sintering temperature, etc., but may be generally in the range of from 1 to 48 hours.

The high-refraction films in the invention may be formed by vaporizing the composition for vapor deposition as defined above using any method of vacuum evaporation, sputtering, ion plating or the like under ordinary conditions. These conventional methods are described in more detail in Handbook of Thin Film Technology Edited by Leon I. Maissel and Reinhard Glang. That is, from the composition for vapor deposition is

generated a vapor of the mixed oxide of the composition, and the resulting vapor is deposited on a substrate. The temperature of the synthetic resin substrate to be heated varies depending on the heat resistance of the synthetic resin, but may be in the range of, for example, from 70 to 85°C.

According to the method of the invention, even in the case where the film formation must be carried out at a low temperature ranging from 70 to 85°C in terms of the heating temperature of the substrate at vaporization as in synthetic resin substrates, the antireflection film having good heat resistance, the heat resistance of which is hardly lowered with time, can be obtained.

[0018]

The optical element having an antireflection film of the invention may be used not only for lenses for spectacles but also for lenses for cameras, windshields for automobiles, optical filters to be fitted to displays of word processors, etc.

[0019]

Examples

The invention is described in detail with reference to the following Examples. The physical properties of the optical elements having an antireflection film produced in the following Examples and Comparative Examples were measured according to the test methods mentioned below.

(1) Melt condition of composition for vapor deposition:

The melt condition was checked according to the following

criteria:

- UA: Not splashed.
- A: Splashed a little.
- B: Splashed frequently.
- C: Always splashed.

In the context of the present invention, "splashing" is defined as the degree of condition regarding the surface of the composition for vapor deposition.

(2) Attachment condition of fine foreign materials :

After finishing vapor deposition, the state of attachment condition of fine particles on a lens surface in vapor deposition by splashing was checked by means of naked eyes and evaluated according to the following criteria:

- UA: No fine foreign materials found.
- A: 1 to 5 fine foreign materials found.
- B: 6 to 10 fine foreign materials found.
- C: 11 or more fine foreign materials found.

(3) Alkali resistance test:

Lenses were dipped in an aqueous 10 wt % NaOH solution of a temperature of 20 °C. After 30 minutes and 60 minutes, they were checked as to whether or not the coating film had been peeled, and as to whether or not the lens surface had been roughened.

- UA: Few peeled dots are found.

A: Small peeled dots of at most 0.1 mm in size were found on the entire surface, or a few peeled dots of around 0.3 mm in diameter were found.

B: The density of peeled dots was higher than in the rank A, and the proportion of larger peeled dots was higher than in the rank A.

C: Peeled dots of around 0.3 mm in size were found everywhere on the surface, or the density of small peeled dots was high.

D: A lot of peeled dots were found everywhere on the surface, and the surface looked white. All the others inferior to those samples are in the rank D.

(4) Scratch resistance test:

The surface was rubbed with steel wool of #0000 and under a weight of 1 kg being applied thereto. After 20 strokes of rubbing, the surface condition was checked according to the following criteria:

- UA: Scratched little
- A: Scratched slightly.
- B: Much scratched.
- C: Coating film swollen.

(5) Adhesiveness test:

According to JIS-Z-1522, the surface was cut to have 10 × 10 cross-cuts, and tested three times for cross-cut peeling

with an adhesive tape, Cellotape (Trade Name, Produced by Nichiban Corp.). The number of the remaining cross-cuts was counted.

(6) Luminous Reflectance:

Using a spectrophotometer, U-3410 made by Hitachi, Ltd., the luminous reflectance was measured.

(7) Luminous transmittance:

Using a spectrophotometer, U-3410 made by Hitachi, Ltd., the luminous transmittance was measured.

(8) Absorbance:

The absorbance was obtained by subtracting the luminous reflectance and the luminous transmittance from 100 %.

(9) Heat resistance test:

An optical element having an antireflection film immediately after forming a vapor deposition film was heated in an oven for 1 hour, and checked as to whether it was cracked or not. Concretely, it was heated first at 50°C over a period of 60 minutes, and the temperature was elevated at intervals of 5°C (of a duration of 30 minutes for each interval), and the temperature at which it was cracked was read.

Further, an optical element having an antireflection film immediately after forming a vapor deposition film for the heat resistance test with time was exposed to the open air for 2 months, and thereafter subjected to the same heat resistance test and evaluated as above.

[0020]

Example 1, Example 4, Comparative Example 1 and Comparative Example 4:

For the synthetic resin substrate to be coated with an antireflection film, prepared was a plastic lens (CR-39: substrate A) made of diethylene glycol bisallyl carbonate as a major component and containing a UV absorbent, 2-hydroxy-4-n-octoxybenzophenone in a ratio by weight of the former to the latter of 99.97/0.03, and having a refractive index of 1.499.

Formation of hard coat layer (nd 1.50)

The plastic lens was dipped in a coating solution containing 80 mol% of colloidal silica and 20 mol% of γ -glycidoxypropyltrimethoxysilane, and cured to form a hard coat layer A thereon.

[0021]

In Example 1, the plastic lens with the hard coat layer formed thereon was heated at 80°C, and a basic layer made of SiO₂ (having a refractive index of 1.46 and a thickness of 0.4875 λ ($\lambda = 500$ nm)) was formed on the hard coat layer through vacuum evaporation (in vacuum of 2×10^{-5} Torr). Next, a layer (having a refractive index of 2.12 and a thickness of 0.0502 λ) was formed thereon by heating a three-component composition A for vapor deposition (Nb₂O₅:ZrO₂:Y₂O₃ = 76:16.6:7.4 % by weight) prepared by mixing powder of Nb₂O₅, powder of ZrO₂ and powder of Y₂O₃, pressing the resulting mixture under a pressure of 300 kg/cm²,

and sintering it at a temperature of 1300°C under heat with an electronic gun at an output current of 170 mA; and a first low-refraction layer made of SiO₂ (having a refractive index of 1.46 and a thickness of 0.0764 λ) was further formed thereon. On the first low-refraction layer, formed was a high-refraction layer (having a refractive index of 2.12 and a thickness of 0.4952 λ) with the composition A for vapor deposition; and a second low-refraction layer made of SiO₂ (having a refractive index of 1.46 and a thickness of 0.2372 λ) was further formed thereon, to obtain the plastic lens having an antireflection film. The low-refraction layers and the high-refraction layers were formed all in the same manner of vacuum evaporation as that for the basic layer.

In Example 4, an antireflection film was formed in the same manner of vacuum evaporation for which a composition B for vapor deposition prepared by adding 1 % by weight of Al₂O₃ to the composition A for vapor deposition was used for forming the high-refraction layers.

In Comparative Example 1, a conventional vapor source of ZrO₂ was used for forming the high-refraction layers of the antireflection film to coat the plastic lens; and in Comparative Example 4, a vapor source of niobium oxide alone was used for forming them.

[0022]

Example 2, Example 5, Comparative Example 2 and Comparative

Example 5:

142 parts by weight of an organosilicon compound, γ -glycidoxypropylmethoxysilane was put into a glass container, to which were dropwise added 1.4 parts by weight of 0.01 N hydrochloric acid and 32 parts by weight of water with stirring. After the dropwise addition, this was stirred for 24 hours to obtain a solution of hydrolyzed γ -glycidoxypropyltrimethoxysilane. To the solution, added were 460 parts by weight of stannic oxide-zirconium oxide composite sol (dispersed in methanol, having a total metal oxide content of 31.5 % by weight and having a mean particle size of from 10 to 15 nm), 300 parts by weight of ethyl cellosolve, 0.7 parts by weight of a lubricant, silicone surfactant, and 8 parts by weight of a curing agent, aluminum acetylacetonate. The mixture was stirred well and subsequently filtered to prepare a coating solution.

Formation of hard coat layer

A plastic lens substrate (a plastic lens for spectacles made by Hoya Corporation, EYAS (a trade name) having a refractive index of 1.60 - substrate B) was pretreated with an aqueous alkali solution, and dipped in the coating solution. After having been thus dipped therein, this was taken out at a pulling rate of 20 cm/min. Then, the plastic lens was heated at 120°C for 2 hours to form a hard coat layer B.

Next, as indicated in the Table below, a 5-layered

antireflection film was formed to produce plastic lenses, for which the composition A for vapor deposition was used for forming the 2nd and 4th high-refraction layers in Example 2; the composition B for vapor deposition was used for forming the antireflection film in Example 5; a conventional vapor source of ZrO_2 was used for forming the antireflection film in Comparative Example 2; and a vapor source of niobium oxide alone was used for forming the antireflection film in Comparative Example 5.

[0023]

Example 3, Example 6, Comparative Example 3 and Comparative Example 6:

100 parts by weight of an organosilicon compound, γ -glycidoxypropyltrimethoxysilane was put into a glass container, to which were added 1.4 parts by weight of 0.01 N hydrochloric acid and 23 parts by weight of water with stirring. After the addition, this was stirred for 24 hours to obtain a solution of hydrolyzed γ -glycidoxypropyltrimethoxysilane. On the other hand, 200 parts by weight of an inorganic particulate substance, composite sol of particulates made of titanium oxide, zirconium oxide and silicon oxide as major components (dispersed in methanol, having a total solid content of 20 % by weight and having a mean particle size of from 5 to 15 nm - in this, the atomic ratio of Ti/Si in the core particles is 10, and the ratio by weight of the shell to the core is 0.25, this sol can be prepared

according to Japanese Patent Laid-Open No. 270620/1988) was mixed with 100 parts by weight of ethyl cellosolve, 0.5 parts by weight of a lubricant, silicone surfactant, and 3.0 parts by weight of a curing agent, aluminum acetylacetonate. The resulting mixture was added to the hydrolyzed γ -glycidoxypropyltrimethoxysilane, and well stirred. This was filtered to prepare a coating solution.

Formation of hard coat layer

A plastic lens substrate (a plastic lens for spectacles made by Hoya Corporation, Teslalid (a trade name), having a refractive index of 1.71 - substrate C) was pretreated with an aqueous alkali solution, and dipped in the coating solution. After having been thus dipped therein, this was taken out at a pulling rate of 20 cm/min. Then, the plastic lens was heated at 120°C for 2 hours to form a hard coat layer C.

Next, as indicated in the Table below, a 7-layered antireflection film was formed to produce plastic lenses, for which the composition A for vapor deposition was used for forming the 2nd, 4th and 6th high-refraction layers in Example 3; the composition B for vapor deposition was used for forming the antireflection film in Example 6; a conventional vapor source of ZrO_2 was used for forming the antireflection film in Comparative Example 3; and a vapor source of niobium oxide alone was used for forming the antireflection film in Comparative Example 6.

[0024]

Table 1 shows the plastic lens substrates, the hard coat layers, the composition for vapor deposition and the thickness of the constituent layers of the antireflection films, and the data of the physical properties in Examples and Comparative Examples.

In all Examples and in Comparative Examples 4 to 6 in which niobium oxide alone was used for forming the high-refraction layer of the antireflection film, the substrates were pretreated with ions, and the formation of the high-refraction layer was assisted by ions. Concretely, both in the ion-pretreatment and in the ion-assisted process, oxygen gas was used. In the ion-pretreatment, the accelerating voltage was 150 V, the current was 100 mA, and the exposure time was 60 seconds; and in the ion-assisted process, the accelerating voltage was 100 V, and the accelerating current was 20 mA. In Comparative Examples 1 to 3 in which a conventional vapor source of ZrO_2 was used for forming the high-refraction layer of the antireflection film, the substrate was not pretreated with ions, and the formation of the high-refraction layer was not assisted by ions.]

[0025] Table 1

Table 1-1

	Example 1		Example 2		Example 3		Example 4		Example 5		Example 6	
	Substrate A	Substrate B	Substrate B	Substrate B	Substrate C	Substrate A	Substrate B	Substrate B	Substrate B	Substrate C	Substrate C	Substrate C
Hard coat layer	Layer A	Layer B	Layer B	Layer B	Layer C	Layer A	Layer B	Layer B	Layer B	Layer C	Layer C	Layer C
1st Layer	SiO ₂ 0.4875	SiO ₂ 0.0947	SiO ₂ 0.0947	SiO ₂ 0.0908	SiO ₂ 0.0908	SiO ₂ 0.3871	SiO ₂ 0.0426	SiO ₂ 0.0426	SiO ₂ 0.0426	SiO ₂ 0.0727	SiO ₂ 0.0727	SiO ₂ 0.0727
2nd Layer	Composition A 0.0502	Composition A 0.0348	Composition A 0.0348	Composition A 4044	Composition A 4044	Composition B 0.052	Composition B 0.0498	Composition B 0.0498	Composition B 0.0498	Composition B 0.0226	Composition B 0.0226	Composition B 0.0226
3rd Layer	SiO ₂ 0.0764	SiO ₂ 0.5839	SiO ₂ 0.5839	SiO ₂ 0.5839	SiO ₂ 0.5839	SiO ₂ 0.022	SiO ₂ 0.0227	SiO ₂ 0.0227	SiO ₂ 0.0227	SiO ₂ 0.033	SiO ₂ 0.033	SiO ₂ 0.033
4th Layer	Composition A 0.4952	Composition A 0.132	Composition A 0.132	Composition A 0.5809	Composition A 0.5809	Composition B 0.5204	Composition B 0.5004	Composition B 0.5004	Composition B 0.5004	Composition B 0.5402	Composition B 0.5402	Composition B 0.5402
5th Layer	SiO ₂ 0.2372	SiO ₂ 0.0691	SiO ₂ 0.0691	SiO ₂ 0.1297	SiO ₂ 0.1297	SiO ₂ 0.2572	SiO ₂ 0.0781	SiO ₂ 0.0781	SiO ₂ 0.0781	SiO ₂ 0.1097	SiO ₂ 0.1097	SiO ₂ 0.1097
6th Layer	Composition for vapor deposition Thickness (λ)	Composition for vapor deposition Thickness (λ)	Composition for vapor deposition Thickness (λ)	Composition A 0.1747	Composition A 0.1747	Composition A 0.2572	Composition B 0.0781	Composition B 0.0781	Composition B 0.0781	Composition B 0.0226	Composition B 0.0226	Composition B 0.0226
7th Layer	Composition for vapor deposition Thickness (λ)	Composition for vapor deposition Thickness (λ)	Composition for vapor deposition Thickness (λ)	SiO ₂ 0.2853	SiO ₂ 0.2853	SiO ₂ 0.2572	SiO ₂ 0.0781	SiO ₂ 0.0781	SiO ₂ 0.0781	SiO ₂ 0.2527	SiO ₂ 0.2527	SiO ₂ 0.2527
Melt condition of composition for vapor deposition	UA	UA	UA	UA	UA	UA	UA	UA	UA	UA	UA	UA
Attachment of fine particles	UA	UA	UA	UA	UA	UA	UA	UA	UA	UA	UA	UA
Alkali resistance	UA	UA	UA	UA	UA	UA	UA	UA	UA	UA	UA	UA
Scratch resistance	UA	UA	UA	UA	UA	UA	UA	UA	UA	UA	UA	UA
Film adhesiveness	100	100	100	100	100	100	100	100	100	100	100	100
Luminous reflectance Y (%)	0.458	0.48	0.48	0.5	0.5	0.476	0.561	0.561	0.561	0.486	0.486	0.486
Luminous transmittance Z (%)	99.01	99.223	99.223	99.289	99.289	99.002	99.23	99.23	99.23	99.301	99.301	99.301
Absorbance, 100-Y-Z (%)	0.532	0.297	0.297	0.211	0.211	0.522	0.209	0.209	0.209	0.213	0.213	0.213
Heat resistance (°C)	100	100	100	100	100	100	100	100	100	100	100	100
Heat resistance (°C) after exposure to the open air for 2 months	85	85	85	85	85	80	80	80	80	80	80	80

[0026] Table 2

Table 1-2

	Comp. Example 1	Comp. Example 2	Comp. Example 3	Comp. Example 4	Comp. Example 5	Comp. Example 6
	Substrate A Layer A	Substrate B Layer B	Substrate C Layer C	Substrate A Layer A	Substrate B Layer B	Substrate C Layer C
Plastic lens substrate						
Hard coat layer						
1st Layer Composition for vapor deposition Thickness (λ)	SiO ₂ 1.2444	SiO ₂ 0.3625	SiO ₂ 0.561	SiO ₂ 0.3871	SiO ₂ 0.0426	SiO ₂ 0.0727
2nd Layer Composition for vapor deposition Thickness (λ)	ZrO ₂ 0.0635	ZrO ₂ 0.0636	ZrO ₂ 0.0637	Nb ₂ O ₅ 0.0518	Nb ₂ O ₅ 0.0598	Nb ₂ O ₅ 0.0126
3rd Layer Composition for vapor deposition Thickness (λ)	SiO ₂ 0.0587	SiO ₂ 0.0588	SiO ₂ 0.0589	SiO ₂ 0.022	SiO ₂ 0.0227	SiO ₂ 0.033
4th Layer Composition for vapor deposition Thickness (λ)	ZrO ₂ 0.4204	ZrO ₂ 0.4205	ZrO ₂ 0.4206	Nb ₂ O ₅ 0.5129	Nb ₂ O ₅ 0.5044	Nb ₂ O ₅ 0.5329
5th Layer Composition for vapor deposition Thickness (λ)	SiO ₂ 0.253	SiO ₂ 0.2531	SiO ₂ 0.2832	SiO ₂ 0.2572	SiO ₂ 0.0781	SiO ₂ 0.1097
6th Layer Composition for vapor deposition Thickness (λ)			ZrO ₂ 0.4206			Nb ₂ O ₅ 0.0526
7th Layer Composition for vapor deposition Thickness (λ)			SiO ₂ 0.253			SiO ₂ 0.2527
Melt condition of composition for vapor deposition	UA	UA	UA	B	B	B
Attachment of fine particles	UA	UA	UA	B	B	B
Alkali resistance	UA to A	UA	UA	UA to A	UA to A	A
Scratch resistance	UA to A	UA	UA	UA	UA	UA
Film adhesiveness	98	99	98	100	100	100
Luminous reflectance Y (%)	0.476	0.476	0.476	1.025	1.442	1.352
Luminous transmittance Z (%)	99.002	99.002	99.002	97.568	96.89	97.063
Absorbance, 100-Y-Z (%)	0.522	0.522	0.522	1.407	1.668	1.585
Heat resistance (°C)	85	85	85	85	85	85
Heat resistance (°C) after exposure to the open air for 2 months	50	50	60	80	80	80

[0027]

As indicated in Table 1, the compositions A and B for vapor deposition of the invention used in Examples 1 to 6 were prevented from splashing, and stably deposited. Accordingly, attachment of fine particles by splashing was not found on the lens surface, and an excellent thin optical film was obtained.

Also as in Table 1, the antireflection film-coated plastic lenses of Examples 1 to 6 in which was used any of the composition A or B for vapor deposition of the invention all had better heat resistance as compared with the antireflection film-coated plastic lenses obtained in Comparative Examples 1 to 6, and their heat resistance lowered little with time.

[0028]

Example 7 to Example 18:

In the same manner as in Examples 1 to 6 but not assisted by ions, an antireflection film was formed under the condition as in Table 2 and Table 3, and tested for their properties. Though not assisted by ions, were obtained good physical properties as in Table 2 and Table 3.

In the Tables, λ indicates the wavelength of the light applied, and $\lambda = 500$ nm.

[0029] Table 3

	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12
Plastic lens substrate	Substrate A	Substrate B	Substrate C	Substrate A	Substrate B	Substrate C
Hard coat layer	Layer A	Layer B	Layer C	Layer A	Layer B	Layer C
1st Layer Composition for vapor deposition Thickness (λ)	SiO ₂ 0.0971	SiO ₂ 0.4728	SiO ₂ 0.0843	SiO ₂ 0.0501	SiO ₂ 0.4728	SiO ₂ 0.0843
2nd Layer Composition for vapor deposition Thickness (λ)	Composition A 0.01	Composition A 0.0759	Composition A 0.0379	Composition B 0.0382	Composition B 0.0759	Composition B 0.0379
3rd Layer Composition for vapor deposition Thickness (λ)	SiO ₂ 0.5783	SiO ₂ 0.0455	SiO ₂ 0.5031	SiO ₂ 0.6107	SiO ₂ 0.0455	SiO ₂ 0.5031
4th Layer Composition for vapor deposition Thickness (λ)	Composition A 0.0533	Composition A 0.4209	Composition A 0.065	Composition B 0.0625	Composition B 0.4209	Composition B 0.065
5th Layer Composition for vapor deposition Thickness (λ)	SiO ₂ 0.0681	SiO ₂ 0.2315	SiO ₂ 0.0456	SiO ₂ 0.072	SiO ₂ 0.2315	SiO ₂ 0.0456
6th Layer Composition for vapor deposition Thickness (λ)	Composition A 0.4777	Composition A	Composition A 0.4362	Composition B 0.5104	Composition B	Composition B 0.4362
7th Layer Composition for vapor deposition Thickness (λ)	SiO ₂ 0.2365	SiO ₂ 0.2365	SiO ₂ 0.2347	SiO ₂ 0.2511	SiO ₂ 0.2347	SiO ₂ 0.2347
Melt condition of composition for vapor deposition	UA	UA	UA	UA	UA	UA
Attachment of fine particles	UA	UA	UA	UA	UA	UA
Alkali resistance	UA	UA	UA	UA	UA	UA
Scratch resistance	UA	UA	UA	UA	UA	UA
Film adhesiveness	100	100	100	100	100	100
Luminous reflectance Y (%)	0.86	0.85	0.86	0.86	0.85	0.86
Luminous transmittance Z (%)	99.01	99.01	99	99.002	99.02	99
Absorbance, 100-Y-Z (%)	0.13	0.14	0.14	0.138	0.13	0.14
Heat resistance (°C)	100	100	100	100	100	100
Heat resistance (°C) after exposure to the open air for 2 months	85	85	85	85	85	85

Table 2

[0030] Table 4

Table 3

	Example 13	Example 14	Example 15	Example 16	Example 17	Example 18
Plastic lens substrate	Substrate A	Substrate B	Substrate C	Substrate A	Substrate B	Substrate C
Hard coat layer	Layer A	Layer B	Layer C	Layer A	Layer B	Layer C
1st Layer Composition for vapor deposition Thickness (λ)	SiO ₂ 0.459 Composition A 0.0458	SiO ₂ 0.4568 Composition A 0.0549	SiO ₂ 0.0698 Composition A 0.0407	SiO ₂ 0.801 Composition A 0.032	SiO ₂ 0.6121 Composition A 0.0465	SiO ₂ 0.1123 Composition A 0.0287
2nd Layer Composition for vapor deposition Thickness (λ)	SiO ₂ 0.0809 Composition A 0.14	SiO ₂ 0.0671 Composition A 0.1194	SiO ₂ 0.5275 Composition A 0.1179	SiO ₂ 0.102 Composition A 0.143	SiO ₂ 0.1004 Composition A 0.16	SiO ₂ 0.5762 Composition A 0.1035
3rd Layer Composition for vapor deposition Thickness (λ)	SiO ₂ 0.0597 Composition A 0.172	SiO ₂ 0.0543 Composition A 0.1658	SiO ₂ 0.0873 Composition A 0.1731	SiO ₂ 0.0584 Composition A 0.1603	SiO ₂ 0.0519 Composition A 0.1685	SiO ₂ 0.1017 Composition A 0.1484
4th Layer Composition for vapor deposition Thickness (λ)	SiO ₂ 0.2795 Composition A 0.172	SiO ₂ 0.2673 Composition A 0.1658	SiO ₂ 0.2839 Composition A 0.1731	SiO ₂ 0.287 Composition A 0.1603	SiO ₂ 0.2911 Composition A 0.1685	SiO ₂ 0.309 Composition A 0.1484
5th Layer Composition for vapor deposition Thickness (λ)	UA	UA	UA	UA	UA	UA
Melt condition of composition for vapor deposition	UA	UA	UA	UA	UA	UA
Attachment of fine particles	UA	UA	UA	UA	UA	UA
Alkali resistance	UA	UA	UA	UA	UA	UA
Scratch resistance	UA	UA	UA	UA	UA	UA
Film adhesiveness	100	100	100	100	100	100
Luminous reflectance Y (%)	0.84	0.84	0.92	0.8	1.02	1.05
Luminous transmittance Z (%)	99.01	99	98.9	99	98.74	98.7
Absorbance, 100-Y-Z (%)	0.15	0.16	0.18	0.2	0.24	0.25
Heat resistance (°C)	100	110	100	100	110	100
Heat resistance (°C) after exposure to the open air for 2 months	85	95	85	85	95	85

[0031]

Composition A and Composition B in the Tables above mean that the layer was formed of the composition A or the composition B.

The inventive examples of the present application describe preferred embodiments of the present invention. However, compositions having compositional ratios between the compositions of the examples are also preferred. Similarly, antireflection films having thicknesses between those disclosed in the examples are also preferred. Finally, optical elements, having layer structures between those disclosed in the examples are also preferred.

Advantages of the Invention

As is obvious from the above-mentioned Examples, the invention has made it possible to obtain an optical element having an antireflection film and having good heat resistance, which lowers little with time, even on a synthetic resin substrate that must be processed at low temperatures for vapor deposition thereon.

In addition, using the composition of the invention and according to the method for forming an antireflection film of the invention, high-refraction layers can be formed within a shorter period of time, and the good physical properties

intrinsic thereto are not worsened at all. The composition and the method of the invention ensure high working efficiency.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A composition comprising from 60 to 90% by weight of niobium oxide, calculated in terms of Nb_2O_5 , from 5 to 20% by weight of zirconium oxide, calculated in terms of ZrO_2 , and from 5 to 35% by weight of yttrium oxide, calculated in terms of Y_2O_3 , based on the total amount of the composition.
2. The composition according to claim 1, additionally comprising aluminum oxide.
3. The composition according to claim 2, wherein the aluminum oxide content, calculated in terms of Al_2O_3 , is from 0.3 to 7.5% by weight of the total of niobium oxide, zirconium oxide and yttrium oxide.
4. A method for forming an antireflection film comprising:
 - sintering a composition as defined in claim 1, 2 or 3;
 - vaporizing the resulting oxide; and
 - depositing the vapor on a substrate.
5. The method according to claim 4, wherein the substrate is a plastic substrate.
6. The method according to claim 5, wherein the plastic substrate has one or more coating layers.
7. The method according to claim 4, 5 or 6, which is combined with an ion-assisted process.
8. An antireflection film comprising, in an alternating fashion, at least one layer of silicon dioxide and at least

one layer obtainable as defined in any one of claims 4 to 7.

9. An optical element comprising a hard coat layer on a plastic substrate and an antireflection film as defined in claim 8.

10. An optical element according to claim 9, comprising a lens for spectacles, a lens for a camera, a windshield for an automobile, or an optical filter to be fitted to a display of a word processor.