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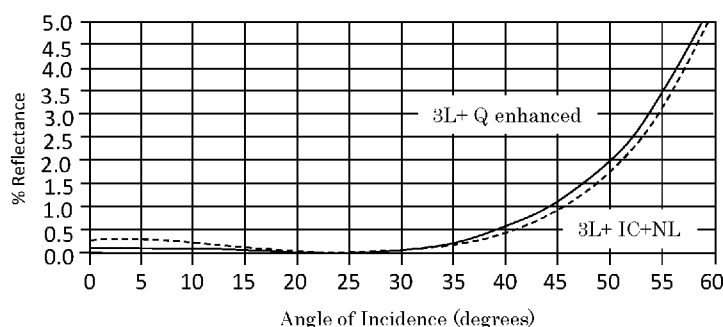


FIG. 9

(57) Abstract: A method of depositing an anti-reflection (AR) coating on an optical element, such as a lens, is disclosed, the method including tailoring an AR layer thickness on the optical element by tilting/masking in physical vapor deposition and depositing a nanolaminate capping layer overtop the AR layer by atomic layer deposition. A total thickness of the nanolaminate capping layer is less than about 30 nm.



SPECTRAL SHIFT FREE ANTI-REFLECTION COATINGS

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority under 35 U.S.C. §119 of U.S. Provisional Application Serial No. 63/617450 filed on January 4, 2024, the content of which is relied upon and incorporated herein by reference in its entirety.

FIELD

[0002] The disclosure generally relates to anti-reflection coatings, and in particular to AR coatings comprising an environmentally protective cap.

BACKGROUND

[0003] Anti-reflection (AR) coatings are an important aspect to precision optical elements, such as optical lenses used in laser applications. Many of these coatings, for example PVD fluoride films, can be porous and may absorb moisture when exposed to normal laboratory environments, e.g., 45% relative humidity (RH) at a room temperature. As a result, the coated lens may exhibit a spectral redshift due to changes in refractive index of the film.

[0004] What is needed is a spectral-shift-free AR coating for precision optics that maintains optical element surface reflectance to less than 0.5% for a prolonged lab exposure, i.e., a couple of days to a few weeks, instead of a few hours, and/or suitable for deep ultra-violet (DUV) precision optics objective coatings in a range from about 193 nm to about 266 nm. This extended time window can allow the completion of potting, testing, and final assembly of the DUV objectives.

SUMMARY

[0005] In a first aspect, an optical element is disclosed comprising a substrate comprising CaF_2 , SiO_2 , or F-SiO_2 , an AR coating deposited on the substrate, the AR coating comprising a PVD-deposited AR layer. The PVD-deposited layer comprises a plurality of discrete AR layers, the discrete AR layers comprising a first discrete AR layer comprising a high refractive index material or a low refractive index material and a second discrete AR layer deposited on the first discrete AR layer, the second discrete AR layer comprising a low refractive index material if

the first discrete AR layer is a high refractive index material or a high refractive index material if the first discrete AR layer is a low refractive index material. A nanolaminate capping layer is disposed over the PVD-deposited AR layer, the nanolaminate capping layer comprising an ALD-deposited Al_2O_3 layer and an ALD-deposited SiO_2 capping layer, the nanolaminate capping layer comprising a total thickness equal to or less than about 30 nm.

[0006] In a second aspect, the total thickness of the nanolaminate capping layer may be equal to or less than about 20 nm.

[0007] In a third aspect, the total thickness of the nanolaminate capping layer is equal to or less than about 10 nm.

[0008] In a fourth aspect, the nanolaminate capping layer comprises a plurality of capping layers and a thickness of each capping layer of the plurality of capping layers is equal to or less than about 0.5 nm.

[0009] In a fifth aspect, the AR coating may comprise an SiO_2 barrier layer disposed between the AR layer and the nanolaminate capping layer.

[0010] In a sixth aspect, the optical element comprises a lens comprising at least one curved surface and the AR coating is deposited on the curved surface.

[0011] In a seventh aspect, a reflectance of the optical element at an external surface of the AR coating is equal to or less than about 0.5% at an angle of incidence in a range from 0 degrees to 35 degrees at a wavelength of 193.4 nanometers.

[0012] In an eighth aspect, a reflectance of the optical element at an external surface of the AR coating is equal to or less than about 0.5% at an angle of incidence in a range from 0 degrees to 40 degrees at a wavelength of 266 nanometers.

[0013] In a ninth aspect, the SiO_2 capping layer is in contact with the Al_2O_3 capping layer.

[0014] In a tenth aspect, the PVD-deposited AR layer comprises a first layer of Al_2F_3 deposited on the substrate, a second layer of GdF_3 deposited on the first layer, a third layer of Al_2F_3 deposited on the second layer, the optical element further comprising an SiO_2 barrier layer deposited on the PVD-deposited AR layer, the nanolaminate capping layer deposited on the SiO_2 barrier layer.

[0015] In an eleventh aspect, the PVD-deposited AR layer comprises a first layer of HfO_2 deposited on the substrate, a second layer of SiO_2 deposited on the first layer, a third layer of HfO_2 deposited on the second layer, and a fourth layer of SiO_2 deposited on the third layer.

[0016] In a twelfth aspect, a method of making an AR-coated optical element is disclosed, comprising depositing on a substrate by PVD an AR layer comprising a high refractive index

material layer and a low refractive index material layer, the substrate comprising CaF_2 , SiO_2 , or F- SiO_2 . The method further comprises depositing over the AR layer by atomic layer deposition a nanolaminate capping layer with a total thickness equal to or less than about 30 nm, the nanolayer capping layer comprising an Al_2O_3 capping layer and an SiO_2 capping layer.

[0017] In a thirteenth aspect, the total thickness of the nanolaminate capping layer is equal to or less than about 10 nm.

[0018] In a fourteenth aspect, the total thickness of the nanolaminate capping layer is equal to or less than about 5 nm.

[0019] In a fifteenth aspect, the method may further comprise depositing an SiO_2 barrier layer on the AR layer prior to the depositing the nanolaminate capping layer.

[0020] In a sixteenth aspect, a thickness of the SiO_2 barrier layer is in a range from about 5 nm to about 60 nm.

[0021] In a seventeenth aspect, the SiO_2 capping layer is in contact with the Al_2O_3 capping layer.

[0022] In an eighteenth aspect, an optical axis of the optical element is tilted away from at least one of a source of the high refractive index material or a source of the low refractive index material during the depositing at least one of the AR layer or the nanolaminate capping layer.

[0023] Additional features and advantages will be set forth in the detailed description which follows, and in part will be readily apparent to those skilled in the art from that description or recognized by practicing the embodiments as described herein, including the detailed description which follows, the claims, as well as the appended drawings.

[0024] It is to be understood that both the foregoing general description and the following detailed description are merely exemplary and are intended to provide an overview or framework to understanding the nature and character of the claims. The accompanying drawings are included to provide a further understanding and are incorporated in and constitute a part of this specification. The drawings illustrate one or more embodiments, and together with the description explain principles and operation of the various embodiments.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025] FIG. 1 is a plot of reflectance in percent as a function of the angle of incidence of impinging light on an optical element (e.g., lens), showing spectral performance of a 3L + QR AR-coated lens vs. a 3L AR-coated lens;

[0026] FIG. 2 is a cross-sectional view of a lens assembly comprising 15 lens elements numbered E1-E15;

[0027] FIG. 3 is a plot of reflectance in percent as a function of the angle of incidence of impinging light on an optical element (e.g., lens), showing spectral performance of a 3L + QR AR-coated lens vs. a 3L + Q enhanced AR-coated lens;

[0028] FIG. 4 is a plot of reflectance as a function of wavelength in nanometers (nm) showing a redshift due to environmental exposure;

[0029] FIG. 5 is a schematic view of a lens assembly comprising 10 lens elements numbered E1 to E10;

[0030] FIG. 6A is a schematic view of a deposition process utilizing tilted physical vapor deposition;

[0031] FIG. 6B is a schematic view of a deposition process not utilizing tilted physical vapor deposition;

[0032] FIG. 7 is a plot of reflectance as a function of wavelength in nanometers (nm) showing a redshift due to environmental exposure;

[0033] FIG. 8 is a cross-sectional side view of an exemplary calcium fluoride (CaF_2) optical element comprising a fluoride-based AR coating (3L + IC + NL) comprising a 3-layer (3L) PVD-deposited fluoride AR layer and an ALD nanolaminate (NL) cap;

[0034] FIG. 9 is a plot of reflectance in percent as a function of angle of incidence in degrees for the exemplary optical element of FIG. 8, with the optical performance of a 3L+Q enhanced AR coated lens shown for comparison;

[0035] FIG. 10 is a cross-sectional side view of an exemplary optical element comprising an HPFS lens, a four layer (4L) AR layer, and an ALD deposited nanolaminate (NL) cap, with the spectral performance of a 4L AR coated optical element without capping layer shown for comparison; and

[0036] FIG. 11 is a plot of reflectance in percent as a function of angle of incidence in degrees for the exemplary optical element of FIG. 10.

DETAILED DESCRIPTION

[0037] In the following detailed description, for purposes of explanation and not limitation, example embodiments disclosing specific details are set forth to provide a thorough understanding of various principles of the present disclosure. However, it will be apparent to one having ordinary skill in the art, having had the benefit of the present disclosure, that the

present disclosure may be practiced in other embodiments that depart from the specific details disclosed herein. Moreover, descriptions of well-known devices, methods and materials may be omitted so as not to obscure the description of various principles of the present disclosure. Finally, wherever applicable, like reference numerals refer to like elements.

[0038] Ranges can be expressed herein as from “about” one particular value, and/or to “about” another particular value. When such a range is expressed, another embodiment includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent “about,” it will be understood that the particular value forms another embodiment. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint.

[0039] Unless otherwise expressly stated, it is in no way intended that any method set forth herein be construed as requiring that its steps be performed in a specific order. Accordingly, where a method claim does not actually recite an order to be followed by its steps, or it is not otherwise specifically stated in the claims or descriptions that the steps are to be limited to a specific order, it is no way intended that an order be inferred, in any respect. This holds for any possible non-express basis for interpretation, including matters of logic with respect to arrangement of steps or operational flow; plain meaning derived from grammatical organization or punctuation; the number or type of embodiments described in the specification.

[0040] As used herein, the singular forms “a,” “an” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to a “component” includes aspects having two or more such components, unless the context clearly indicates otherwise.

[0041] For brevity, ranges of values disclosed herein, including compositional ranges or attribute (performance) ranges, or series of ranges, may be appended by the phrase “including all ranges and subranges therebetween,” which is to be interpreted as including whole number or decimal subranges as though explicitly presented. Thus, by way of example, a range between 6 and 8 (units omitted) implicitly includes a subrange between 6.4 and 8, or a subrange between 6 and 7.2, or a subrange between 6 and 7, and so forth. Additionally, a series of ranges, such as “in a range from 6 to 11 or in a range from 6 to 8” implicitly includes a range from 7 to 10, or subranges therebetween, such as 7.2 to 10.4, as though explicitly presented, provided the range does not exceed the minimum or maximum endpoints of the explicitly presented range or series of ranges. Thus, for example, “in a range from 6 to 11 or in a range from 6 to 8” has as endpoints 6 and 11.

[0042] Anti-reflection coatings find use in the manufacture of precision optical elements, such as optical lenses used in laser applications. Many of these coatings, such as physical vapor deposited (PVD) fluoride coatings, e.g., coatings applied by evaporation, can be porous and may absorb moisture when exposed to normal laboratory environments, e.g., 45% relative humidity (RH) at room temperature, e.g., 22°C. PVD is a line-of-sight deposition process and may pose a problem for steep lens surfaces wherein the coating material arrives at very large impingement angles relative to a normal to the lens surface. As a result, coating thickness and mechanical properties can be substantially different toward the edge of the lens surface compared to the center of the lens surface. For example, the coating may be thinner and have a reduced packing density toward the edge of the lens full clear aperture (CA), which is the largest aperture of a lens that meets a predetermined optical specification. As a result, a standard PVD coating on a hemispherical lens may result in a thickness uniformity as low as 20% of the coating thickness at the center of the lens. This reduced coating thickness uniformity may lead to high spectral reflectance and polarization split at the edge of the lens. Tilting of the lens during coating deposition can improve coating uniformity on steep surfaces but may reduce coating packing density toward the center of the lens, leading to increased scattering loss at the lens center. Plasma interaction with the tilted surface may be difficult when a high tilt angle is selected to achieve a desired uniformity. Moreover, the effectiveness of plasma densification is reduced at high ion impingement angles and/or high angles of deposition for precision optics and plasma ion densification is ineffective when a lens is tilted away from the plasma source. Additionally, some lens fixture design challenges may accompany tilting during coating deposition. Tilting increases the coating deposition angle ($> 60^\circ$) at the 0 CA. High deposition angle results in high porosity.

[0043] Masking is another approach that may improve PVD coating uniformity, including stationary masks and moving masks. Stationary masking may work better for large optics, whereas moving masks may improve uniformity distribution over small optics. However, both tilting and masking are based on PVD processes.

[0044] It is desirable to have an AR coating with good uniformity, particularly on curved surfaces. Atomic layer deposition (ALD) is a thin film deposition process based on sequential exposure of a substrate to self-limiting surface half-reactions. Advantages of ALD for optical coatings include the placement of conforming layers on curved surfaces enabling application of AR coatings on both sides of a lens element simultaneously, simplified lens fixture design, and reduced risk of mechanically damaging the lens element during the coating process.

[0045] Environmentally stable deep ultraviolet (DUV) AR coatings have been developed for laser optics by employing a half-wave silica barrier layer overtop the AR coating. The barrier layer comprises a thin protective silica layer Q and a thicker plasma-ion densified layer R. The Q layer may be a thin F-SiO₂ layer deposited using PVD at about 300°C without plasma involvement. The densified R layer typically utilizes plasma-ion assisted deposition (PIAD) of an F-SiO₂ layer as an outermost densified layer. By way of example, the Q and R layer thicknesses may be 10 nanometer (nm) and 52 nm, respectively, for a 3-layer (3L) fluoride AR coating at 193.4 nm and a normal (90°) angle of incidence (AOI) of incoming light rays. While the densified R layer can effectively prevent moisture penetration with full densification, the Q layer protects the underlying AR coating from plasma-induced damage during deposition of the densified R layer using a PIAD process. The densified R layer may have a packing density, for example, of 100%. FIG. 1 is a plot showing a side-by-side comparison of reflectance in percent as a function of AOI for incoming light rays for 3L (without QR barrier layers) and 3L+QR AR coatings at 193.4 nm. The total optical thickness of the QR layer corresponds to a half-wave optical thickness at 193.4 nm. The environmental protection afforded by the QR barrier layer comes at the cost of reduced anti-reflection properties. The data show that for an AOI of 40 degrees the 3L anti-reflection layer provides a reflectance of about 0.5%, while the 3L+QR AR coating provided a reduced reflectance of about 3%. However, the 3L+QR AR coating produced environmentally stable optical performance: A spectral shift-free AR was confirmed even after a 6-month lab exposure.

[0046] Lens assembly and testing is a complex and time-consuming process. Coated optical elements may sit in a testing facility (e.g., laboratory) longer than desired, wherein the optical element may be exposed to a greater humidity or temperature than desired. As a result, a well-aligned optical element, for example an objective lens in an optical assembly, may need disassembly to conduct additional ultraviolet-ozone (UVO) cleaning to bring axial transmission into specified parameters. A prolonged lab exposure may lead to a spectral redshift that results in an increase in reflectance at 193.4 nm up to about 1%. If all surfaces have 1% reflectance, an axial transmission of the system may be only 74%, which can be out of specification. This spectral redshift not only reduces the manufacturing productivity of precision optics but may impact system performance of the optical system in which the precision optical component is used.

[0047] Extending the barrier layer concept to wide angle AR coatings for high numerical aperture (NA) objectives is therefore considered. For example, a complex optical lens

assembly shown in FIG. 2 comprises high purity fused silica (HPFS) and calcium fluoride (CaF₂) lens elements. The lens assembly comprises 15 lens elements E1-E15 and therefore 30 optical surfaces (left to right) with various surface curvatures. The angle of incidence at 100CA (or 100% clear aperture, i.e., including marginal rays) may be beyond 40 degrees for several HPFS and CaF₂ lens elements in the system while an axial transmission greater than 76% may be one of the system requirements. Wide-angle AR coatings have been specifically developed for precision optics, where the Q layer thickness is increased by 50% (e.g., from about 10 nm to about 15 nm). A densified R layer may or may not be used. This enhanced Q layer eliminates moisture penetration into the underlying AR (e.g., fluoride) coating layers during lens testing and assembly phases while maintaining a reflectance less than 0.5% over a wide range of angle of incidence. FIG. 3 is a plot showing a side-by-side comparison of a 3L+Q enhanced AR coating and a 3L+QR AR coating in terms of reflectance as a function of angle of incidence at 193.4 nm. The thickness of the enhanced Q layer (Q enhanced) may be about 15 nm for precision optics applications, whereas the Q layer thickness can be about 10 nm in the 3L+QR design for laser optical elements. As can be seen, the 3L+Q enhanced AR coating provides a broader angle of incidence, from about 0 degrees to about 40 degrees, when compared to an angle of incidence range of 0 degrees to about 30 degrees for a 3L+QR AR coating having a reflectance value of 0.5%. Combining masking and/or lens tilting during deposition along with ultraviolet-ozone (UVO) cleaning, the 3L+Q enhanced AR coating can meet the system requirement. By using this 15 nm Q layer, axial transmission can be as high as 86% for the 30-surface lens assembly of FIG. 2. As an example, such an axial transmission value corresponds to an optical loss less than about 0.5% per surface for the 30-surface system.

[0048] UVO cleaning vaporizes absorbed moisture within the AR coatings. The enhanced Q layer reduces the rate of moisture re-penetration into the underlying AR coating. No noticeable spectral redshift occurs within a couple of hours after exposing a UVO-cleaned coated lens to lab conditions without N₂ or dry-clean-air (DCA) purging. This operation window allows lens testing and assembly to be performed.

[0049] Still, there may be a problem in practice. Sometimes, the coated lens elements may sit in a lab longer than expected, during which time a coated lens may be exposed to a humidity or a temperature higher than desired. FIG. 4 plots an initial reflectance (dashed curve) as a function of wavelength at 0 CA of E15R1 (where R1 denotes the first surface of the 15th lens element, left side in the figure) with the 3L+Q enhanced AR coating. Initial reflectance is determined after UVO cleaning to remove absorbed moisture. The solid curve shows

reflectance as a function of wavelength after several hours at room temperature (i.e., 22 °C) and 45% RH. The data show, for example, that the brief environmental exposure resulted in an approximately 12 nm shift in minimum reflectance, illustrating the wavelength dependence of the AR coating. A prolonged lab exposure may lead to spectral redshift that results in a reflectance increase to about 1% at 193.4 nm. If all surfaces have 1% reflectance, an axial transmission of the system is only 74%, which may be out of specification.

[0050] There is a need, therefore, for a spectral-shift-free AR coating for precision optics that maintains reflectance to less than about 0.5% for a prolonged lab exposure, e.g., a couple of days to a few weeks, instead of a few hours. This extended time window allows completion of potting, testing, and final assembly of DUV optical assemblies.

[0051] Also needed is a spectral-shift-free PIAD-oxide AR coating for tilt-applied coatings for precision optical assemblies at 266 nm. PIAD-SiO₂ and PIAD-HfO₂ 4-layer AR coatings may be used to address this challenge and to explain why there is a need even for PIAD-oxide AR coated lens. FIG. 5 is a cross-sectional optical diagram of a 266 nm optical assembly comprising 10 HPFS lenses. The first surface of lens element 9 (E9R1) has a convex shape with steep surface slopes. This surface is tilted from the optical axis at an angle of 47 degrees for the AR coating deposition. Also included is E1R1, a relatively flat surface, for comparison.

[0052] The advantages of PVD and atomic level deposition (ALD) are combined to provide high performance AR coatings for demanding precision optical systems at wavelengths in a range from about 190 nm to about 270 nm, e.g., 193 nm, 213 nm, and/or 266 nm. PVD is used to tailor a desired AR coating layer thickness distribution and ALD is used to deposit an Al₂O₃-SiO₂ nanolamination barrier layer to seal the PVD-deposited AR coating, thereby providing a spectral-shift-free AR coating.

[0053] FIGS. 6A and 6B are schematic diagrams showing a tilted AR coating application for E9R1 (FIG. 6A) and a non-tilted AR coating for E1R1 (FIG. 6B). Both E9R1 and E1R1 AR coatings use a 4-layer alternating PIAD-HfO₂ and PIAD-SiO₂ coating. The AR coating on the E1R1 lens surface is spectral-shift-free, whereas the AR coating on the E9R1 lens surface is sensitive to lab exposure. Accordingly, exposure of E9R1 to a lab environment may lead to a spectral redshift in optical performance.

[0054] FIG. 7 plots initial (dashed curved) and redshifted (solid curve) spectral reflectance of E9R1 at 0 CA and 8 degrees AOI. As shown, the redshift moves the minimum spectral reflectance from 290 nm to 345 nm. The 55 nm red-shift leads to an increase of reflectance from 0.3% to 2.5% at 266 nm.

[0055] The present disclosure combines the advantages of PVD and ALD to deliver high performance AR coatings for demanding precision optical systems at 193 nm, 213 nm, and 266 nm. PVD is used to tailor a desired coating layer thickness distribution and ALD derived Al_2O_3 - SiO_2 nanolamination is used to seal the PVD AR coating, leading to spectral-shift-free AR coatings for precision optics.

[0056] FIG. 8 is a schematic diagram of an ALD nanolaminate (NL) capping layer over a 3L fluoride-based AR coating (3L + IC + NL) 100 on a calcium fluoride (CaF_2) lens 102, the AR coating comprising a 3-layer PVD-fluoride AR layer (3L) 104 including a first AR layer 106 of aluminum fluoride (AlF_3), a second AR layer 108 of gadolinium fluoride (GdF_3), and a third AR layer 110 of AlF_3 . A 5 nm PVD-Q (SiO_2) barrier layer 112 (IC) is deposited overtop AR layer 104, and a nanolaminate (NL) capping layer 114 is deposited overtop the barrier layer, such as in contact with the barrier layer, NL capping layer 114 comprising at least a first capping layer 116 comprising Al_2O_3 and optionally a second capping layer 118 comprising SiO_2 overtop the Al_2O_3 capping layer. NL capping layer 114 is deposited by ALD. A total thickness of NL capping layer 114 may be equal to or less than about 30 nm, for example equal to or less than about 20 nm, such as equal to or less than about 10 nm, equal to or less than about 5 nm, or even equal to or less than about 1 nm, including all ranges and subranges therebetween. The NL capping layer thickness may be measured, for example, by spectroscopic ellipsometry. As described, NL capping layer 114 may comprise a plurality of individual discrete capping layers. Individual capping layers may each be equal to or less than about 0.5 nm, for example equal to or less than about 0.3 nm. While two capping layers are shown, NL capping layer 114 may have more than two capping layers. By way of example, lens surface 118 is the E14R1 surface from the 30-surface lens system of FIG. 2 and the reflectance curve in percent reflectance as a function of AOI at 193.4 nm is plotted in FIG. 9. A curve of a 3L + Q enhanced coated lens is shown for comparison. FIG. 9 shows a reflectance of the optical element at an external surface of the AR coating equal to or less than about 0.5% at an angle of incidence in a range from 0 degrees to equal to or greater than 35 degrees at a wavelength of 193.4 nanometers after exposure of the optical element to a temperature of 22°C and 45% RH for 48 hours. The ALD nanolaminate-capped AR coating 100 achieves similar spectral reflectance as that of the initial PVD 3L+Q enhanced AR coating at 193.4 nm but enables a substantially spectral-shift-free performance.

[0057] Fig. 10 is a cross-sectional schematic diagram of a 4L ALD deposited nanolaminate (NL) capped AR coating 200 on an HPFS lens 202 similar to that shown in FIG. 8. AR coating

200 comprises a 4-layer PIAD-oxide AR layer 202 (TL + NL) including a first AR layer 206 of hafnium oxide (HfO_2), a second AR layer 208 of silica (SiO_2), a third AR layer 210 of HfO_2 , and a fourth AR layer 212 of silica. A nanolaminate (NL) capping layer 214 is deposited overtop AR layer 202, for example in contact with AR layer 202, NL capping layer 214 comprising a first capping layer 216 of Al_2O_3 and a second capping layer 218 of SiO_2 overtop the Al_2O_3 such that the silica capping layer is exposed to the external environment. NL capping layer 214 is deposited by ALD. A total thickness of NL capping layer 214 is equal to or less than about 30 nanometers, for example equal to or less than about 20 nm, such as equal to or less than about 10 nm, equal to or less than about 5 nm, or equal to or less than about 1 nm. NL capping layer 214 may comprise a single capping layer or a plurality of individual capping layers. Individual capping layers may be equal to or less than about 0.5 nm, for example equal to or less than about 0.3 nm. While two capping layers are shown, NL capping layer 214 may have fewer than two layers or more than two capping layers. The lens surface 220 is the E9R1 surface from the 10-lens system previously described and the reflectance curve at 193.4 nm is plotted in FIG. 11. FIG. 11 shows a reflectance of the optical element at an external surface of the AR coating is equal to or less than about 0.5% at an angle of incidence in a range from 0 degrees to equal to or greater than 40 degrees at a wavelength of 266 nanometers after exposure of the optical element to a temperature of 22°C and 45% RH for 48 hours. A 47-degree tilt was employed in both cases for the PVD process. A curve of a 4L AR coated lens is shown for comparison. Again, the ALD nanolaminate capped AR coating achieves similar spectral reflectance as that of the initial PVD 4L AR at 266 nm but enables spectral-shift-free performance.

[0058] It will be apparent to those skilled in the art that various modifications and variations can be made to embodiments of the present disclosure without departing from the spirit and scope of the disclosure. Thus, it is intended that the present disclosure cover such modifications and variations provided they come within the scope of the appended claims and their equivalents.

What is claimed is:

1. An optical element, comprising:
 - a substrate comprising CaF_2 , SiO_2 , or F-SiO_2 ;
 - an AR coating deposited on the substrate, the AR coating comprising:
 - a PVD-deposited AR layer comprising a plurality of discrete AR layers, the discrete AR layers comprising:
 - a first discrete AR layer comprising a high refractive index material or a low refractive index material;
 - a second discrete AR layer deposited on the first discrete AR layer, the second discrete AR layer comprising a low refractive index material if the first discrete AR layer is a high refractive index material or a high refractive index material if the first discrete AR layer is a low refractive index material; and
 - a nanolaminate capping layer disposed over the PVD-deposited AR layer, the nanolaminate capping layer comprising an ALD-deposited Al_2O_3 capping layer and an ALD-deposited SiO_2 capping layer, the nanolaminate capping layer comprising a total thickness equal to or less than about 30 nm.
2. The optical element of claim 1, wherein the total thickness of the nanolaminate capping layer is equal to or less than about 20 nm.
3. The optical element of claim 1, wherein the total thickness of the nanolaminate capping layer is equal to or less than about 10 nm.
4. The optical element of any one of claims 1 to 3, wherein the nanolaminate capping layer comprises a plurality of capping layers and a thickness of each capping layer of the plurality of capping layers is equal to or less than about 0.5 nm.
5. The optical element of any one of claims 1 to 4, wherein the AR coating comprises an SiO_2 barrier layer disposed between the AR layer and the nanolaminate capping layer.

6. The optical element of any one of claims 1 to 5, wherein the optical element comprises a lens comprising at least one curved surface and the AR coating is deposited on the curved surface.
7. The optical element of any one of claims 1 to 6, wherein a reflectance of the optical element at an external surface of the AR coating is equal to or less than about 0.5% at an angle of incidence in a range from 0 degrees to 35 degrees at a wavelength of 193.4 nanometers.
8. The optical element of any one of claims 1 to 6, wherein a reflectance of the optical element at an external surface of the AR coating is equal to or less than about 0.5% at an angle of incidence in a range from 0 degrees to 40 degrees at a wavelength of 266 nanometers.
9. The optical element of any one of claims 1 to 7, wherein the SiO₂ capping layer is in contact with the Al₂O₃ capping layer.
10. The optical element of any one of claims 1 to 9, wherein the PVD-deposited AR layer comprises a first layer of Al₂F₃ deposited on the substrate, a second layer of GdF₃ deposited on the first layer, a third layer of Al₂F₃ deposited on the second layer, the optical element further comprising an SiO₂ barrier layer deposited on the PVD-deposited AR layer, the nanolaminate capping layer deposited on the SiO₂ barrier layer.
11. The optical element of any one of claims 1 to 9, wherein the PVD-deposited AR layer comprises a first layer of HfO₂ deposited on the substrate, a second layer of SiO₂ deposited on the first layer, a third layer of HfO₂ deposited on the second layer, and a fourth layer of SiO₂ deposited on the third layer.
12. A method of making an AR-coated optical element, comprising:
 - depositing on a substrate by PVD an AR layer comprising a high refractive index material layer and a low refractive index material layer, the substrate comprising CaF₂, SiO₂, or F-SiO₂;
 - depositing over the AR layer by atomic layer deposition a nanolaminate capping layer with a total thickness equal to or less than about 30 nm, the nanolayer capping layer comprising an Al₂O₃ capping layer and an SiO₂ capping layer.

13. The method of claim 12, wherein the total thickness of the nanolaminate capping layer is equal to or less than about 10 nm.
14. The method of claim 12, wherein the total thickness of the nanolaminate capping layer is equal to or less than about 5 nm.
15. The method of any one of claims 12 to 14, further comprising depositing an SiO₂ barrier layer on the AR layer prior to the depositing the nanolaminate capping layer.
16. The method of claim 15, wherein a thickness of the SiO₂ barrier layer is in a range from about 5 nm to about 60 nm.
17. The method of any one of claims 12 to 16, wherein the SiO₂ capping layer is in contact with the Al₂O₃ capping layer.
18. The method of any one of claims 12 to 17, wherein an optical axis of the optical element is tilted away from at least one of a source of the high refractive index material or a source of the low refractive index material during the depositing at least one of the AR layer or the nanolaminate capping layer.

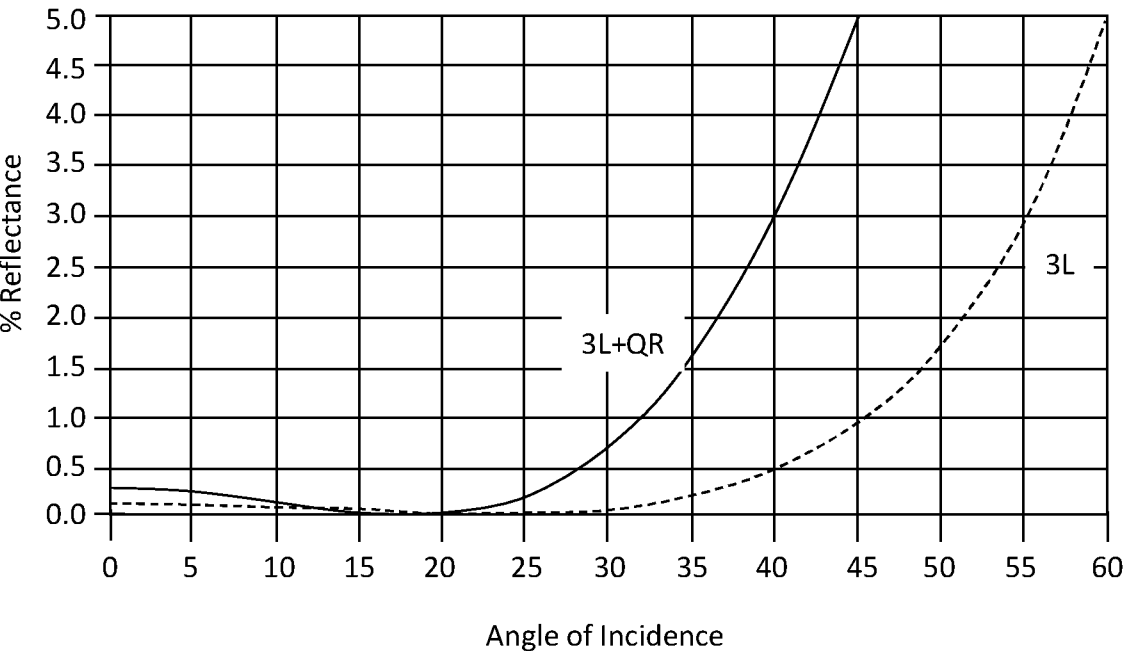


FIG. 1

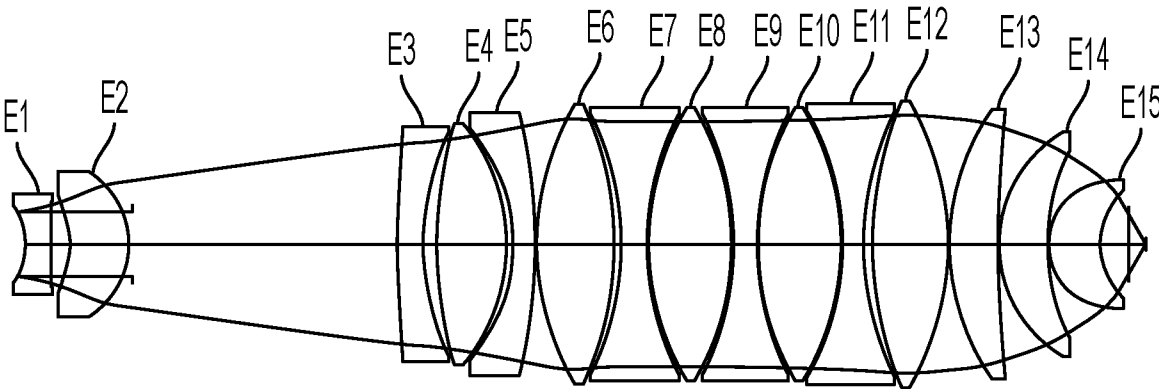


FIG. 2

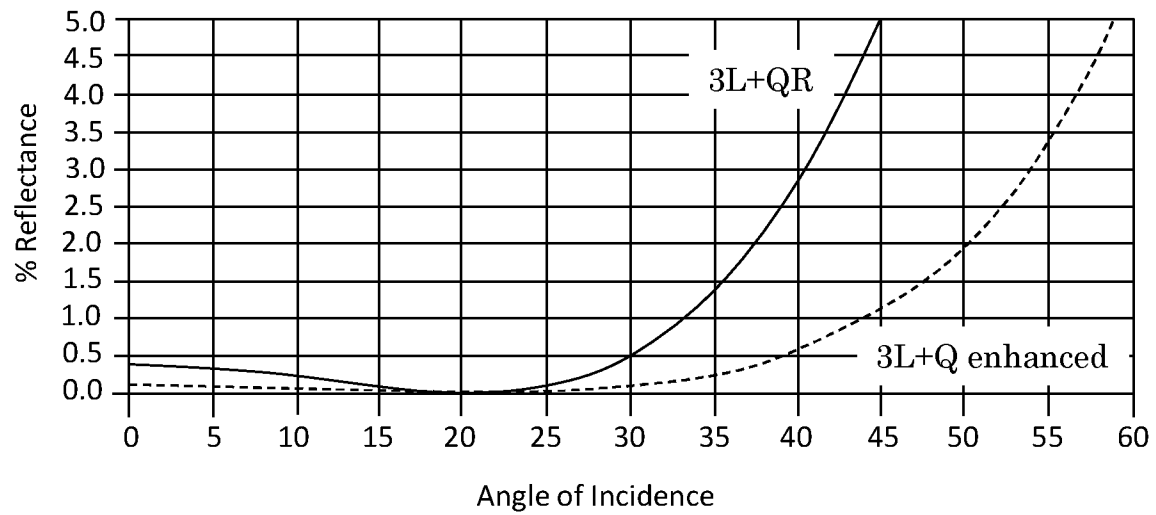


FIG. 3

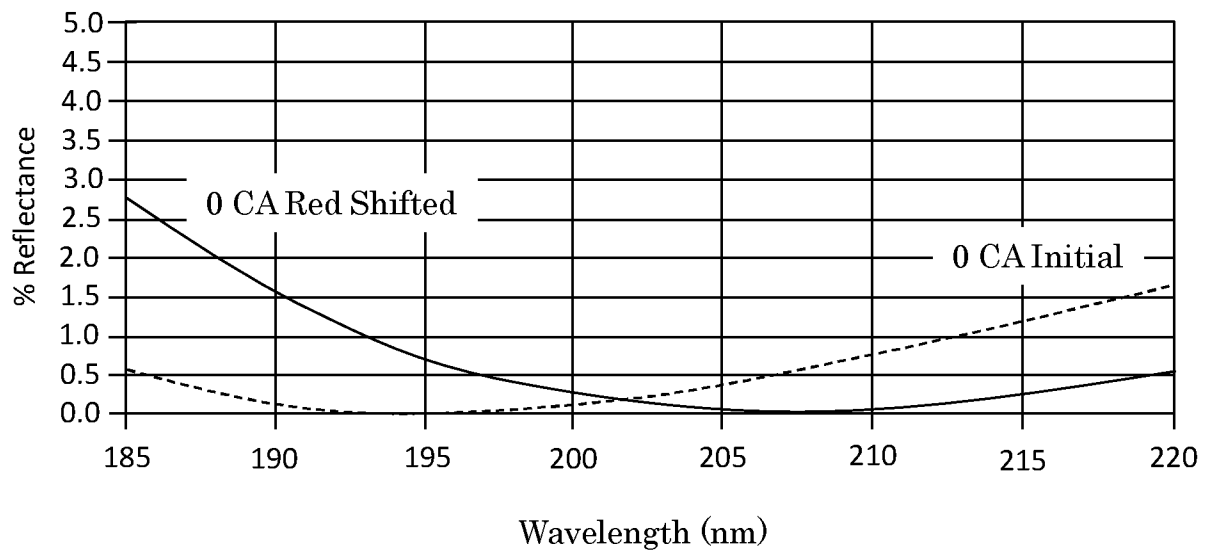


FIG. 4

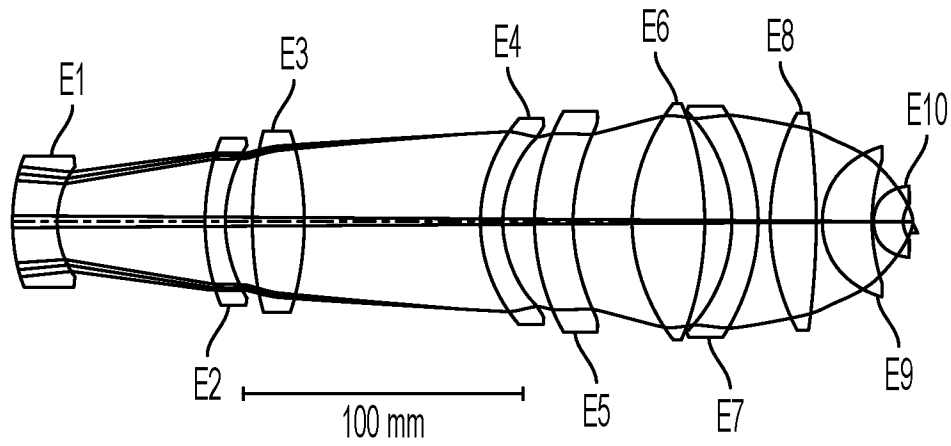


FIG. 5

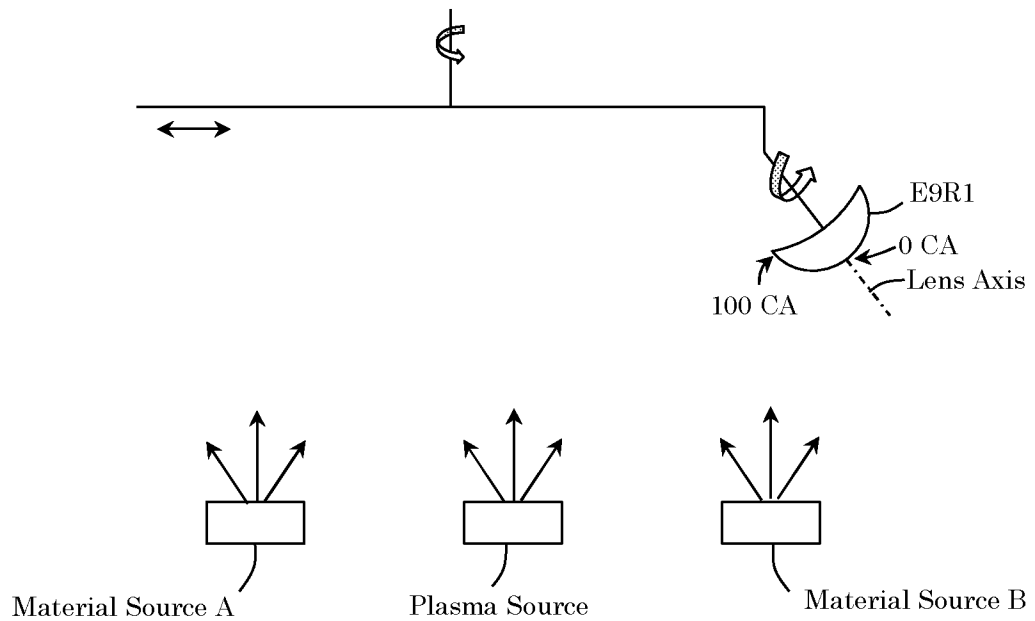


FIG. 6A

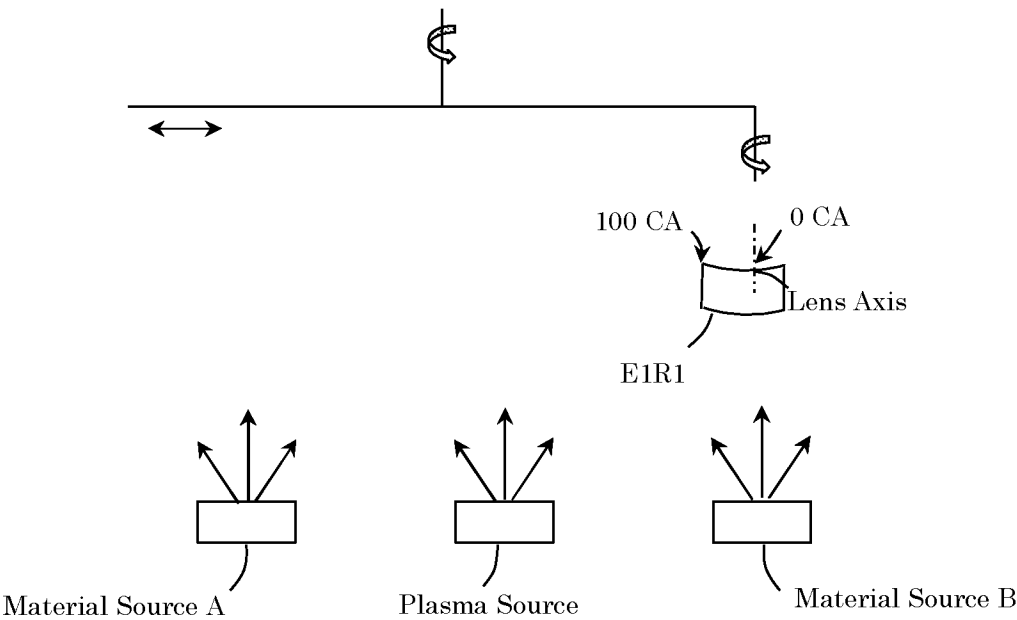


FIG. 6B

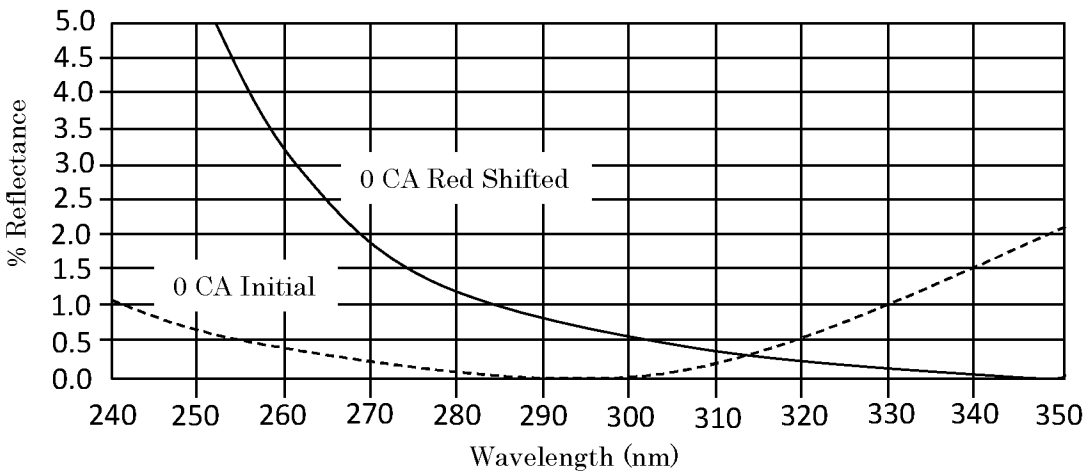


FIG. 7

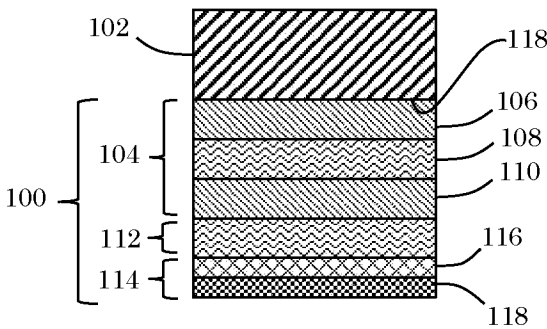


FIG. 8

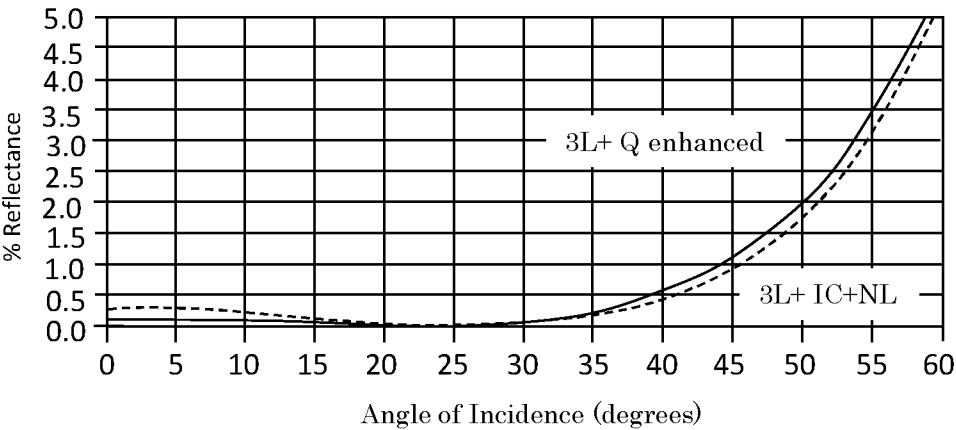


FIG. 9

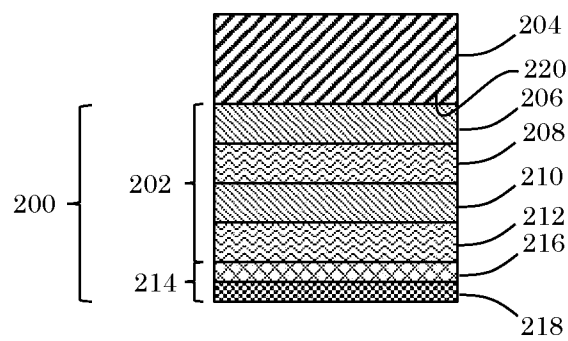


FIG. 10

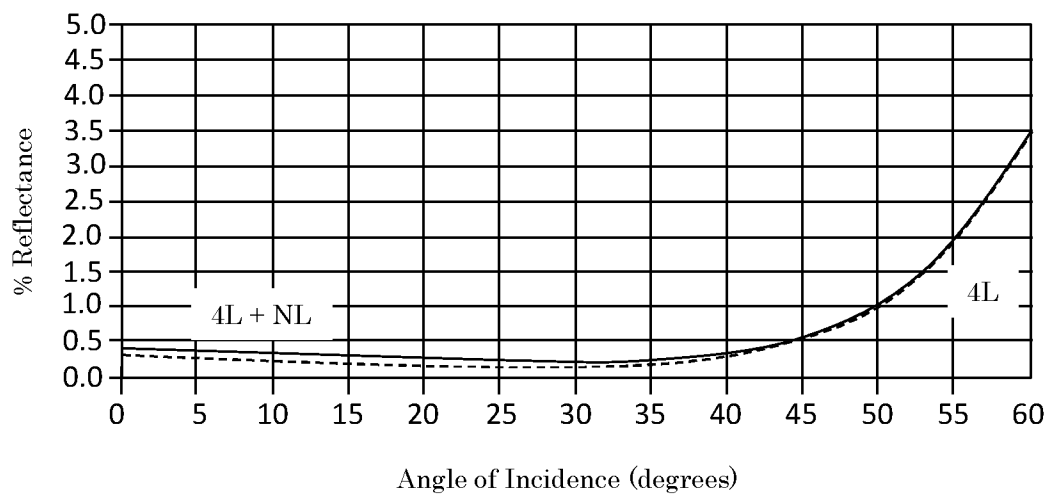


FIG. 11

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2024/059097

A. CLASSIFICATION OF SUBJECT MATTER					
INV.	G02B1/14	G02B1/115	G02B13/14	C23C16/30	C23C16/455
	G03F7/00	C23C14/08			
ADD.					
According to International Patent Classification (IPC) or to both national classification and IPC					
B. FIELDS SEARCHED					
Minimum documentation searched (classification system followed by classification symbols)					
G02B C23C G03F					
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched					
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)					
EPO-Internal					
C. DOCUMENTS CONSIDERED TO BE RELEVANT					
Category*	Citation of document, with indication, where appropriate, of the relevant passages				Relevant to claim No.
Y	US 2012/212716 A1 (SHIRAI TAKESHI [JP] ET AL) 23 August 2012 (2012-08-23) paragraphs [0017] - [0035], [0059], [0238] - [0244], [0288] - [0294], [0353]; figure 7; tables 1, 8				1-18
Y	US 2023/287557 A1 (HU YIMIN [US] ET AL) 14 September 2023 (2023-09-14) paragraphs [0014] - [0061]				1-18
A	US 2023/123796 A1 (ALLEN DONALD ERWIN [US] ET AL) 20 April 2023 (2023-04-20) the whole document				1-17
A	US 11 714 212 B1 (GUSTAFSON TIMOTHY M [US] ET AL) 1 August 2023 (2023-08-01) column 10				5,15,16
	- / - -				
☒ Further documents are listed in the continuation of Box C.					
☒ See patent family annex.					
* Special categories of cited documents :					
"A" document defining the general state of the art which is not considered to be of particular relevance			"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention		
"E" earlier application or patent but published on or after the international filing date			"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone		
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)			"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art		
"O" document referring to an oral disclosure, use, exhibition or other means			"&" document member of the same patent family		
"P" document published prior to the international filing date but later than the priority date claimed					
Date of the actual completion of the international search			Date of mailing of the international search report		
24 March 2025			03/04/2025		
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016			Authorized officer Knorn, Raphaela		

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2024/059097

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	ZHANG LICHAO ET AL: "High performance fluoride optical coatings for DUV optics", 7TH INTERNATIONAL SYMPOSIUM ON ADVANCED OPTICAL MANUFACTURING AND TESTING TECHNOLOGIES: ADVANCED OPTICAL MANUFACTURING TECHNOLOGIES, vol. 9281, 6 August 2014 (2014-08-06), page 92810A, XP093249570, DOI: 10.1117/12.2068115 the whole document -----	10
A	WANG JUE ET AL: "Characterization of reactive plasma ion assisted HfO₂ films for low loss optical coatings in the DUV and MWIR", PROCEEDINGS OF SPIE; [PROCEEDINGS OF SPIE ISSN 0277-786X VOLUME 10524], SPIE, US, vol. 10181, 11 May 2017 (2017-05-11), pages 101810P-101810P, XP060088765, DOI: 10.1117/12.2271889 ISBN: 978-1-5106-1533-5 the whole document -----	11
A	WO 2022/256520 A1 (META PLATFORMS TECH LLC [US]) 8 December 2022 (2022-12-08) paragraphs [0001], [0017] - [0020], [0044]; figure 1 -----	18
A	US 2015/226881 A1 (TAKAHASHI HIROKI [JP] ET AL) 13 August 2015 (2015-08-13) paragraphs [0003], [0038] - [0040]; figure 2 -----	18

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/059097

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims;; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-17

An optical element comprising an anti-reflective (AR) coating, the AR coating comprising AR layers deposited by physical vapour deposition (PVD), and a nanolaminate capping layer. Details regarding the material of the AR layers and the capping layer, deposited by atomic layer deposition (ALD). And a method of forming the optical element.

2. claim: 18

A method of forming an optical element comprising an AR coating, the AR coating comprising a PVD-deposited AR layer and a nanolaminate capping layer, wherein an optical axis of the optical element is tilted away from the deposition source during the PVD-based coating of the AR layers.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2024/059097

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2012212716 A1	23-08-2012	US 2006203218 A1 US 2012212716 A1	14-09-2006 23-08-2012
US 2023287557 A1	14-09-2023	NONE	
US 2023123796 A1	20-04-2023	CN 118076764 A EP 4419730 A1 JP 2024537029 A KR 20240093699 A US 2023123796 A1 WO 2023069226 A1	24-05-2024 28-08-2024 10-10-2024 24-06-2024 20-04-2023 27-04-2023
US 11714212 B1	01-08-2023	NONE	
WO 2022256520 A1	08-12-2022	NONE	
US 2015226881 A1	13-08-2015	CN 104755967 A JP 5796140 B2 JP WO2014065371 A1 US 2015226881 A1 WO 2014065371 A1	01-07-2015 21-10-2015 08-09-2016 13-08-2015 01-05-2014