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(54) **ENGINEERED FLUORIDE-COATED ELEMENTS FOR LASER SYSTEMS**

(76) Inventors: **Jue Wang**, Fairport, NY (US); **Horst Schreiber**, Rochester, NY (US)

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(57) **ABSTRACT**

The invention is directed to elements having fluoride coated surfaces having multiple layers of fluoride material coatings for use in laser systems, and in particular in laser systems operating at wavelength <200 nm. In a particular embodiment the invention is directed to highly reflective mirrors for use in wavelengths <200 nm laser systems. The invention describes the mirrors and a method of making them that utilizes a plurality of periods of fluoride coatings, each period comprising one layer a high refractive index fluoride material and one layer low refractive index fluoride material, and additionally at least one layer of an amorphous silica material. The silica material can be inserted between each period, inserted between a stack consisting of a plurality of periods, and, optionally, can also be applied as the final layer of the finished element to protect the element.

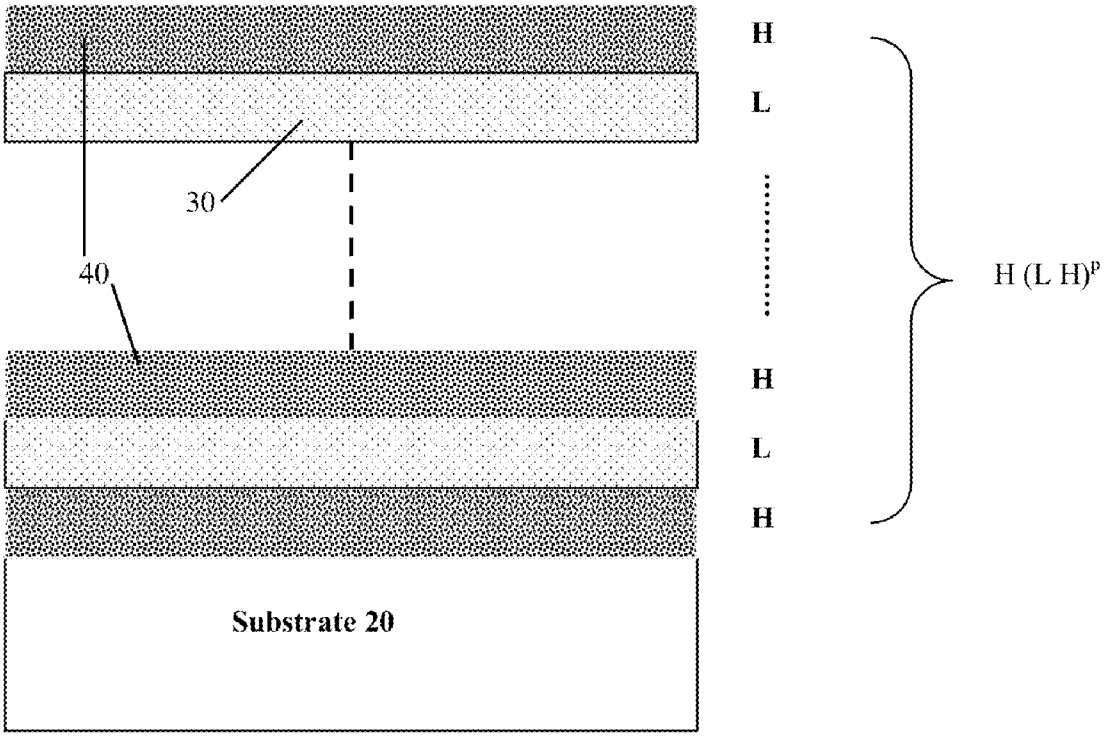


Figure 1

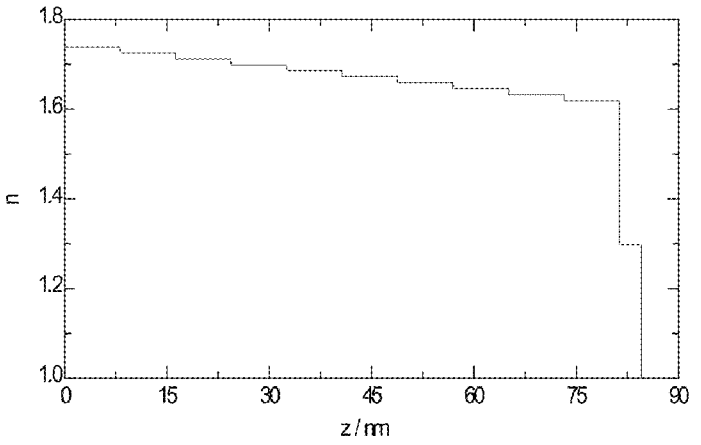


Figure 2 A

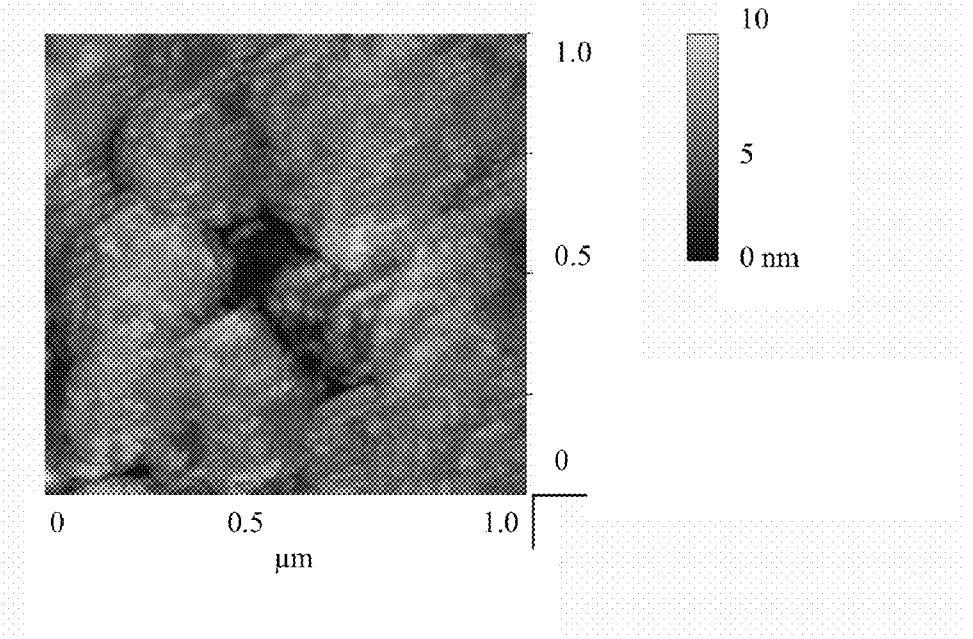


Figure 2B

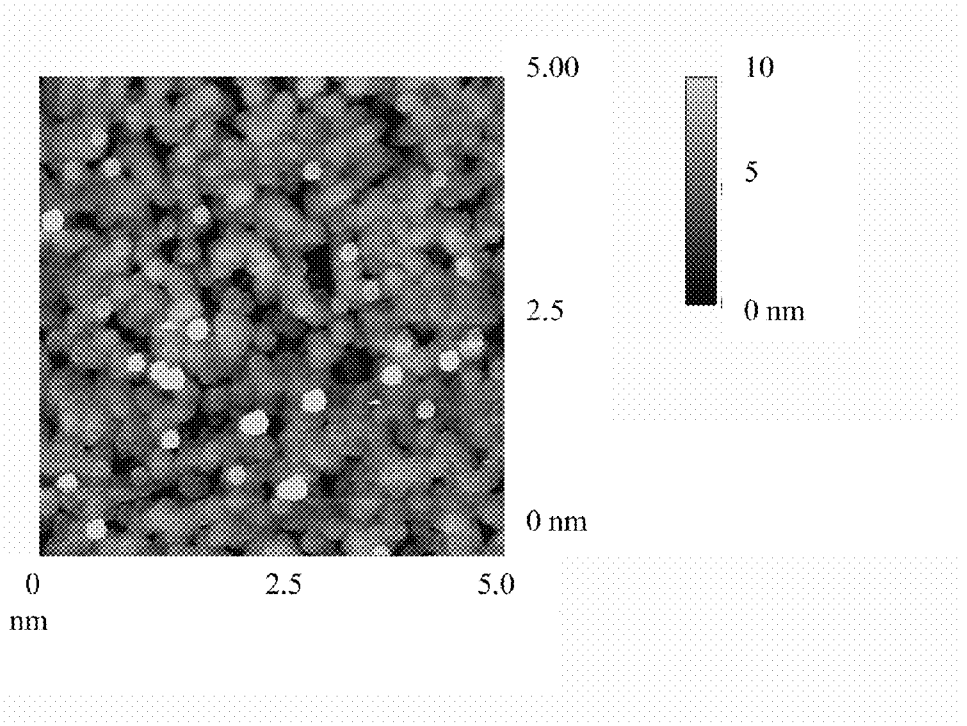


Figure 3

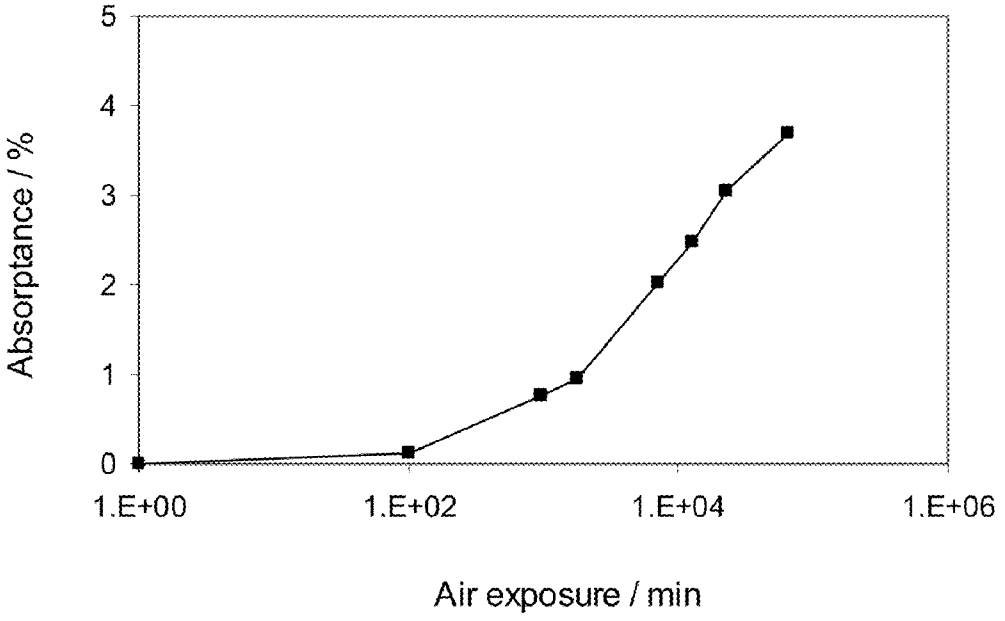


Figure 4

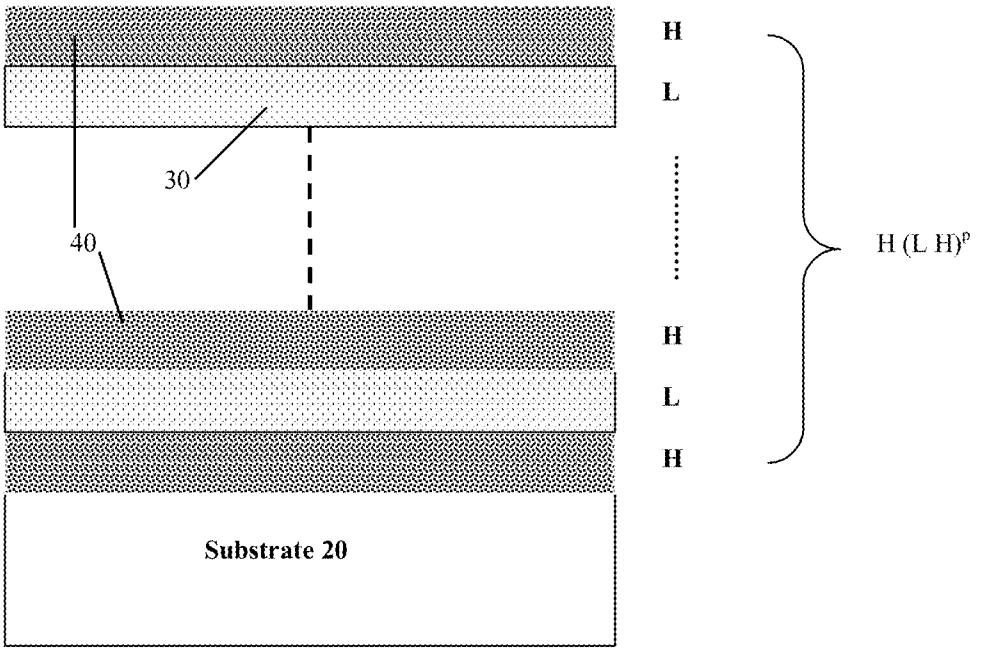


Figure 5

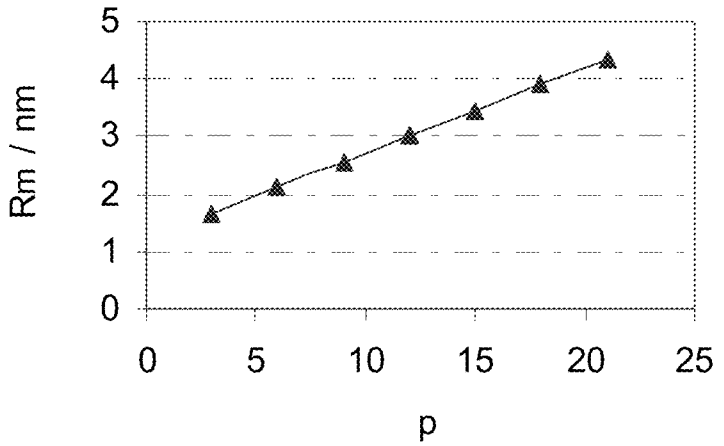


Figure 6

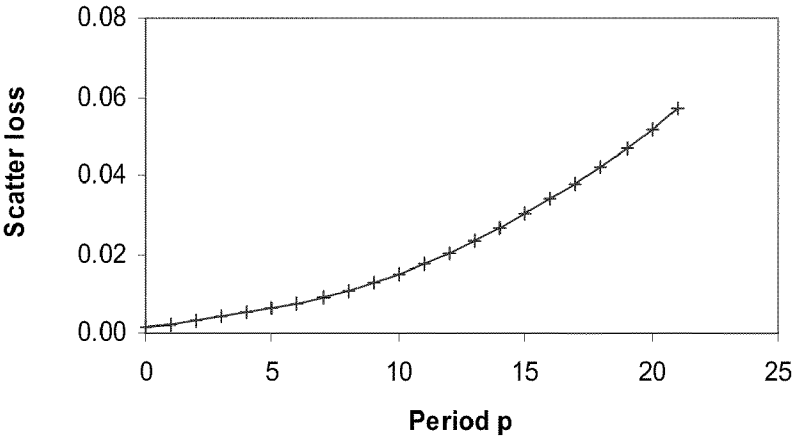


Figure 7

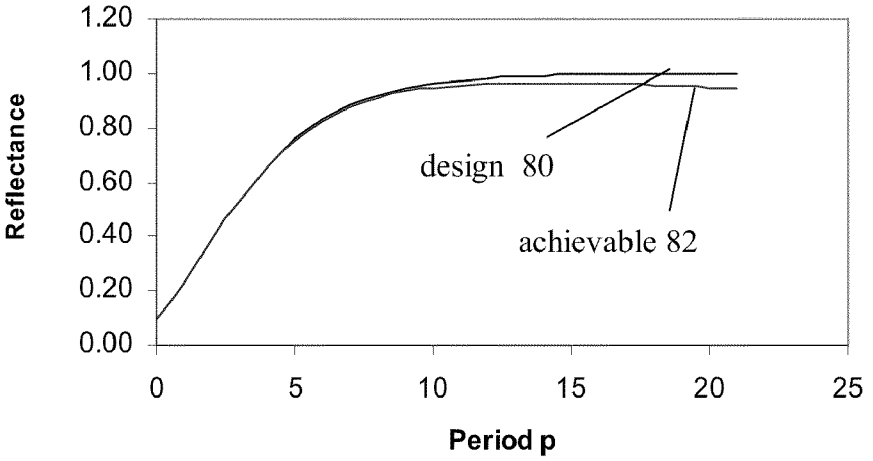


Figure 8A

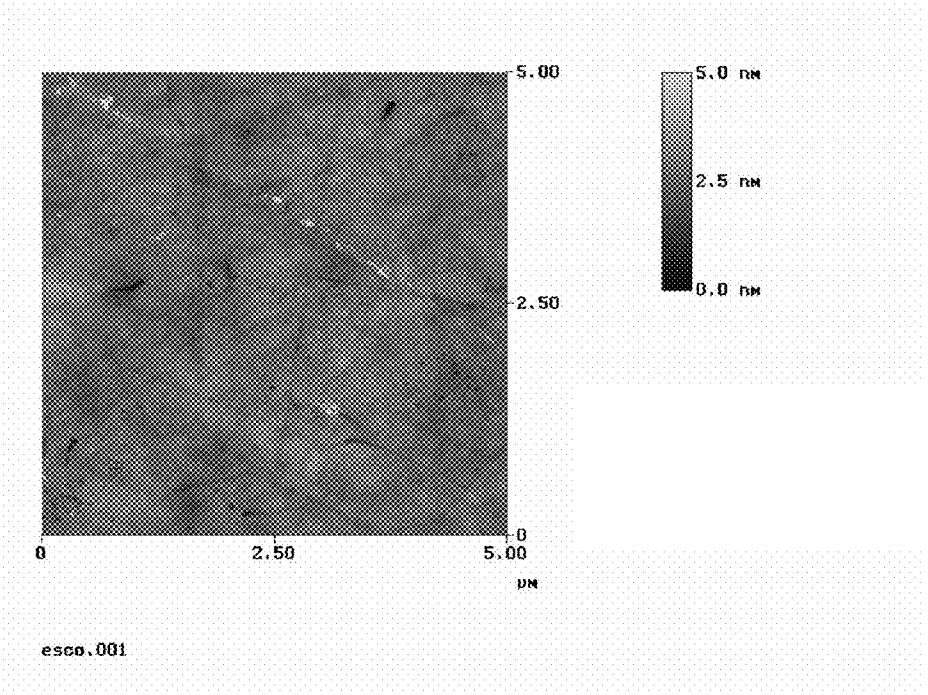


Figure 8B

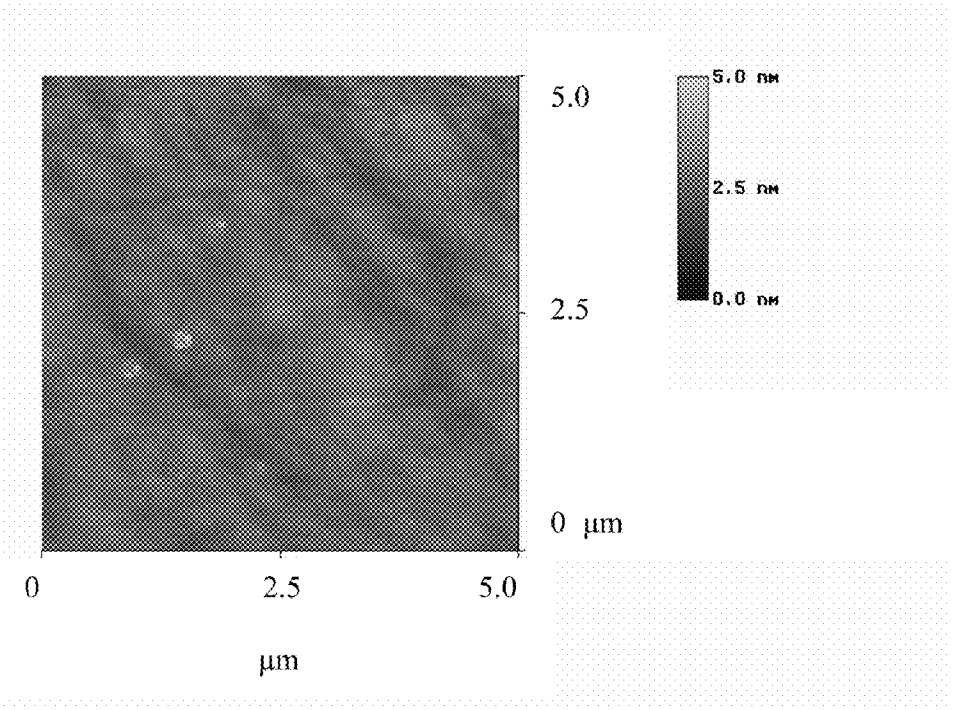


Figure 9

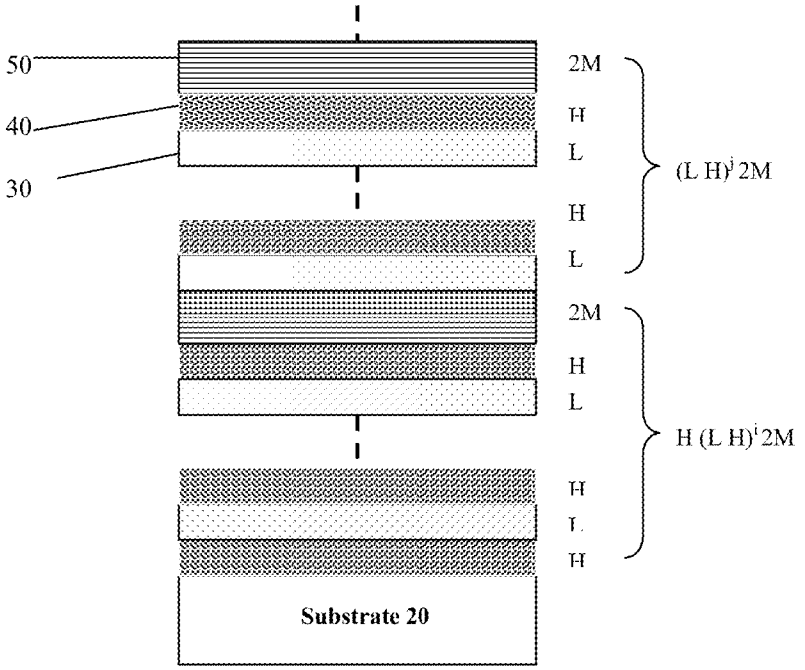


Figure 10

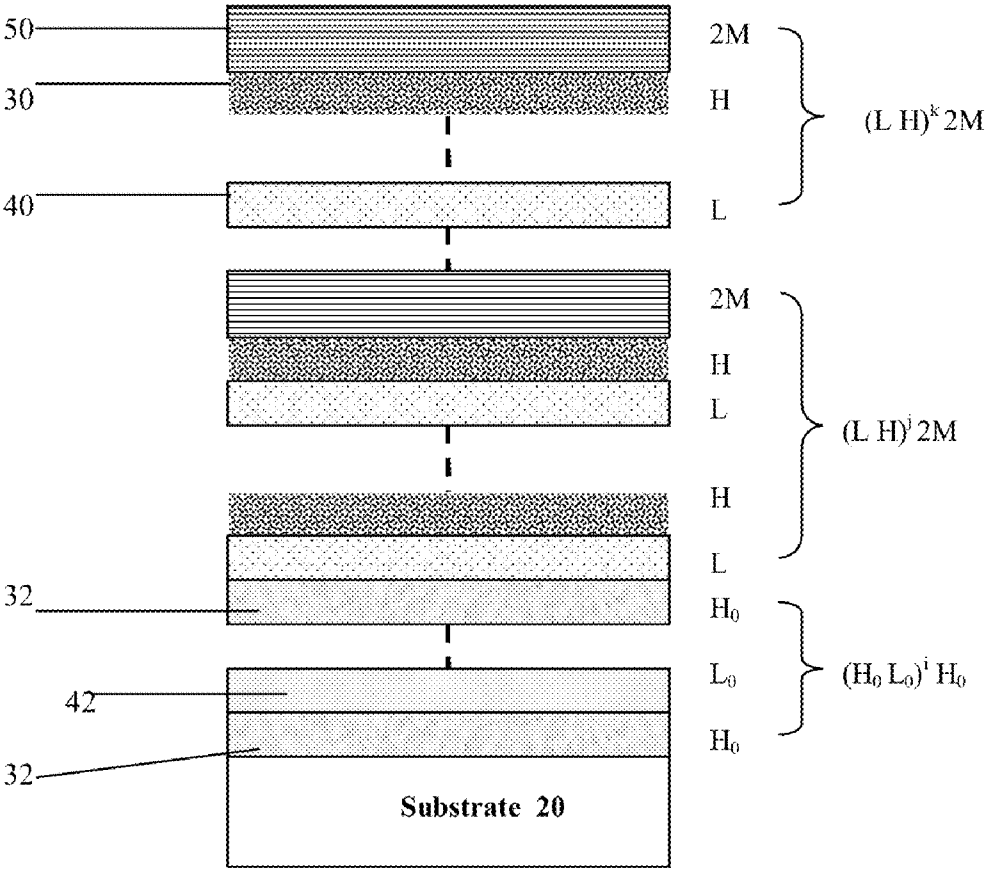
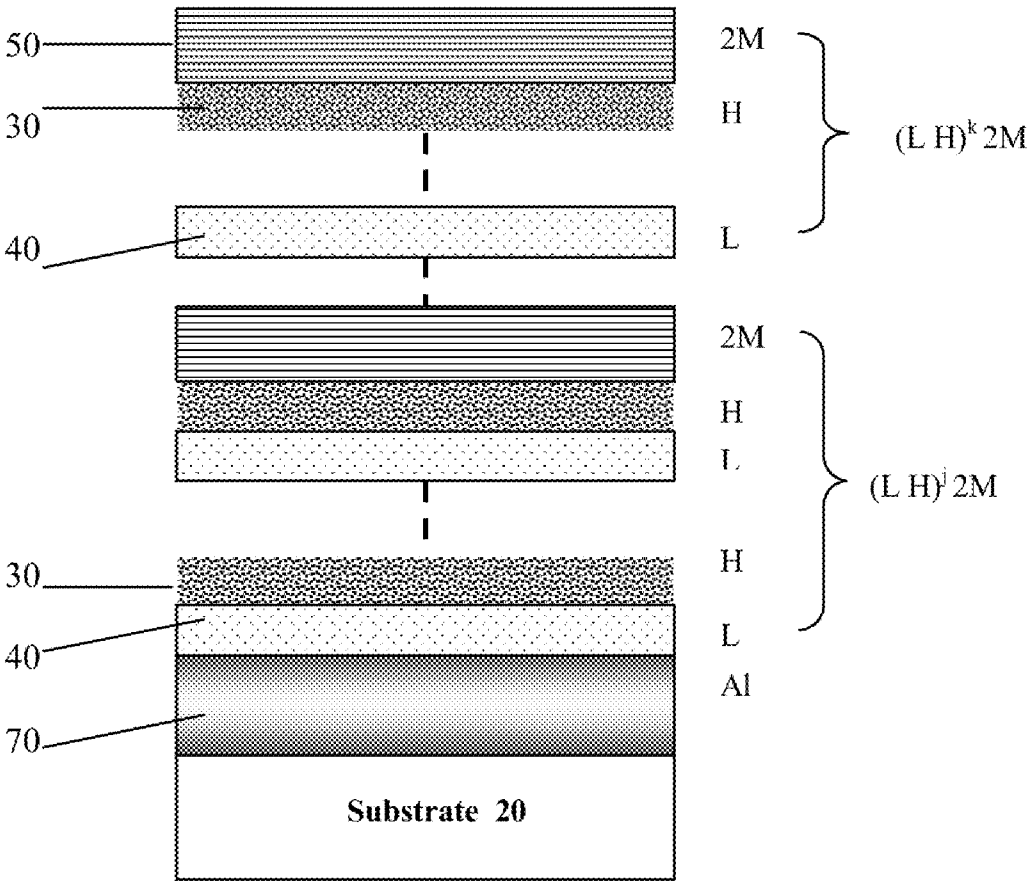

50
30
40
32
42
32
2M
H
L
(L H)^k 2M
2M
H
L
H
L
(L H)^j 2M
H0
L0
H0
(H0 L0)^i H0
Substrate 20

Figure 11



ENGINEERED FLUORIDE-COATED ELEMENTS FOR LASER SYSTEMS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This is a divisional of U.S. patent application Ser. No. 12/072,427 filed on Feb. 26, 2008, which claims the benefit of priority under 35 U.S.C. §119(e) of U.S. Provisional Application Ser. No. 60/904,132 filed on Feb. 28, 2007, the content of which is relied upon and incorporated herein by reference in its entirety, and the benefit of priority under 35 U.S.C. §120 is hereby claimed.

FIELD

[0002] The invention is directed to fluoride coated surfaces and elements having multiple layers of fluoride material coatings for use in laser systems. In particular, the invention is directed to surfaces, for example, highly reflective mirrors for use with 193 nm lasers that have multiple layers of coatings of fluoride materials.

BACKGROUND

[0003] ArF excimer lasers are the illumination sources of choice for the microlithographic industry. The industry constantly demands more performance from excimer laser sources. As a result, greater demands are constantly placed on excimer laser optical components, for example, the highly reflective mirrors that are used in 193 nm wavelength excimer lasers that operate at high repetition rates. These highly reflective mirrors are typically made using at least one high refractive index material and one low refractive index material. Among the very limited number of materials that can be used for such mirrors, GdF_3 and LaF_3 are considered as high refractive index materials and MgF_2 and AlF_3 are the low refractive index materials that are used for wavelengths below 200 nm. [see D. Ristau et al., "Ultraviolet optical and microstructural properties of MgF_2 and LaF_3 coating deposited by ion-beam sputtering and boat and electron-beam evaporation", *Applied Optics* 41, 3196-3204 (2002); R. Thielsch et al., "Development of mechanical stress in fluoride multilayers for UV-applications", Proc. *SPIE* 5250, 127-136 (2004); C. C. Lee et al., "Characterization of AlF_3 thin films at 193 nm by thermal evaporation", Applied Optics 44, 7333-7338 (2005); R. Thielsch et al, "Optical, structural and mechanical properties of gadolinium tri-fluoride thin films grown on amorphous substrates", Proc. *SPIE* 5963, 59630O1-12 (2005); and Jue Wang and Robert L. Maier, "Nano-structure of GdF_3 thin film evaluated by variable angle spectroscopic ellipsometry", Proc. *SPIE* 6321, p6321071-10 (2006)]. At the present time there is renewed research interest in wide band-gap fluoride thin films for ArF laser optics applications. The application of energetic deposition processes, such as plasma ion-assisted deposition (PIAD), ion assisted deposition (IAD) and ion beam sputtering (IBS), are restricted for fluoride materials because of the nature of fluoride materials. As a result, the industry has accepted thermal resistance evaporation for fluoride film deposition without introducing fluorine depletion. However, when thermal resistance evaporation is used as the film deposition method, the resulting fluoride film packing density is low (that is, it is porous) and the film structure is inhomogeneous. Neither of these is desirable because a porous structure can harbor environmental contamination and increases scatter losses. Various approaches have been applied to improve fluoride film structure including substrate temperature and deposition rate. Recently, the effect of substrate crystal orientation has also been taken into account, but no significant improvements have been reported. [see Y. Taki and K. Muramatsu, "Hetero-epitaxial growth and optical properties of LaF_3 on CaF_2", Thin Solid Films 420-421, 30-37 (2002), and U.S. Pat. No. 6,809,876 to Y. Taki et al., titled "OPTICAL ELEMENT EQUIPPED WITH LANTHANUM FLUORIDE FILM"].

[0004] Another problem arises from the fact that many periods of high index and low index layers (one period equals one high and one low refractive index layer) are required in order to get high reflectivity at 193 nm. However, the surface/interface roughness and inhomogeneity increase as number of layers and the overall thickness increases. The control of the multilayer fluoride film structure is critical for achieving high reflectivity at 193 nm. In addition to their use in microlithography, fluoride coated mirrors are also required for those areas where ArF excimer laser have other, non-lithographic application, for example minimal invasive brain-, vascular- and eye surgery; ultra-precision machining & measurement; large-scale integrated electronic devices; and components for communication. In view of the problems extant with the present fluoride coated elements, for example mirrors, that are used in below 200 nm, and particularly in 193 nm, lithography, it is desirable to have fluoride coated elements that overcome these problems. In addition to mirrors, the invention can also be applied to beamsplitters, prisms, lenses, output couplers and similar elements used in <200 nm laser systems.

SUMMARY

[0005] The invention is directed to elements for use in <200 nm laser systems, the element comprising a substrate; one or a plurality of periods of fluoride coating materials, each of said periods comprising at least one layer of a high refractive index fluoride material and at least one layer of a low refractive fluoride material; and at least one layer of an amorphous SiO_2 material selected from the group consisting of amorphous silica, amorphous F-doped SiO_2, amorphous Al_2O_3-doped SiO_2, and amorphous N-doped SiO_2. In accordance with the invention the amorphous SiO_2 material can be inserted after each period of the fluoride coating material or after a stack consisting of a plurality of periods of fluoride coating material. Optionally, a layer of the amorphous SiO_2 material can be applied to the substrate prior to the application of the first period of fluoride coating materials. The fluoride coating materials are metal fluoride materials having a high refractive index and low refractive index, and these materials are applied in alternating layers to the substrate or amorphous SiO_2 coated substrate. In some embodiments the high refractive index fluoride material has an index in the range of 1.65 to 1.75 and said low refractive fluoride material has an index in the range of 1.35 to 1.45. Substrates that can be used for the elements are glass and glass-ceramic substrates; alkaline metal fluoride single crystal substrates; metallic substrates, for example without limitation, substrates made from aluminum, titanium, and other metals known in the art that are know to be resistant to deterioration in a 200 nm laser environment such as found in ArF and F_2 lasers; and other materials resistant to deterioration in a 200 nm laser environment such as found in ArF and F_2 lasers, for example silicon nitride (Si_3N_4). The amorphous SiO_2 material includes amorphous SiO_2 itself and doped amorphous SiO_2 materials such as silica

materials doped with fluorine (F), silica materials doped with Al_2O_3, and silica materials doped with nitrogen (N), fluoride (F) and Al_2O_3. Each period of fluoride coating has a thickness in the range of 50 nm to 90 nm, and within the period the high refractive index material has a thickness in the range of 20 nm to 40 nm, and the low refractive index material has a thickness in the range of 30 nm to 50 nm. The SiO_2 layer applied to the substrate before coating (optional), or after a period or stack of periods, has a thickness in the range of 5 nm to 75 nm. The final layer of SiO_2 applied to element after the deposition of all the fluoride coating periods has a thickness in the range of 10 nm to 150 nm.

[0006] The invention is further directed to a method for preparing fluoride coated elements and in particular highly reflective fluoride coated mirrors for use in <200 nm laser systems. The method has at least the steps of providing a substrate; coating the substrate with one or a plurality of periods of fluoride coating materials using an energetic deposition technique, each such period having at least one layer of a high refractive index fluoride material and at least one layer of a low refractive index fluoride coating material; and further coating using an amorphous SiO_2 material including amorphous SiO_2 material itself and doped amorphous SiO_2 materials. In one embodiment of the method the SiO_2 is applied as a layer after each fluoride coating period. In another embodiment of the method the SiO_2 layer is applied after a stack of a plurality of fluoride coating material periods. In another embodiment of the method a SiO_2 layer is applied to the substrate prior to the applying the first period of fluoride coating materials. Energetic deposition techniques that can be used in practicing the invention include PIAD (plasma ion-assisted deposition), IAD (ion-assisted deposition), and IBS (ion beam sputtering).

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] FIG. **1** (Prior Art) is a graph illustrating the refractive index depth profile of a GdF_3 film grown on CaF_2 (111).

[0008] FIGS. **2**A and **2**B (Prior Art) are AFM images of GdF_3 single layer grown on a CaF_2 (111) single crystal.

[0009] FIG. **3** (Prior Art) is a graph illustrating the absorbance of a GdF_3 film at 193 nm as a function of air exposure time.

[0010] FIG. **4** (Prior Art) is a schematic diagram illustrating of a standard fluoride mirror having high and low refractive index materials coated on a substrate.

[0011] FIG. **5** (Prior Art) is a graph illustrating the surface roughness of standard fluoride mirrors as a function of stack period.

[0012] FIG. **6** (Prior Art) is a graph illustrating the scatter loss of standard fluoride mirrors as a function of stack period.

[0013] FIG. **7** (Prior Art) is a graph illustrating the reflectance of standard fluoride mirrors as a function of stack period.

[0014] FIGS. **8**A and **8**B are AFM images comparing the PIAD smoothed SiO_2 film of FIG. **8**A with the uncoated SiO_2 substrate of **8**B.

[0015] FIG. **9** is a schematic diagram illustrating the surface and interface of an engineered fluoride mirror.

[0016] FIG. **10** is a schematic diagram illustrating the surface and interface of an engineered fluoride-enhanced-oxide mirror.

[0017] FIG. **11** is a schematic diagram illustrating the surface and interface engineered fluoride-enhanced-Al mirror.

DETAILED DESCRIPTION

[0018] As used herein, the terms "fluoride coated mirrors" and "fluoride mirrors" include mirrors in which the fluoride coating is applied to substrates such as alkaline earth metal fluoride single crystal materials (single crystals of CaF_2, BaF_2, SrF_2, BaF_2), glass materials (for example SiO_2, HPSF® (Corning Incorporated), BK7™ and SF10™ (Schott Glass)), metallic materials (for example, aluminum, titanium) and other materials (for example, Si, Si_3N_4). Also as used herein, the term "period" as applied to fluoride coatings means one high refractive index layer and one low refractive index layer. The term "stack" as used herein means two or more periods of fluoride materials coated on the substrate which lie between the substrate and the SiO_2 films of the invention or between two SiO_2 films.

[0019] In wavelengths <200 nm laser systems, for example, ArF laser systems which operate at 193 nm, scatter and contamination are the main factors that degrade the performance of fluoride mirrors and fluoride enhanced mirrors. Fluorine depletion generates significant absorption at 193 nm if advanced energetic deposition processes are used to improve fluoride film structure and reduce scatter loss. Among the problems associated with standard fluoride mirrors, including fluoride-enhanced-oxide mirrors and fluoride-enhanced-Al mirrors are:

[0020] (1) it is difficult to obtain a reflectivity over 97% at 193 nm,

[0021] (2) the reflectivity is environmental sensitive,

[0022] (3) the porous structure of fluoride films harbors contamination, leading to absorption at 193 nm, and

[0023] (4) laser durability is low

The present invention overcomes these problems by insertion of amorphous silica (SiO_2) layers between a period or stack of periods of the high and low refractive index materials that are use to coat the mirror blanks (substrates). In general, the invention is directed to using a PIAD smoothed SiO_2 layer is periodically inserted into fluoride stacks and also use SiO_2 as the top, capping or final layer. More specifically, the invention relates to:

[0024] (1) inserting amorphous SiO_2 layer to eliminate the growth of inhomogeneous fluoride film structure,

[0025] (2) using PIAD to smooth the amorphous SiO_2 layer surface,

[0026] (3) continuously growing fluoride films on the smoothed SiO_2 surface, and

[0027] (4) using the dense smoothed SiO_2 as capping layer to reduce the fluoride exposed surface area by a factor of $\sim 10^{-5}$ and thus to seal the engineered fluoride mirror.

[0028] [1]. The Surface Roughness of a Fluoride Single Layer

[0029] Standard fluoride mirrors comprise multiple layers of fluoride materials; in particular, alternating layers of a high refractive index material and a low refractive index material. The fluoride film growth mechanism was investigated using a GdF_3 single layer as an example, and the results indicate that the layer has an inhomogeneous structure and a rough surface. FIG. **1** (Prior Art) shows the refractive index (at 193 nm) depth profile of a GdF_3 film grown on CaF_2 (111) surface. The refractive index is proportional to film packing density. In

general for the GdF_3 film, high refractive index originates from a dense film, whereas low refractive index corresponds to a porous film structure. As can be seen in FIG. **1**, at the beginning of the GdF_3 film formation a dense thin layer is formed on the substrate leading to a refractive index of 1.738. As the film thickness increases, the growth mechanisms of columnar and polycrystalline microstructure may introduce gaps between crystal grains. As a consequence, the film density decreases as the layer thickness accumulates. At the end of film growth the refractive index has further dropped to 1.62, corresponding to a mean porosity of 15.8%. A refractive index of 1.35 represents a 3.5 nm surface roughness layer in FIG. **1**. High refractive index fluoride materials have an index of refraction n in the range of 1.65 to 1.75, and low refractive index fluoride material has an index on the range of 1.35 to 1.45.

[0030] FIGS. **2**A and **2**B (Prior Art) exhibits AFM (atomic force microscopy) images over 1μ×1μ and 5μ×5μ scanning areas of the GdF_3 layer, respectively. The grain and the pore sizes shown in FIGS. **2**A and **2**B range from 300 nm to 350 nm. The AFM images clearly reveal the nano-porous morphology of GdF_3 film growth on a CaF_2 (111) surface. As can be seen in the 1μ×1μ image of FIG. **2**A, there are some gaps between the accumulated dense grains, leading to the formation of porous structure. By increasing AFM scanning size to 5μ×5μ as shown in FIG. **2**B, the porous network is obvious on the film growth plane. As predicted by ellipsometric modeling, the inhomogeneity of the GdF_3 film is a result of film porosity changes during growth. The randomly distributed porous structure with relatively high internal surface area may connect to each other to some degree and may harbor environmental contamination.

[0031] FIG. **3** (Prior Art) shows the absorbance of the GdF_3 film at 193 nm as a function of laboratory ambient exposure (air exposure). The film absorbance increases over exposure time to air. In summary, fluoride films are inhomogeneous and porous in general. As layer thickness increases, film surface roughness increases. The porous film structure and rough surface lead to high absorption and scatter loss at 193 nm wavelength.

[0032] [2]. Surface and Interface of Standard Fluoride Mirror

[0033] Based on our experimental results, the surface roughness of standard fluoride mirror, R_m, can be described by Equation (1),

$$R_m=\alpha p+\beta R_s \quad (1)$$

where α and β are fluoride material and deposition process related parameters, Rs is the surface roughness of the substrate, and p is the stack period. A stack period is defined as a combination of low refractive index and high refractive index layers. Parameter α is related to the high and the low refractive fluoride layers used for the period such as GdF_3/MgF_2, LaF_3/MgF_2, GdF_3/AlF_3 and LaF_3/AlF_3, the deposition rate and substrate temperature for each material. Parameter β is dominated by the substrate material properties and surface finishing condition. Using standard fluoride mirrors, for example, at a normal angle of incidence, i.e., 0°, the fluoride mirrors compromise stacks of high and low refractive index layers as represented by Formula (2):

$$Sub_H(LH)^p \quad (2)$$

where H and L corresponds to a quarter-wave high index GdF_3 and a quarter-wave low index AlF_3, respectively, and p is a stack period. A schematic of the mirror is shown in FIG. **4** (Prior Art). [Note: In all the figures, the substrate is numbered as **20**; H is numbered as **30**; L is numbered as **40**, the SiO_2 layer 2M is numbered as **50**.]

[0034] FIG. **5** (Prior Art) is a graph showing the surface roughness of standard fluoride mirrors as a function of stack period. The surface roughness is linearly proportional to the stack period as described in formula (1). That is, the more periods a standard mirror contains the rougher the surface becomes. FIG. **6** (Prior Art) shows surface and interfacial scatter loss of fluoride mirrors as a function of stack period. Generally, a large number of stack periods (p>16) are required in order to achieve high reflectivity in the final mirror product. As can be seen from FIG. **6**, scatter loss increases slowly when the stack period is a small number. However, FIG. **6** shows that the slope of the curve increases along with an increasing number of stack periods. In other words, scatter loss increases faster than the additional reflectivity gain due to adding more stack periods into standard fluoride mirror. As a result, there is an optimized number of stack periods which offers the highest reflectivity when one takes into account of scatter loss.

[0035] FIG. **7** (Prior Art) shows reflectance of standard fluoride mirror as a function of stack period. According to the design calculations (design curve is numeral **80**), the reflectance as a function of stack period can be separated into 3 zones which are:

[0036] 1. a fast increasing region (up to 6 periods),

[0037] 2. a slow increasing region (more than 16 periods) and

[0038] 3. transition region from the fast increase to the slow increase.

[0039] The achievable reflectance (numeral **82**), which also has 3 zones, is plotted in the same figure for comparison. The fast increasing region of the achievable reflectance is almost the same as that of the design reflectance. The transition zone for the achievable reflectance is very similar to the design, but there is a small separation when the stack period number is located at the high end of the zone. The main difference between the achievable reflectance and the design reflectance is located in the region where the period number is greater than 16. Instead of a slow increase of reflectance as shown for the design reflectance, a slow decrease of reflectance appears in the high period region for the achievable reflectance because of scatter loss. Consequently, in order to successfully make a high reflectance fluoride mirror it is necessary to eliminate surface and interface roughness. As discussed above, energetic deposition techniques cannot be used to make dense smooth fluoride films without generating fluorine depletion. The invention describes high reflectance fluoride mirrors which utilize SiO_2 based oxide layers to smooth-out fluoride films to achieve high reflectivity.

[0040] [3]. Smoothed Amorphous SiO_2 by Energetic Deposition

[0041] In accordance with the invention, an amorphous but dense and smooth, SiO_2 film is inserted into a fluoride stack by means of energetic deposition. Dense smooth SiO_2 films can be deposited by PIAD, IAD and IBS. Here PIAD deposited SiO_2 is used as an example. FIG. **8**A is an AFM image of PIAD smoothed SiO_2 film on a SiO_2 substrate. The surface roughness of the uncoated substrate is 0.35 nm. After depositing a 200 nm SiO_2 film, the surface roughness has been reduced to 0.29 nm. The result shows that the smoothed SiO_2 film reduces roughness of an uncoated substrate. FIG. **8**B illustrates how a SiO_2 film can be also used to improve, that is, decrease, the surface smoothness of a coated substrate. In accordance with the invention, at least one PIAD deposited SiO_2 layer has been inserted into standard fluoride mirror to protect fluoride films from plasma ion direct bombardment, and to smooth out the fluoride film's accumulated rough structure. Fluoride stacks can be continuously deposited on the smoothed SiO_2 film layer. In preferred embodiments the final layer is a SiO_2 film layer. In FIG. **8**B, the surface roughness is 0.29 nm after application of the SiO_2 film. Before application of the SiO_2 film the surface roughness was 0.35 nm.

[0042] [4]. Surface and Interface Engineered Fluoride Mirror

[0043] Surface and interface engineered fluoride mirrors can be described by Formula (3):

$$\text{Sub_H(LH)}^{i}\text{2M(LH)}^{j}\text{2M} \ldots \text{(LH)}^{k}\text{2M} \quad (3)$$

where 2M represents a half-wave SiO_2 layer; H and L are high index and low index fluoride layers, respectively; and i, j . . . and k are stack periods. According to Equation (3), a SiO_2 layer is inserted into standard fluoride mirror every i, j . . . k stack periods. FIG. **9** shows a schematic of surface and interfacial engineered fluoride mirror as represented by Formula (3). Table 1 lists a comparison of standard and surface/interface engineered fluoride mirrors with a stack period of 21, where 3 nm surface and interface roughness is used for the engineered mirror.

TABLE 1

Comparison of standard and surface/interface engineered mirrors

	Standard mirror	Engineered mirror
Scatter loss (%)	5.69	1.16
Reflectance design (%)	99.96	99.57
Reflectance achievable (%)	94.27	98.41

[0044] Although the designed reflectance of the standard mirror (99.96%) is higher than the engineered mirror (99.57%), the scatter loss of the standard mirror is 4.9 times greater than that of the engineered mirror. The final achievable reflectance is 94.27% and 98.41% for the standard and the engineered mirrors, respectively. In some embodiments of the invention the top layer of the engineered mirror ends with a dense SiO_2 layer as shown in formula (3). This top layer of SiO_2 seals and smoothes the porous structure as is shown in the AFM images of FIGS. **8**A and **8**B. In addition, as a result of applying a dense SiO_2 film as described herein, the risk for environmental contamination penetrating into the porous fluoride structure is eliminated. This is a further difference between the surface/interface engineered mirrors of the invention as compared to the standard fluoride mirror which can easily be contaminated due to porosity as is illustrated by GdF_3 single layer data shown in FIG. **3** (Prior Art).

[0045] [5]. Surface/Interface Engineered Fluoride-Enhanced-Oxide Mirror

[0046] The invention, in another embodiment, is also directed to fluoride-enhanced-oxide mirrors in which the fluoride enhanced stacks are smoothed by inserting PIAD deposited SiO_2 layers in a Formula (4)

$$\text{Sub_H}_0(\text{L}_0\text{H}_0)^{i}\text{(LH)}^{j}\text{2M} \ldots \text{(LH)}^{k}\text{2M} \quad (4)$$

or Formula (5)

$$\text{Sub_(H}_0\text{L}_0)^{i}\text{H(LH)}^{j}\text{2M} \ldots \text{H(LH)}^{k}\text{2M} \quad (5)$$

where H_0 and L_0 corresponds to a quarter-wave high index Al_2O_3 and a quarter-wave low index SiO_2, respectively; 2M represents a half-wave SiO_2 layer; and H and L are high index and low index fluoride layers, respectively. A schematic of surface and interface engineered fluoride-enhanced-oxide mirror is shown in FIG. **10** where H_0 is numeral **32**; L_0 is numeral **42**; and H, L and 2M are represented by numerals as previously indicated.

[0047] [6]. Surface/Interface Engineered Fluoride-Enhanced-Aluminum Mirror

[0048] The invention, in another embodiment, is also directed to fluoride-enhanced-aluminum mirror, in which the fluoride enhanced stacks are smoothed by inserting PIAD deposited SiO_2 layers as represented by Formula (6):

$$\text{Sub_A(LH)}^{j}\text{2M} \ldots \text{(LH)}^{k}\text{2M} \quad (6)$$

or Formula (7)

$$\text{Sub_AH(LH)}^{j}\text{2M} \ldots \text{(LH)}^{k}\text{2M} \quad (7)$$

where A is a thickness aluminum (Al) layer; 2M represents a half-wave SiO_2 layer; and H and L are high index and low index fluoride layers, respectively. A schematic of surface and interface engineered fluoride-enhanced-Al mirror is shown in FIG. **11**, the aluminum layer (Al) being represented by numeral **70**; and H, L and 2M are represented by numerals as previously indicated.

[0049] To summarize the characteristics of the invention:

[0050] H can be any high refractive index fluoride material, for example, GdF_3, LaF_3, and other high refractive index metal fluoride materials known in the art.

[0051] L can be any low refractive index fluoride material, for example, AlF_3, MgF_2, CaF_2 and other low refractive metal fluoride materials known in the art

[0052] SiO_2 based layer can be SiO_2 or modified SiO_2, for example, F-doped SiO_2, N-doped SiO_2, and Al_2O_3-doped SiO_2,

[0053] Energetic smoothing technique that can be used in practicing the invention can be PIAD (plasma ion-assisted deposition), IAD (ion assisted deposition), IBS (ion beam sputtering), and similar energetic techniques

known in the art as being useful for the deposition of the oxide materials and particularly oxide materials.

[0054] The layer order of H and L in Formulas (3)-(7) can be changed. For example, the order in Formula (3) may change from

$$Sub_H(LH)^i2M(LH)^j2M \ldots (LH)^k2M \quad (3)$$

to

$$Sub_(HL)^i2MH(LH)^j2M \ldots (LH)^k2M \quad (8)$$

or

$$Sub_(LH)^i2M(LH)^j2M \ldots (LH)^k2M \quad (9)$$

[0055] Formulas 4-7 may similarly be changed.

[0056] Changing the optical thickness in Formulas (3)-(7) enables one to apply the invention to S-polarization or P-polarization mirrors at high angle of incidence at 193 nm. Typically the thickness of the high refractive index layer is in the range of 20 to 35 nm, and the thickness of the low refractive index material is in the range of 30 to 45 nm. The thickness of the SiO_2 film inserted, in accordance with the invention, after a period or a stack of periods is typically in the range of 5 to 75 nm. The thickness can be changed to 22 to 39 nm for the high refractive index material and 36 to 54 nm for the low refractive index material for applications to S-polarization or P-polarization mirrors at high angle of incidence at 193 nm.

[0057] The element can be selected from the group consisting of reflective mirrors, beamsplitters, prisms, lenses, and output couplers.

[0058] The high refractive index material can be selected from the group consisting of GdF_3 and LaF_3.

[0059] The low refractive index material can be selected from the group consisting of MgF_2, CaF_2 and AlF_3.

[0060] The thickness of the amorphous SiO_2 layer inserted between the periods of high and low refractive index materials can be in the range of 5 nm to 75 nm.

Changing optical thickness in Equations (3)-(7) also enables one to apply the invention to other DUV laser wavelengths, for example, other <200 nm laser systems that operate at such <200 nm wavelengths such as 157 nm, 198.5 nm.

[0061] While the invention has been described with respect to a limited number of embodiments, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope of the invention as disclosed herein. Accordingly, the scope of the invention should be limited only by the attached claims.

We claim:

1. A method for making a fluoride coated element suitable for use <200 nm laser systems, said method comprising the steps of:

providing a substrate;

coating, using an energetic deposition technique, the substrate with one or a plurality of periods of fluoride coating materials using an energetic deposition technique, and

further coating, using an energetic deposition technique, with an amorphous SiO_2 material to thereby form a fluoride coated element suitable for use in <200 nm laser systems;

wherein coating the substrate with one or a plurality of periods of fluoride coating materials means coating such that each period comprises a layer of a high refractive index fluoride coating material and a layer of a low refractive index coating material.

2. The method according to claim **1**, wherein said method further comprises coating said substrate with a layer of an amorphous SiO_2 material prior to the application of the first period of fluoride coating materials.

3. The method according to claim **1**, wherein coating using an energetic deposition technique comprises coating using deposition techniques selected form the group consisting of plasma ion-assisted deposition, ion-assisted deposition and ion beam sputtering.

4. The method according to claim **1**, wherein the method further comprises coating said element with a final layer of an amorphous silica after the coating with a plurality of fluoride materials is completed.

5. The method according to claim **1**, wherein coating with said amorphous silica material means coating with a silica material selected from the group consisting of silica, F-doped SiO_2, N-doped SiO_2 and Al_2O_3-doped SiO_2.

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