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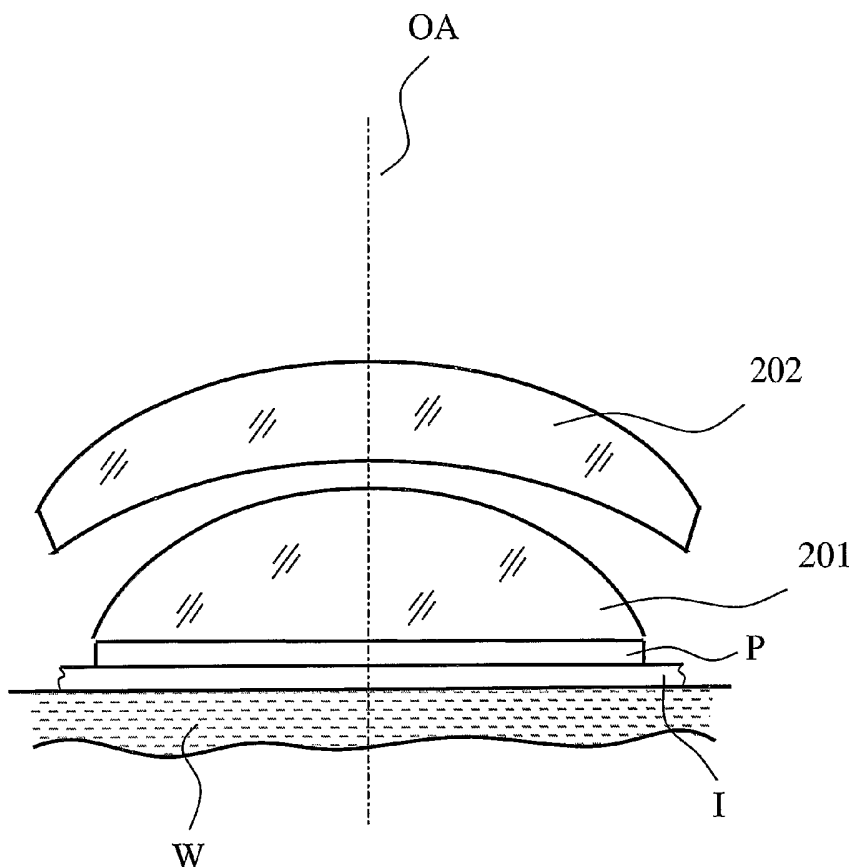
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(54) Title: OPTICAL ELEMENT



(57) Abstract: An optical element is suggested which is made of a mixed crystal with at least two metal oxides and a semiconductor oxide, like, for example $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, $\text{Al}_2\text{Mg}_2\text{CaSi}_3\text{O}_{12}$, and $\text{Al}_2\text{MgCa}_2\text{Si}_3\text{O}_{12}$. An optical element of this kind can be used in a projection objective for microlithography, in particular for immersion lithography. In one embodiment of the invention the composition of the mixed crystal can be chosen in such a way that the overall intrinsic birefringence of the optical element is adjusted to a particular value, preferably minimized.

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Optical Element

- 5 The invention relates to an optical element, an objective with at least one optical element, a projection objective, as well as a microlithography projection exposure apparatus with a projection objective.
- 10 In the time ahead, there will be a need in the field of microlithography for materials of exceptionally high refractivity. This holds particularly for the last lens or several last lenses, which are located adjacent to the wafer. Such highly refractive materials take on a special importance
- 15 in the areas of immersion lithography or optical near-field lithography.

The invention has the object to propose an optical element which in addition to a high index of refraction also has good

20 transmissivity for DUV wavelengths, in particular the wavelength of 193 nm.

This object is attained through an optical element in accordance with the independent claims 1 and 7. Advantageous

25 further developed embodiments are presented in the dependent claims 2 to 6 and 8 to 17.

It is a further object of the invention to propose an objective, in particular a projection objective, whose

30 transmissivity is as high as possible at the aforementioned wavelengths and which has refractive indices that are suitable for obtaining a high resolution and depth of focus.

The latter object is attained through the use of a material in accordance with claim 18. Advantageous further embodiments are presented in the dependent claims 19 to 23.

5 As a material for an optical element, in particular for use in an objective in a microlithography projection exposure apparatus, a crystal is proposed which comprises at least two metal oxides and a semiconductor oxide. For example, this could be a mixed crystal consisting of two metal oxides and a
10 semiconductor oxide. In another example, it could be a mixed crystal consisting of three metal oxides and a semiconductor oxide.

It is particularly advantageous to use pyrope, which is a
15 mixed crystal of MgO , Al_2O_3 and SiO_2 . Its crystal structure is cubic. Its chemical formula is $\text{Al}_2\text{O}_3 \cdot 3\text{MgO} \cdot 3\text{SiO}_2$ or $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$. The refractive index of pyrope at a wavelength of 193 nm is close to the refractive index of magnesium spinel (MgAl_2O_4), which at 193 nm has a refractive index of 1.8.

20 It is likewise very advantageous to use grossularite, a mixed crystal which, instead of the MgO found in pyrope, contains CaO . Accordingly, the chemical formula of grossularite is $\text{Al}_2\text{O}_3 \cdot 3\text{CaO} \cdot 3\text{SiO}_2$ or $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$. Like pyrope, it has a
25 cubic/isotropic crystal structure. Its refractive index is notably higher than for pyrope.

At a wavelength of 193 nm the refractive index of pure MgO is around 2.0, while the refractive index of CaO is around 2.7.
30 Accordingly, as the component 3MgO in pyrope crystal is replaced by 3CaO , the refractive index of grossularite is notably higher in comparison to pyrope.

Besides mixed crystals of two metal oxides and a semiconductor oxide, other materials that can be considered for optical elements, in particular for use in an objective of a microlithography projection exposure apparatus, include
5 crystal materials that are formed of three different metal oxides and a semiconductor oxide.

Particularly advantageous among these materials is a mixed crystal of Al_2O_3 , MgO , CaO and SiO_2 with the composition
10 $\text{Al}_2\text{O}_3 \cdot 2\text{MgO} \cdot \text{CaO} \cdot 3\text{SiO}_2$ or $\text{Al}_2\text{Mg}_2\text{CaSi}_3\text{O}_{12}$. Likewise a possible choice is a mixed crystal with the same components, but with different proportions of CaO and MgO , such as for example $\text{Al}_2\text{O}_3 \cdot \text{MgO} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$ or $\text{Al}_2\text{MgCa}_2\text{Si}_3\text{O}_{12}$.

15 Calcium oxide CaO and magnesium oxide MgO exhibit intrinsic birefringence at DUV wavelengths, particularly at 193 nm. At these wavelengths the sign of the intrinsic birefringence of CaO is opposite to the sign of the intrinsic birefringence of MgO : While MgO exhibits a positive intrinsic birefringence,
20 the birefringence of CaO is negative. The inventor has found that in a mixed crystal of at least two, in particular three, metal oxides and a semiconductor oxide, these mutually countervailing effects can be put to use by specifically selecting the respective proportions of the positive-
25 birefringent MgO and the negative-birefringent CaO so that the overall intrinsic birefringence of the mixed crystal becomes minimal, with particular preference zero. The value of the intrinsic birefringence is strongly dependent on the wavelength of the transmitted radiation. Accordingly, the
30 wavelength has to be taken into account in optimizing the composition of the mixed crystal.

It is in this context particularly advantageous to use a mixed crystal of the composition $\text{Al}_2\text{O}_3 \cdot 3[\text{A MgO} \cdot \text{B CaO}] \cdot 3\text{SiO}_2$,

wherein $A + B = 1.0$, with A and B being factors for the respective proportions of MgO and CaO. This mixed crystal, too, has a cubic crystal structure. The factors A and B are preferably selected in such a way that the intrinsic
5 birefringence of the crystal at a given wavelength is minimized, for example if the optical element is used in an objective of a projection exposure apparatus. It is further advantageous if A and B are selected in such a way that the resultant mixture is eutectic.

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In comparison to pure metal oxide crystals, the foregoing crystal composition with variable shares of MgO and CaO has the further advantage that its absorption edge is located farther away from 193 nm. This is true in particular in the
15 case of a eutectic mixture.

In a microlithography projection objective, particularly for applications in the areas of immersion lithography or near-field lithography, it is advantageous to select a material of
20 the highest refractivity possible, such as for example MgO, YAG (yttrium aluminum garnet, $Y_3Al_5O_{12}$) or grossularite for the optical element that is located closest to the image plane. Adjacent to this element, as a further optical element, it is advantageous to provide an optical element of one of the
25 aforementioned materials which is suitable to compensate the birefringence of the optical element that lies closest to the image plane. This adjacent optical element can have a lower refractive index. Consequently a larger selection of materials is available that can be used for compensating the
30 intrinsic birefringence. Particularly suited for this is a mixed crystal of the composition $Al_2O_3 \cdot 3[A \text{ MgO} \cdot B \text{ CaO}] \cdot 3SiO_2$, wherein $A + B = 1.0$, because its intrinsic birefringence can be adjusted by varying the factors A and B.

It is particularly advantageous, especially for applications in lithography, to select the composition of the oxide-based mixed crystal in such a way that the refractive index is above 1.7 and that at the same time an intrinsic birefringence is achieved with an absolute value of less than 100 nm/cm, preferably less than 50 nm/cm, and with special preference less than 30 nm/cm.

Each of the preceding types of crystals can also be compensated by itself through four crystal orientations, which requires four lens elements that are distributed in the objective, preferably also following each other in a direct sequence. This can be achieved, for instance, by providing four lens elements, for example made of pyrope, which are either positioned adjacent to each other or distributed in the objective and whose crystal orientations are shifted with respect to each other. This technique is frequently referred to as "clocking".

As another advantageous means for minimizing the intrinsic birefringence, optical elements made of a mixed crystal with a positive overall intrinsic birefringence are compensated by other optical elements made of a mixed crystal with a negative overall intrinsic birefringence, and vice versa. When implementing this concept, it is particularly advantageous to orient the optical elements in such a way that the crystallographic axis with the highest symmetry runs parallel to the optical axis of the objective.

Besides the aforementioned mixed crystals of at least two metal oxides and a semiconductor oxide, there are further oxide-based mixed crystals that could be chosen, in particular for objectives in microlithography projection exposure apparatus. These include in particular: calcium spinel

(CaAl_2O_4), gahnite (ZnAl_2O_4), scandium spinel (ScAl_2O_4), strontium spinel (SrAl_2O_4), excess-magnesium spinel ($\text{MgO} \cdot 3\text{Al}_2\text{O}_3$) and excess calcium spinel ($\text{CaO} \cdot 3\text{Al}_2\text{O}_3$), which in regard to their structure are related to magnesium spinel (MgAl_2O_4).

5 Furthermore, scandium oxide (Sc_2O_3), magnesium gallium oxide (MgGaO_4), scandium aluminum garnet ($\text{Sc}_3\text{Al}_5\text{O}_{12}$) and hydro-grossularite ($\text{Ca}_3\text{Al}_2\text{SiO}_8(\text{SiO}_4)_{1-m}(\text{OH})_{4m}$) are also suitable choices.

10 The invention will be explained in more detail based on the drawing, wherein:

Figure 1 shows a schematic representation of a projection exposure apparatus for applications in immersion lithography, with a projection objective, and

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Figure 2 schematically illustrates the two lens elements of in the last positions on the image side of a projection objective.

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Figure 1 schematically illustrates a microlithography projection exposure apparatus 1 designed for manufacturing highly integrated semiconductor elements by means of immersion lithography. As a light source, the projection exposure apparatus 1 includes an excimer laser 3 with an operating wavelength of 193 nm. Alternatively, it is also possible to use light sources with different operating wavelengths, for example 248 nm or 157 nm. An illumination system 5 following next in the light path produces in its exit plane or object plane 7 a large illumination field which is sharply delimited, very homogeneously illuminated, and matched to the telecentricity requirements of the projection objective 11 which follows in the light path. The illumination system 5 includes devices for the control of the pupil illumination and

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for setting a predetermined state of polarization of the illumination light. In particular, a device is provided which polarizes the illumination light in such a way that the plane of oscillation of the electrical field vector is oriented
5 parallel to the structures of the mask 13.

Downstream in the light path after the illumination system, a device (called reticle stage) for holding and moving a mask 13 is arranged in such a way that the mask 13 is positioned in
10 the object plane 7 of the projection objective 11 and is movable in this plane in a travel direction 15 to work in a scanning mode.

After the object plane 7 which is also referred to as mask
15 plane, the projection objective 11 follows next, projecting an image of the mask in a reduced scale onto a substrate 19, for example a silicon wafer, which carries a light-sensitive lacquer, also called resist 21. The substrate 19 is arranged in such a way that the planar surface of the substrate
20 carrying the resist 21 substantially coincides with the image plane 23, which is one of the field planes of the projection objective 11. The substrate is held by a mechanism 17 which includes a drive source to move the substrate 19 synchronously with the mask 13. The mechanism 17 also includes manipulators
25 which serve to move the substrate 19 in the z-direction parallel to the optical axis 25 of the projection objective 11 as well as in the x- and y-directions perpendicular to the optical axis 25. A tilting device is integrated in the mechanism with at least one tilt axis running perpendicular to
30 the optical axis 25.

The mechanism 17 (wafer stage) which serves to hold the substrate 19 is designed for use in immersion lithography applications. The mechanism 17 includes a receiving device 27

that is movable by a scanner drive and whose bottom has a shallow recess to receive the substrate 19. With a surrounding border 29, a shallow, liquid-tight receiving cavity that is open at the top is formed for an immersion liquid 31. The height of the border is dimensioned so that when the immersion liquid 31 is in place, it can completely cover the substrate surface with the resist 21, and so that the end portion of the projection objective 11 on the exit side of the latter can penetrate into the immersion liquid, if the operating distance between the exit of the objective and the substrate surface has been correctly adjusted.

The projection objective 11 has an image-side numerical aperture of at least $NA = 0.8$, but preferably more than 1.0, and with the highest preference more than 1.3. Thus, the projection objective 11 is specifically adapted for the use of immersion liquids with a high refractive index.

The projection objective 11 has as its last optical element closest to the image plane 11 a hemispherical planar-convex lens 33 whose exit surface 35 is the last optical surface of the projection objective 11. When the projection exposure apparatus is operating, the exit surface of the last optical element is completely immersed in the immersion liquid 31 and is wetted by the latter. An additional adjacent optical element 34 is arranged above the planar-convex lens 33.

Figure 2 schematically illustrates the last lens elements on the image side of a projection objective for immersion lithography, serving to project an image onto a wafer 219. An immersion liquid 231 is arranged between the last optical element 233 on the image side and the wafer 219, for example water, cyclohexane, or a perfluorated ether compound. On the last lens element 233 on the image side, a protective layer

system P is deposited which can consist for example of an anti-reflection layer system in combination with an SiO₂ layer forming an enclosure against the immersion liquid 231 and thereby protecting the optical element 233 from chemical
5 attack by the immersion liquid 231. A further lens element 234 is arranged adjacent to the last lens element 233 on the image side.

Example 1:

10 In a first exemplary embodiment, the last element 233 on the image side consists of MgO with a refractive index of 2.0 at a wavelength of 193 nm and with a positive intrinsic birefringence. The adjacent lens element 234, on the other hand, consists of Al₂O₃·MgO·2CaO·3SiO₂. The refractive index
15 of this material is somewhat lower than the refractive index of MgO. As a result of the contribution of CaO, which has a negative birefringence to the overall properties of the mixed crystal, the crystal overall has a negative intrinsic birefringence, so that by combining the lens elements 233 and
20 234, the overall intrinsic birefringence of the lens group consisting of the last lens element 233 and the adjacent lens element 234 is reduced.

Example 2:

25 The last lens element 233 on the image side in a second exemplary embodiment consists of YAG. The adjacent lens element 234 consists of Al₂O₃·MgO·2CaO·3SiO₂. As in the first example above, combining these materials minimizes the overall intrinsic birefringence.

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Example 3:

The last lens element 233 on the image side in a third exemplary embodiment consists of pyrope (Al₂O₃·3MgO·3SiO₂).

The adjacent lens element 234 consists of grossularite $\text{Al}_2\text{O}_3 \cdot 3\text{CaO} \cdot 3\text{SiO}_2$. As the respective intrinsic birefringence values of MgO and CaO have opposite signs, the overall intrinsic birefringence is minimized by combining the two lens elements. In this example, the last lens element 233 on the image side has a lower refractive index than the adjacent lens element 234.

Example 4:

In a fourth example of an embodiment, both the last lens element 233 on the image side and the adjacent lens element 234 consist of a eutectic mixture of the composition $\text{Al}_2\text{O}_3 \cdot 3[\text{A MgO} \cdot \text{B CaO}] \cdot 3\text{SiO}_2$, wherein A and B are selected so that the intrinsic birefringence is minimized at a operating wavelength of 193 nm.

Example 5:

In a fifth example of an embodiment, the last lens element 233 on the image side consists of grossularite ($\text{Al}_2\text{O}_3 \cdot 3\text{CaO} \cdot 3\text{SiO}_2$).

The adjacent lens element 234 consists of pyrope ($\text{Al}_2\text{O}_3 \cdot 3\text{MgO} \cdot 3\text{SiO}_2$). As in the third example, the overall intrinsic birefringence is minimized due to the opposite signs of the respective birefringence properties of pyrope and grossularite. In contrast to the third example, the optical element 233 closest to the image has in this case the higher refractive index.

Even though the invention has been described with reference to specific embodiments, those skilled in the art will also see numerous variations and alternative embodiments, for example by combination and/or replacement of features of individual embodiments. A person skilled in the art will accordingly understand that such variations and alternative embodiments of

the present invention are also covered, and the scope of the invention is restricted only in the sense of the attached patent claims and their equivalents.

Patent Claims:

1. Optical element of a mixed crystal with at least two metal oxides and a semiconductor oxide.
- 5 2. Optical element according to claim 1, characterized in that the mixed crystal is formed of at least three metal oxides and a semiconductor oxide.
- 10 3. Optical element according to claim 1 or 2, characterized in that the mixed crystal is selected from the group that consists of $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, $\text{Al}_2\text{Mg}_2\text{CaSi}_3\text{O}_{12}$, and $\text{Al}_2\text{MgCa}_2\text{Si}_3\text{O}_{12}$.
- 15 4. Optical element according to claim 1 or 2, characterized in that the proportions of the metal oxides in the composition of the mixed crystal are adjusted so that the intrinsic birefringence of the mixed crystal is minimized.
- 20 5. Optical element according to claim 4, characterized in that the mixed crystal is composed of $\text{Al}_2\text{O}_3 \cdot 3[\text{A MgO} \cdot \text{B CaO}] \cdot 3\text{SiO}_2$, wherein $\text{A} + \text{B} = 1$.
- 25 6. Optical element according to claim 5, characterized in that the mixed crystal is a nearly eutectic mixture.
- 30 7. Optical element of a mixed crystal, characterized in that the mixed crystal is selected from the group that consists of calcium spinel CaAl_2O_4 , gahnite ZnAl_2O_4 , scandium spinel ScAl_2O_4 , strontium spinel SrAl_2O_4 , excess-magnesium spinel $\text{MgO} \cdot 3\text{Al}_2\text{O}_3$, excess calcium spinel $\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, scandium oxide Sc_2O_3 , magnesium gallium oxide MgGaO_4 , scandium aluminum garnet $\text{Sc}_3\text{Al}_5\text{O}_{12}$, and hydro-grossularite $\text{Ca}_3\text{Al}_2\text{SiO}_8(\text{SiO}_4)_{1-m}(\text{OH})_{4m}$.

8. Objective with at least a first optical element according to at least one of the claims 1 to 7.

5 9. Objective according to claim 8 with at least a second optical element according to one of the claims 1 to 7.

10. Objective according to claim 9, characterized in that the first optical element and the second optical element are
10 arranged adjacent to each other.

11. Objective according to claim 10, characterized in that the first optical element and the second optical element consist of different materials.

15 12. Objective according to claim 11, characterized in that the material of the first optical element and the material of the second optical element exhibit intrinsic birefringence with, respectively, opposite signs.

20 13. Objective according to one of the claims 8 to 12, having a field plane, characterized in that the first optical element is the optical element which is located closest to the field plane.

25 14. Projection objective for projecting an image of an object plane into an image plane, consisting of an objective according to claim 13, characterized in that the field plane is the image plane.

30 15. Projection objective according to claim 14, characterized in that an immersion liquid is arranged between the first optical element and the image plane.

16. Microlithography projection exposure apparatus with a projection objective according to one of the claims 14 or 15.
- 5 17. Projection exposure apparatus according to claim 16, characterized in that the projection exposure apparatus is operated at a wavelength of less than 250 nm, in particular less than 200 nm.
- 10 18. Use of a mixed crystal of at least two metal oxides and a semiconductor oxide as material for an optical element in a microlithography projection objective.
- 15 19. Use in accordance with claim 18, characterized in that the mixed crystal is formed of at least three metal oxides and a semiconductor oxide.
- 20 20. Use in accordance with claim 19, characterized in that the mixed crystal is selected from the group consisting of $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, $\text{Al}_2\text{Mg}_2\text{CaSi}_3\text{O}_{12}$, and $\text{Al}_2\text{MgCa}_2\text{Si}_3\text{O}_{12}$.
- 25 21. Use in accordance with one of the claims 18 to 20, characterized in that the projection objective is designed for light with an operating wavelength of less than 250 nm, in particular less than 200 nm.
- 30 22. Use in accordance with claim 21, characterized in that the respective proportions of the metal oxides in the composition of the mixed crystal are adjusted so that the intrinsic birefringence of the mixed crystal at the operating wavelength is minimized.

23. Use in accordance with claim 22, characterized in that the mixed crystal is composed of $\text{Al}_2\text{O}_3 \cdot 3[\text{A MgO} \cdot \text{B CaO}] \cdot 3\text{SiO}_2$, wherein $\text{A} + \text{B} = 1$.

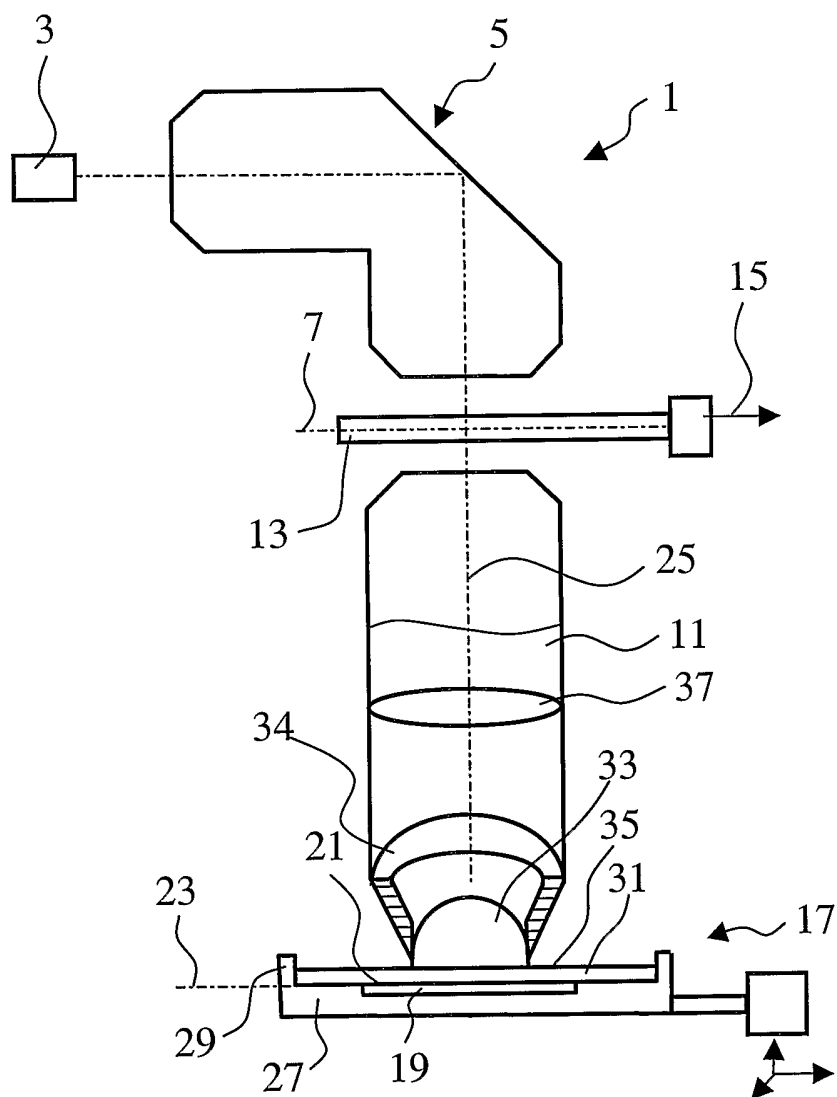
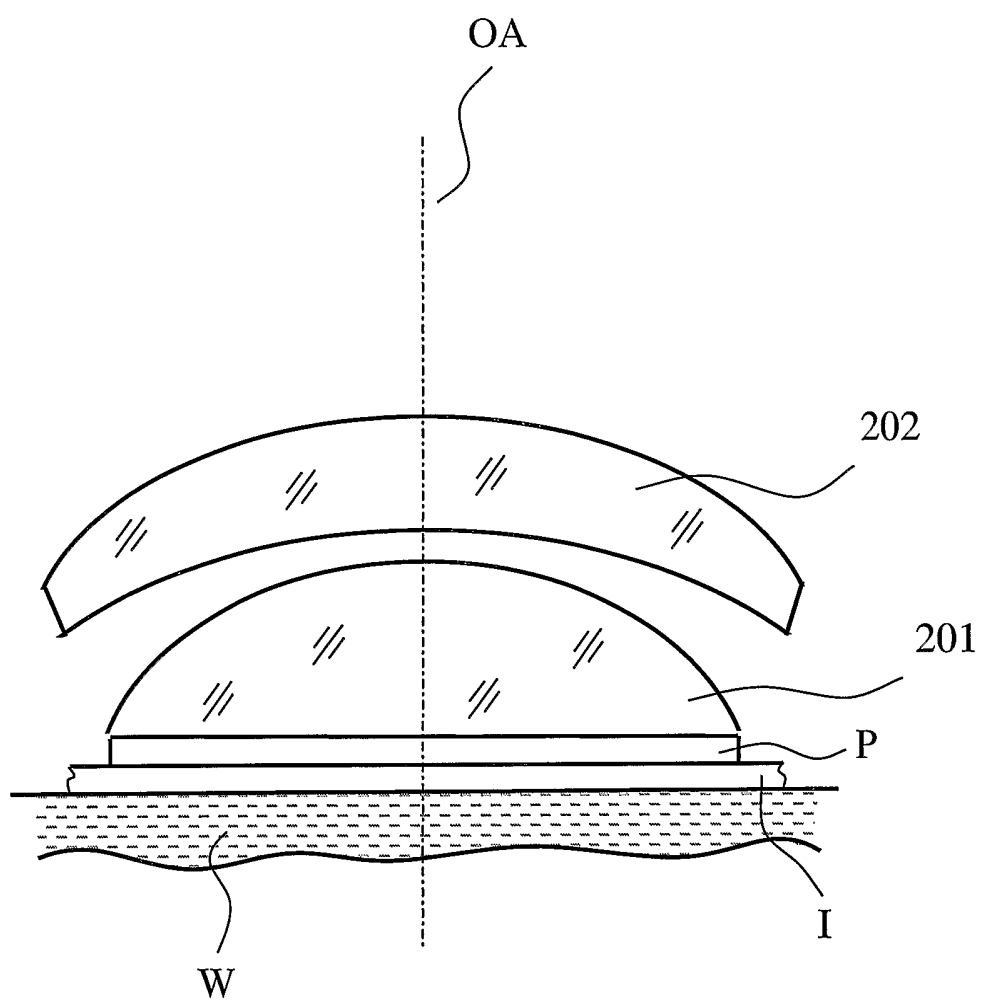
FIG.1

FIG.2

INTERNATIONAL SEARCH REPORT

PCT/EP2005/013572

A. CLASSIFICATION OF SUBJECT MATTER

INV. G02B1/02 G02B13/14 C30B29/22 C30B29/28

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 C30B

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 practical, search terms used)

EPO-Internal, WPI Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	BURNETT J H ET AL: "HIGH INDEX MATERIALS FOR 193 NM IMMERSION LITHOGRAPHY" PROCEEDINGS OF THE SPIE; CONFERENCE: OPTICAL MICROLITHOGRAPHY XVIII, SAN JOSE, CA, USA; CONFERENCE DATE: 1 MARCH 2005, vol. 5754, May 2004 (2004-05), pages 611-621, XP002376239 BELLINGHAM, VA, US abstract page 615 - page 616 page 620	1-23
X	US 5 021 302 A (BRANDLE, JR. ET AL) 4 June 1991 (1991-06-04) abstract; example 2 ----- -/--	1,2



Further documents are listed in the continuation of Box C.



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Date of the actual completion of the international search

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Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

PCT/EP2005/013572

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	BOSENICK ANNE ET AL: "LOCAL CA-MG DISTRIBUTION OF MG-RICH PYROPE-GROSSULAR GARNETS SYNTHESIZED AT DIFFERENT TEMPERATURES REVEALED BY 29SI MAS NMR SPECTROSCOPY" AMERICAN MINEROLOGIST, vol. 84, 1999, pages 1422-1432, XP002376240 abstract -----	1-23
A	SLUITER MARCEL H ET AL: "INTERMIXING TENDENCIES IN GARNETS: PYROPE AND GROSSULAR" PHYSICAL REVIEW B, November 2004 (2004-11), pages 184120-1-184120-4, XP002376241 the whole document -----	1-23
A	BURNETT J H ET AL: "HIGH INDEX MATERIALS FOR 193 NM AND 157 NM IMMERSION LITHOGRAPHY" INTERNATIONAL SYMPOSIUM ON IMMERSION & 157 NM LITHOGRAPHY, [POWERPOINT PRESENTATION], [Online] 8 February 2004 (2004-02-08), XP001207229 VANCOUVER, CANADA Retrieved from the Internet: URL:http://www.sematech.org/resources/litho/meetings/immersion/20040803/DAY_1_presentations/1-11_NIST_Burnett.pdf [retrieved on 2006-04-07] the whole document -----	1-23
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US 5021302	A	04-06-1991	NONE