

Method for producing a capping layer composed of silicon oxide on an EUV mirror, EUV mirror, and EUV lithography apparatus

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Cross-reference to Related Applications

This application claims priority under 35 U.S.C. §119(a) to German Patent Application No. 10 2011 083 461, filed September 27, 2011, the entire
10 disclosure of which is considered part of and is incorporated by reference in the disclosure of this application.

Background of the invention

15 The invention relates to a method for producing a capping layer composed of silicon oxide on a coating of a mirror, said coating reflecting EUV radiation. The invention likewise relates to a mirror comprising a capping layer composed of silicon oxide, and to an EUV lithography apparatus comprising such a mirror. It goes without saying that the mirror can also be used in a different optical device
20 than an EUV lithography apparatus, e.g. in an EUV mask metrology system.

Projection exposure apparatuses for microlithography serve for producing microstructured components by means of a photolithographic method. In this case, a structure-bearing mask, the so-called reticle, is imaged onto a
25 photosensitive layer with the aid of a projection optical unit. The minimum feature size that can be imaged with the aid of such a projection optical unit is determined by the wavelength of the imaging light used. The smaller the wavelength of the imaging light used, the smaller the structures that can be imaged with the aid of the projection optical unit. Imaging light having the
30 wavelength of 193 nm or – in so-called EUV lithography apparatuses – imaging light having a wavelength in the range of the extreme ultraviolet (EUV), i.e.

5 nm – 30 nm, is principally used nowadays. Reflective optical elements (EUV mirrors) are exclusively used in EUV lithography apparatuses since no optical materials having a sufficiently high transmission at these wavelengths are known.

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An EUV mirror for such an EUV lithography apparatus comprises a substrate and a reflective coating having a plurality of layers, said reflective coating being applied to the substrate. Such a multilayer coating generally consists of alternating layers composed of materials having high and low refractive indices, e.g. alternating layers composed of molybdenum and silicon, the layer thicknesses of which are coordinated with one another such that the coating fulfils its optical function and a high reflectivity is ensured. The reflective multilayer coating typically has a capping layer in order to protect the underlying layers against oxidation. Said capping layer can consist of a metallic material, e.g. of ruthenium, rhodium or palladium.

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EP 1 065 568 A2 discloses using carbides as materials for the capping layer, e.g. boron carbide (B_4C) or silicon carbide (SiC). Nitrides, for example silicon nitride (Si_3N_4) or titanium nitride (TiN), are also specified there as materials for the capping layer. Analogously, US 2006/0066940 A1 describes an EUV mirror comprising a capping layer system, wherein alongside silicon nitride (Si_3N_4) boron nitride (BN), too, and alongside boron carbide (B_4C) molybdenum carbide (MoC) and silicon dioxide (SiO_2), too, are proposed as materials for the capping layer system.

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It is also known inter alia from the article "Top Layer Oxidation in Mo/Si Multilayer X-Ray Mirror" by Khanh Nguyen et al., Mat. Res. Soc. Symp. Proc. Vol. 306, 1993 (Materials Research Society) that in the case of an Mo/Si multilayer coating in which a layer of silicon forms the terminating or capping layer, a thin film of silicon dioxide (SiO_2) forms in ambient air, the thickness

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thereof typically being between approximately 10 Angstroms and 20 Angstroms.

US 2010/0190113 A1 describes a mirror comprising a capping layer system
5 having a plurality of layers. The topmost layer of the capping layer system can be formed from silicon dioxide, for example, which is applied by means of a reactive sputtering process.

During the operation of an EUV mirror with such a capping layer composed of
10 silicon dioxide and produced by sputtering in an EUV lithography apparatus, it has been found that during hydrogen cleaning in which the surface of the capping layer is brought into contact with activated hydrogen in order to remove contaminations such as carbon or possibly tin from said layer, a partial conversion or reduction of the silicon dioxide takes place, during which silanes
15 are possibly formed, which has a disadvantageous effect on the reflectivity and/or the uniformity of the reflectivity.

Object of the invention

20 It is an object of the invention to provide a method for producing a capping layer composed of silicon oxide, a mirror comprising such a capping layer, and an EUV lithography apparatus, in which the capping layer has an increased stability of its optical properties during cleaning e.g. with activated hydrogen.

25 Subject matter of the invention

This object is achieved by means of a method of the type mentioned in the introduction, comprising: irradiating a capping layer composed of silicon nitride SiN_x or composed of silicon oxynitride SiN_xO_y for converting the silicon nitride
30 SiN_x or the silicon oxynitride SiN_xO_y of the capping layer into silicon oxide (SiO_x). The invention proposes producing a capping layer composed of silicon

oxide by subjecting a capping layer composed of silicon nitride or silicon oxynitride SiN_xO_y to radiation until practically the entire nitrogen in the capping layer has been replaced by oxygen, thus resulting in the formation of a capping layer composed of silicon oxide SiO_x . A capping layer composed of silicon
5 oxide and produced in this way has proved to be stabler during hydrogen cleaning than a capping layer composed of silicon oxide and produced by direct vapor deposition. The radiation used for the conversion should have wavelengths of less than 390 nm (UV or DUV), wherein in particular EUV radiation, i.e. radiation having wavelengths of less than 30 nm, has proved to
10 be advantageous for the conversion. If appropriate, X-ray radiation, i.e. radiation having wavelengths of less than 5 nm, can be used for the irradiation. The irradiation is typically performed in a gas atmosphere containing oxygen or an oxygen compound.

15 It is possible, during the irradiation, not to subject the entire surface of the capping layer to radiation, such that the complete conversion of the material of the capping layer takes place only within an irradiated region surrounded, if appropriate, by unirradiated or only weakly irradiated regions in which the capping layer material is not completely converted. In general, however, it is
20 advantageous to irradiate the entire capping layer (in particular homogeneously) in order to convert the material of the entire capping layer into silicon oxide SiO_x .

In one variant, the capping layer is irradiated at its surface with EUV radiation
25 having a power density of 200 mW/mm^2 or more, in particular of 250 mW/mm^2 or more, if appropriate 1000 mW/mm^2 or more. It has been found that the power density of the EUV radiation is a determining parameter for the replacement of nitrogen by oxygen in the matrix of the silicon nitride SiN_x or of the silicon oxynitride SiN_xO_y material of the capping layer. In principle, it holds
30 true that high power densities, which are in particular above the threshold value

mentioned above, enable fast conversion of the capping layer into a silicon oxide layer.

In a further variant of the method, the irradiation of the capping layer is carried out in an EUV lithography apparatus in which the mirror is arranged (typically prior to an exposure operation of the EUV lithography apparatus). An EUV lithography apparatus typically comprises an EUV light source which can generate the power densities specified above. Therefore, it is appropriate to use an EUV lithography apparatus for the irradiation. In this case, the irradiation is typically effected before the actual exposure operation, wherein the mirrors having the capping layers composed of silicon nitride or silicon oxynitride can, if appropriate, firstly be brought to suitable positions for the irradiation (in particular in proximity to the EUV radiation source) in order to subject them to EUV radiation having a high power density. After the complete conversion of the capping layer, the EUV mirrors can then be brought to the position respectively provided for exposure operation. Alternatively, the irradiation of the EUV mirrors can also be performed in-situ, i.e. at a position corresponding to the position during later exposure. If appropriate, in this case, the beam path from the EUV light source to the mirror can be changed by comparison with the exposure beam path, such that as few reflective optical elements as possible are situated between a mirror respectively to be irradiated and the EUV light source.

Alternatively, the irradiation can also be performed by means of an EUV light source, a UV light source or by means of an X-ray source which is not part of an EUV lithography apparatus. In this case, the irradiation process typically takes place in an irradiation apparatus specially provided for this purpose.

In a further variant, the irradiation of the capping layer is carried out in a residual gas atmosphere having an oxygen partial pressure $p(\text{O}_2)$ of between 10^{-7} mbar and 10^{-11} mbar, preferably about approximately 10^{-9} mbar and/or a

water partial pressure $p(\text{H}_2\text{O})$ of between 10^{-5} mbar and 10^{-9} mbar, preferably about approximately 10^{-7} mbar. Such an oxygen and/or water partial pressure promotes the replacement of nitrogen by oxygen in the capping layer and can therefore be used for the pre-irradiation of the capping layer. The residual gas
5 atmosphere can be produced in a vacuum environment of the (pre-)irradiation apparatus or in an EUV lithography apparatus. A higher oxygen partial pressure and/or water partial pressure are/is typically used for the pre-irradiation than during operation of the EUV mirror in an EUV lithography apparatus or in an EUV mask metrology system.

10 Preferably, the capping layer is applied to a silicon layer of the reflective coating in order to promote the deposition of the silicon nitride material or of the silicon oxynitride material. The reflective coating typically has a plurality of individual layers consisting alternately of materials having different refractive indices. If
15 EUV radiation at a wavelength in the range of 13.5 nm is used, then the individual layers usually consist of molybdenum and silicon. Other material combinations such as e.g. molybdenum and beryllium, ruthenium and beryllium or lanthanum and B_4C are likewise possible. In addition to the individual layers described, a reflective coating can also comprise intermediate layers for
20 preventing diffusion and the above-described capping layer for preventing oxidation or corrosion.

In a further variant, the method comprises in a step preceding the irradiation: applying the capping layer composed of silicon nitride or composed of silicon
25 oxynitride by vapor deposition. Since the substrate materials of EUV mirrors typically cannot withstand excessively high temperatures, it is known e.g. from US 2008/0316595 A1 to implement a capping layer composed of silicon nitride by chemical vapor deposition (CVD) involving plasma enhanced chemical vapor deposition (PE-CVD) or low pressure chemical vapor deposition (LP-CVD).

30 These coating methods enable a deposition at lower temperatures than is the case with a conventional chemical vapor deposition.

It has proved to be advantageous to apply the capping layer composed of silicon nitride or silicon oxynitride by physical vapor deposition (PVD), in particular by sputtering (cathode sputtering). PVD methods have the advantage that they can be carried out at comparatively low temperatures, and so the substrate material is not damaged during coating. Sputtering can be carried out using a magnetron, for example as described in WO 2010/127845 A1, wherein so-called "High Power Impulse Magnetron Sputtering (HiPIMS)" and "High Power Pulsed Magnetron Sputtering (HPPMS)" are used to form nitridic layers.

The method described in WO 2010/127845 A1 is intended to be suitable, in particular, for producing oxynitride layers having different proportions of oxygen and nitride. Inter alia, silicon nitride (Si_3N_4), silicon oxynitride (SiN_xO_y) and, in particular, $\text{Si}_{3-2x}\text{O}_{2x}\text{N}_{4(1-x)}$ (where x is between 0 and 1) are specified as possible types of layers.

In one variant, a nitrogen proportion x in the SiN_x or in the SiN_xO_y of between 0.4 and 1.4, preferably between 0.7 and 1.4, particularly preferably between 1.0 and 1.4 is set when depositing the capping layer. A capping layer which is composed of silicon oxynitride or silicon nitride and is deposited by means of a PVD process with suitably chosen coating parameters is low in nitrogen, i.e. this material has a significantly lower nitrogen proportion than is predefined by the stoichiometry of conventional silicon nitride (Si_3N_4). The nitrogen proportion of the silicon nitride or the silicon oxynitride can be varied within certain limits during coating, for example by suitably choosing the residual gas composition during coating in a vacuum coating apparatus.

In a further variant, an oxygen proportion $y < 0.9$, preferably $y < 0.4$, is set in the SiN_xO_y when applying the capping layer. The oxygen proportion in the silicon oxynitride can also be influenced by the composition of the gas constituents of the residual gas atmosphere.

In a further variant, the method comprises in a step preceding the irradiation: applying the reflective coating to a substrate in such a way that the reflective coating has a reflection maximum at an operating wavelength λ_B in the EUV wavelength range and a maximum or a minimum of the field intensity of a standing wave that forms upon the reflection of radiation at the operating wavelength λ_B at the reflective coating is arranged at a distance of $0.1 \lambda_B$ or less from a surface of the capping layer of the reflective coating which forms the interface between the capping layer and the environment.

The inventors have found that a decrease in reflectivity as a result of the replacement of nitrogen by oxygen in the capping layer turns out to be comparatively small (typically approximately 2% or less) if the maximum or the minimum of the standing wave is situated in the region of the surface of the capping layer or of the reflective coating. In order to achieve this, the optical design of the multilayer coating, in particular the layer thicknesses of the layers, can be chosen suitably. Thus, in particular the thickness of the capping layer and/or the thickness of the layer to which the capping layer is applied can be set such that the standing wave has a maximum or a minimum at the surface. Particularly if a minimum of the field intensity of the standing wave is formed at the surface of the capping layer, the differences in reflectivity between a capping layer composed of silicon nitride or silicon oxynitride and a capping layer composed of silicon oxide are very small. Consequently, even the undesirable case where the entire nitrogen in the capping layer is not replaced by oxygen during irradiation leads only to a comparatively small change in the reflectivity of the EUV mirror.

A further aspect of the invention relates to a mirror for use in an EUV lithography apparatus comprising: a substrate and a coating reflective to EUV radiation, said coating having a capping layer composed of silicon oxide SiO_x which is as stable as possible during hydrogen cleaning. Such a capping layer can be obtained, in particular, by the method described above, i.e. by

converting a capping layer composed of silicon nitride or silicon oxynitride into a capping layer composed of silicon oxide. It has proved to be advantageous if the capping layer has an oxygen proportion where $1.0 < x < 2.0$, in particular where $1.8 < x < 2.0$. The capping layer can, in particular, also have an oxygen
5 proportion of $x = 2.0$. In this case, it differs from a capping layer composed of silicon dioxide SiO_2 , produced by direct vapor deposition (without EUV irradiation), in terms of its crystal structure.

Layers composed of silicon nitride or silicon oxynitride which are applied by
10 physical vapor deposition, in particular, are typically low in nitrogen, i.e. they have a nitrogen proportion of between approximately 0.4 and 1.4, preferably between 0.7 and 1.4, particularly preferably between 1.0 and 1.4.

If the capping layer is produced from SiN_xO_y , it has proved to be advantageous
15 if the oxygen proportion y in the capping layer is less than 0.9, preferably less than 0.4.

Particularly if the capping layer is deposited by means of a sputtering method, it is generally amorphous, which has an advantageous effect on its stability
20 properties.

In one embodiment, the capping layer is applied to a silicon layer of the reflective coating. Applying the capping layer comprised of silicon nitride or silicon oxynitride to a silicon layer has proved to be advantageous for improving
25 the adhesion properties of the capping layer. By contrast, applying the capping layer to a molybdenum layer would possibly lead to the formation of a mixed layer comprising constituents of both the molybdenum layer and the capping layer. Such a mixed layer could consist e.g. of MoSi_2 , MoN or MoOx .

In a further embodiment, the reflective coating has a reflection maximum at an
30 operating wavelength λ_B in the EUV wavelength range and a maximum or a

minimum of the field intensity of a standing wave that forms upon the reflection of radiation at the operating wavelength λ_B at the reflective coating is arranged at a distance of $0.1 \lambda_B$ or less from a surface of the capping layer of the reflective coating, wherein the surface forms the interface between the capping layer and the environment. The operating wavelength λ_B of EUV mirrors in an EUV lithography apparatus is typically approximately 13.5 nm. As explained further above, particularly for the case where the standing wave has an intensity minimum at the surface of the capping layer, it is possible to prevent a decrease in reflectivity even in partial regions of the capping layer in which the irradiation has not led to complete replacement of the nitrogen in the nitride or oxynitride matrix by oxygen.

A further aspect of the invention relates to an EUV lithography apparatus comprising at least one mirror embodied in the manner described above. The mirror is arranged in a residual gas atmosphere situated in an (evacuated) vacuum housing of the EUV lithography apparatus.

As explained further above, the capping layer can be converted into a silicon oxide layer in the EUV lithography apparatus if appropriate in-situ, i.e. the mirrors, during the (pre-)irradiation, are already situated at the position in which they will subsequently be used during exposure operation. Alternatively, the irradiation can also be effected in an irradiation apparatus provided especially for this purpose. In both cases, the irradiation can be restricted, if appropriate, to the regions of the capping layer which are arranged in the beam path of the EUV radiation during exposure operation, while conversion of the capping layer material can be dispensed with, if appropriate, in partial regions of the surface of the capping layer which are not directly subjected to the EUV radiation.

Other features and advantages of the invention are evident from the following description of exemplary embodiments of the invention, with reference to the figures of the drawing, which show details essential to the invention, and from

the claims. The individual features can be realized in each case individually by themselves or as a plurality in any desired combination in a variant of the invention.

5 Drawing

Exemplary embodiments are illustrated in the schematic drawing and are explained in the description below. In the figures:

- 10 Figure 1 shows a schematic illustration of an embodiment of an EUV lithography apparatus according to the invention,
- Figure 2 shows a schematic illustration of an EUV mirror for such an EUV lithography apparatus during irradiation for converting a
- 15 capping layer composed of silicon oxynitride or silicon nitride into a capping layer composed of silicon oxide,
- Figures 3a,b show two spectra obtained during an XPS analysis of a capping layer composed of silicon oxynitride,
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- Figures 4a,b show a comparison of the reflectivity and respectively of the field intensity with regard to the vacuum interface of a standing wave of a reflective coating with a capping layer composed of
- silicon oxynitride and respectively with a capping layer
- 25 composed of silicon oxide as a function of the wavelength, and
- Figures 5a,b show an illustration analogous to Figures 4a,b wherein the standing wave has a maximum of the field intensity at the surface of the capping layer.

Figure 1 schematically shows a projection exposure apparatus for EUV lithography, which is designated hereinafter as EUV lithography apparatus 1 for short. The EUV lithography apparatus 1 comprises a ray generating system 2, an illumination system 3 and a projection system 4, which are accommodated in separate vacuum housings and arranged successively in a beam path 6 proceeding from an EUV light source 5 of the ray shaping system 2. By way of example, a plasma source or a synchrotron can serve as EUV light source 5. The radiation in the wavelength range of between approximately 5 nm and approximately 20 nm that emerges from the light source 5 is firstly concentrated in a collimator 7. With the aid of a downstream monochromator 8, the desired operating wavelength λ_B , which is approximately 13.5 nm in the present example is filtered out by variation of the angle of incidence, as indicated by a double-headed arrow. The collimator 7 and the monochromator 8 are embodied as reflective optical elements.

The radiation treated with regard to wavelength and spatial distribution in the ray generating system 2 is introduced into the illumination system 3, which has a first and second reflective optical element 9, 10. The two reflective optical elements 9, 10 direct the radiation onto a photomask 11 as further reflective optical element, which has a structure that is imaged onto a wafer 12 on a reduced scale by means of the projection system 4. For this purpose, a third and fourth reflective optical element 13, 14 are provided in the projection system 4.

The reflective optical elements 9, 10, 11, 13, 14 each have an optical surface that is subjected to the EUV radiation 6 from the light source 5. In this case, the optical elements 9, 10, 11, 13, 14 are operated under vacuum conditions in a residual gas atmosphere 19. Since the interior of the projection exposure apparatus 1 cannot be baked out, the presence of residual gas constituents in the vacuum environment cannot be completely avoided.

The EUV lithography apparatus 1 has a gas feed device 20 with a feed channel 21, which is connected to a gas reservoir (not shown) and serves for feeding and for discharging different gas constituents into and from the residual gas atmosphere 19 of the EUV lithography apparatus 1. As is shown in Figure 1, nitrogen (N_2), water (H_2O), oxygen (O_2) and hydrogen (H_2) are present, inter alia, as gas constituents in the residual gas atmosphere 19. It goes without saying that corresponding feed channels can also be provided in the illumination system 3 and/or in the ray generating system 2 or else a central feed channel can be provided for the entire EUV lithography apparatus 1. A control device (not shown) serves to control the gas feed device 20 and to control further functions of the EUV lithography apparatus 1.

The construction of one of the reflective optical elements 13 in the EUV lithography apparatus 1, said element also being designated as EUV mirror hereinafter, is described by way of example hereinafter with reference to Figure 2. The EUV mirror 13 has a substrate 15 composed of a material having a low coefficient of thermal expansion, which is typically less than 100 ppb/K at 22°C or over a temperature range of approximately 5°C to approximately 35°C. One material which has these properties is silicate or quartz glass doped with titanium dioxide, which typically has a silicate glass proportion of more than 90%. One such silicate glass that is commercially available is sold by Corning Inc. under the trade name ULE® (Ultra Low Expansion glass). A further group of materials having a very low coefficient of thermal expansion is glass ceramics, in which the ratio of the crystal phase to the glass phase is set such that the coefficients of thermal expansion of the different phases virtually cancel one another out. Such glass ceramics are offered e.g. by Schott AG under the trade names Zerodur®, and by Ohara Inc. under the trade name Clearceram®. For the reflective optical elements 9, 10 arranged in the illumination system 3, an e.g. metallic substrate material can also be used, if appropriate, instead of a zero expansion material.

A reflective coating 16 is applied to the substrate 15, said reflective coating having a plurality of individual layers 17a, 17b consisting alternately of materials having different refractive indices, to be precise silicon and molybdenum in the present case. In addition to the individual layers shown in Figure 2, the
5 reflective coating 16 can also comprise intermediate layers for preventing diffusion or the like. The illustration of such auxiliary layers in the figures has been omitted.

The reflective coating 16 has a capping layer 18 in order to prevent oxidation of
10 the underlying individual layers 17a, 17b and in order to simplify cleaning of contaminating substances attached to the surface 18a of the capping layer 18. The capping layer 18 of the mirror 13 was applied to the topmost silicon layer 17a of the reflecting coating 16 by vapor deposition. The capping layer 18 has a thickness d1 of e.g. approximately 1.5 nm and absorbs the impinging EUV
15 radiation 6 only to a small extent also on account of the small layer thickness. Depending on the application, the layer thickness can be between approximately 1 nm and approximately 20 nm, comparatively large layer thicknesses being used, in particular, in the vicinity of the collector or collimator 7.

20 In the exemplary embodiment illustrated, the EUV mirror 13 has a planar surface 18a. This was chosen thus merely in order to simplify the illustration, that is to say that the EUV mirror 13 can also have a curved surface form, wherein e.g. concave surface forms or convex surface forms are possible,
25 which can be embodied spherically and also aspherically.

Figure 2 shows the capping layer 18 during homogeneous irradiation with EUV radiation 6 in order to convert the material of the capping layer 18, which material was applied during the coating of the EUV mirror in the form of silicon
30 oxynitride SiO_xN_y or of silicon nitride SiN_x , into silicon oxide SiO_x . The irradiation of the EUV mirror 13 can be effected in an apparatus which is

5 specially designed for this purpose and which has an EUV light source. It is more advantageous if the irradiation is performed directly in the EUV lithography apparatus 1 itself, to be precise in particular in-situ, i.e. if the EUV mirror 13 is arranged, during irradiation, at the same location at which it is also used during the exposure operation of the EUV lithography apparatus 1.

10 In order that the EUV mirror 13 as shown in Figure 2 is subjected to EUV radiation 6 as homogeneously as possible during irradiation, if appropriate additional reflective optical elements can be provided in the EUV lithography apparatus, which are introduced into the beam path of the EUV light source 5 only during the pre-irradiation, in order to collimate the EUV radiation 6 before the latter impinges on the EUV mirror 13.

15 Alternatively, it is possible to arrange the EUV mirror 13 for the conversion of the material of the capping layer 18 at a different location than in the EUV lithography apparatus 1, for example in an irradiation apparatus which is provided separately for this purpose and which enables the capping layer 18 to be prepared in a well-defined manner. In such an irradiation apparatus (not illustrated in the figures), in particular EUV radiation 6 with a collimated beam path can be generated, such that the surface 18a, as shown in Figure 2, can be subjected homogeneously to EUV radiation. As an alternative to the irradiation of the surface 18a with EUV light, it is also possible to use radiation at other wavelengths, e.g. UV radiation (having wavelengths of < 390 nm) or X-ray radiation.

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The use of an irradiation apparatus has also proved to be advantageous for producing a high power density (e.g. of more than 200 mW/mm^2 or of more than 1000 mW/mm^2) at the surface 18a of the EUV mirror 13, since said surface 18a can be subjected to the radiation of the EUV light source 5 directly, i.e. without reflections that reduce the power density at a plurality of optical elements.

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While the EUV mirror 13 is subjected to EUV radiation 6 in the EUV lithography apparatus 1 or in an irradiation apparatus in order to achieve the conversion of the material of the capping layer 18, it has proved to be advantageous to
5 provide there a residual gas atmosphere having a high oxygen proportion, wherein suitable oxygen partial pressures are typically in the range of between approximately 10^{-7} mbar and 10^{-11} mbar, in particular around approximately 10^{-9} mbar. Alternatively or additionally, during the irradiation it is also possible to use a water partial pressure of between approximately 10^{-5} mbar and 10^{-9} mbar,
10 preferably around approximately 10^{-7} mbar, in order to promote the conversion of the capping layer 18. A lower oxygen partial pressure and/or water partial pressure is typically used for exposure operation in an EUV lithography apparatus 1 after the conversion of the capping layer 18.

15 The application of the reflective coating 16 to the substrate 15 is described in greater detail below. Firstly, the layers 17a, 17b composed of silicon and composed of molybdenum, respectively, are applied to the substrate 15, for which purpose a PVD method is typically used. The capping layer 18 is then applied to the topmost silicon layer 17a, for which purpose a PVD method is
20 likewise used, to be precise in the present example a sputtering process, as a result of which the deposited silicon oxynitride SiN_xO_y or silicon nitride SiN_x has an amorphous structure. In the coating method, both the nitrogen proportion x of the capping layer 18 and the oxygen proportion y (in the case of a capping layer composed of SiN_xO_y) can be set through a suitable choice of the coating
25 parameters, wherein advantageous values for the nitrogen proportion x are between approximately 0.4 and 1.4, preferably between 0.7 and 1.4, in particular between approximately 1.0 and approximately 1.4. In the case of a capping layer composed of SiN_xO_y , the oxygen proportion y is generally $y = 0.9$, if appropriate $y = 0.4$ or less, wherein a variation of the respective
30 proportions x and y within the capping layer 18 may possibly occur in a process-governed manner. A capping layer 18 having a spatially homogeneous

composition in which $x = 1.0$ or $x > 1.0$ and $y = 0.4$ or $y < 0.4$ is particularly advantageous.

As described above, the exact composition of the silicon oxynitride SiN_xO_y or of the silicon nitride SiN_x is dependent on the coating parameters. During sputtering, a magnetic field can additionally be used (magnetron sputtering) and, if appropriate, pulsed discharges can be used for the coating, as in the case of so-called "High Power Impulse Magnetron Sputtering (HiPIMS)" or in the case of "High Power Pulsed Magnetron Sputtering (HPPMS)", which are described for example in WO 2010/127845 A1 cited in the introduction. Instead of a PVD method, it is also possible, if appropriate, to apply the capping layer 18 by means of a CVD method, in particular a PE-CVD or LP-CVD method, cf. the website of Crystec at <http://www.crystec.com/trinitre.htm> or US 5,773,100 cited in the introduction.

The coating parameters which influence the nitrogen proportion of the capping layer 18 also include the composition of the gas atmosphere during deposition, as described below on the basis of an XPS spectral analysis (cf. Figures 3a,b) of a silicon oxynitride capping layer 18 applied to a silicon layer 17a by means of a sputtering process. The thicknesses of the layers 17a, 17b of the reflective coating 16 were chosen in the present example such that they have a reflection maximum at the operating wavelength λ_B of 13.5 nm.

The graphs in Figures 3a,b illustrate the Si 2p bond of the XPS spectrum (as a function of the bond energy E_B), wherein the intensity I of the photoelectrons which emerge at a shallow angle from the surface 18a of the capping layer 18 is represented by a dashed curve, while the intensity I of photoelectrons which emerge at a steep angle (virtually perpendicularly) with respect to the surface 18a is represented as a solid line. The solid intensity curve thus includes information about the composition of the capping layer 18 at a greater depth,

whereas the dashed intensity curve substantially shows information about a near-surface depth range of approximately 1-2 nm of the capping layer 18.

In Figures 3a,b it can be discerned that the Si 2p spectrum substantially has three peaks at different bond energies E_B . A first bond energy E_B at approximately 103.5 eV is characteristic of the oxide bond, a second bond energy E_B at approximately 102 eV corresponds to the silicon nitride bond, while a third bond energy E_B of approximately 99 eV corresponds to the unbound semiconductor state, i.e. unbound, elemental silicon.

The two graphs in Figure 3a and Figure 3b differ in that additional nitrogen in gaseous form was added during the coating process in Figure 3b, while this was not the case in Figure 3a. Comparison between Figure 3a and Figure 3b clearly reveals that the oxygen peak at approximately 103.5 eV in Figure 3b is significantly smaller than in Figure 3a, and that conversely the peak of the nitride bond at approximately 102 eV has risen significantly, i.e. the composition or the stoichiometry of the silicon oxynitride material essentially depends on the composition of the gas atmosphere during coating.

For the case where, during irradiation, undesirably the capping layer 18 is not subjected to EUV radiation 6 at the entire surface 18a or, in partial regions of the surface 18a, the radiation dose is not high enough for complete conversion of the material of the capping layer 18, it has proved to be advantageous for an antinode or a node of a standing wave that forms in the reflective coating 16 during the irradiation with EUV light 6 to be positioned directly at the surface 18a of the capping layer or – if this is not possible – for the distance between the antinode or node of the standing wave and the surface 18a to be chosen such that it is not more than $0.1 \lambda_S$.

In order to achieve this, in particular the thickness d_1 of the capping layer 18 and the thickness d_2 of the underlying silicon layer 17a (and also, if

appropriate, the thicknesses of further layers 17a, 17b of the reflective coating 16) can be chosen suitably. If the above condition is met, even upon incomplete replacement of the nitrogen by oxygen in the capping layer 18 the change in the reflectivity caused thereby is comparatively small, as can be discerned with
5 reference to Figure 4a, which shows the reflectivity R when using a silicon nitride capping layer as a function of the wavelength λ at which a node of the standing wave is formed at the surface 18a. The coating of the EUV mirror 13, i.e. the thicknesses of the layers 17a, 17b, are in this case optimized for a capping layer composed of silicon nitride, i.e. the maximum reflectivity R is
10 assumed when using a capping layer 18 composed of silicon nitride.

The change in the reflectivity R upon the complete replacement of nitrogen by oxygen is only $\Delta R/R = -0.02\%$ in the case shown in Figure 4a, and so the associated reflectivity curve for the silicon oxide capping layer 18 cannot be
15 discerned in Figure 4a since, with the scaling chosen, it corresponds to the reflectivity curve for silicon nitride. Figure 4b shows the field intensity I at the surface 18a of the capping layer 18 as a function of the wavelength λ , wherein it can clearly be discerned that said field intensity has an intensity minimum $I_{\min}$ (i.e. a node of the standing wave) at the operating wavelength λ_S of 13.5 nm.

20 When an antinode is present at the surface 18a of the capping layer 18, the change in the reflectivity when nitrogen is replaced by oxygen is greater and is $\Delta R/R = -2.1\%$, as is indicated by a dashed reflectivity curve in Figure 5a. As is shown in Figure 5b, the standing wave at the surface 18a of the reflective
25 coating 16 in this case has an intensity maximum $I_{\max}$ approximately at the operating wavelength λ_B of 13.5 nm. In order to minimize a reduction of the reflectivity R upon the replacement of oxygen by nitrogen in the capping layer 18, it is therefore particularly advantageous to position an intensity minimum of the standing wave at the location of the surface 18a.

The use of a stable capping layer 18 composed of silicon oxide has proved to be advantageous in particular for removing impurities or particles, in particular metal compounds containing tin or carbon, from the surface 18a of the EUV mirror 13, for which purpose hydrogen cleaning is advantageously carried out, during which activated hydrogen, in particular in the form of hydrogen radicals or hydrogen ions, is applied to the surface 18a.

The hydrogen cleaning can be carried out by setting a suitable hydrogen partial pressure $p(\text{H}_2)$ in the residual gas atmosphere 19. The hydrogen can be activated by the EUV radiation 6 in proximity to the surface 18a and in the process can be converted into hydrogen ions or hydrogen radicals which clean contaminating substances such as tin or carbon away from the surface 18a. For the hydrogen cleaning it is also possible, however, to provide additional devices in the EUV lithography apparatus 1, for example cleaning heads that serve to generate a hydrogen-containing gas flow directed onto the surface 18a. Cleaning heads of this type are described for example in WO 2009/059614 A1 from this applicant, which is incorporated by reference in the content of this application. The hydrogen in the gas flow can be activated hydrogen, wherein the activation can be effected for example using an electric field, as is described in WO 2009/059614 A1, or possibly by guiding the (molecular) hydrogen along a heating wire for the purpose of activation.

Patent Claims

1. Method for producing a capping layer (18) composed of silicon oxide SiO_x on a coating (16) of a mirror (13), said coating reflecting EUV radiation (6), comprising:
irradiating a capping layer (18) composed of silicon nitride SiN_x or composed of silicon oxynitride SiN_xO_y for converting the silicon nitride SiN_x or the silicon oxynitride SiN_xO_y of the capping layer (18) into silicon oxide SiO_x .
2. Method according to Claim 1, wherein the capping layer (18) is irradiated with EUV radiation (6) having a power density of 200 mW/mm^2 or more.
3. Method according to either of the preceding claims, wherein the irradiation of the capping layer (18) is carried out in an EUV lithography apparatus (1) in which the mirror (13) is arranged.
4. Method according to any of the preceding claims, wherein the irradiation of the capping layer (18) is effected in a residual gas atmosphere (19) having an oxygen partial pressure ($p(\text{O}_2)$) of between 10^{-7} mbar and 10^{-11} mbar and/or a water partial pressure ($p(\text{H}_2\text{O})$) of between 10^{-5} mbar and 10^{-9} mbar.
5. Method according to any of the preceding claims, further comprising: in a step preceding the irradiation: applying the capping layer (18) composed of silicon nitride SiN_x or composed of silicon oxynitride SiN_xO_y by vapor deposition.
6. Method according to Claim 5, wherein the capping layer (18) is deposited by physical vapor deposition.

7. Method according to Claim 5 or 6, wherein a nitrogen proportion x in the SiN_x or in the SiN_xO_y of between 0.4 and 1.4 is set when applying the capping layer (18).
8. Method according to any of Claims 5 to 7, wherein an oxygen proportion $y < 0.9$, preferably $y < 0.4$, is set in the SiN_xO_y when applying the capping layer (18).
9. Method according to any of the preceding claims, further comprising: in a step preceding the irradiation: applying the reflective coating (16) to a substrate (15) in such a way that the reflective coating (16) has a reflection maximum at an operating wavelength λ_B in the EUV wavelength range and a maximum ($I_{\max}$) or a minimum ($I_{\min}$) of the field intensity (I) of a standing wave that forms upon the reflection of radiation at the operating wavelength λ_B at the reflective coating (16) is arranged at a distance of $0.1 \lambda_B$ or less from a surface (18a) of the capping layer (18) of the reflective coating (16).
10. Mirror (13), comprising:
a substrate (15) and a coating (16) reflective to EUV radiation (6),
characterized in that
the reflective coating (16) has a capping layer (18) composed of silicon oxide SiO_x produced by a method according to any of the preceding claims.
11. Mirror according to Claim 10, wherein the oxygen proportion x in the silicon oxide SiO_x is between 1.0 and 2.0, preferably between 1.8 and 2.0.
12. Mirror according to either of Claims 10 and 11, wherein the capping layer (18) is amorphous.

13. Mirror according to any of Claims 10 to 12, wherein the capping layer (18) is applied to a silicon layer (17a) of the reflective coating (16).
14. Mirror according to any of Claims 10 to 13, wherein the reflective coating (16) has a reflection maximum at an operating wavelength λ_B in the EUV wavelength range and a maximum ($I_{\max}$) or a minimum ($I_{\min}$) of the field intensity (I) of a standing wave that forms upon the reflection of radiation at the operating wavelength λ_B at the reflective coating (16) is arranged at a distance of $0.1 \lambda_B$ or less from a surface (18a) of the capping layer (18) of the reflective coating (16).
15. EUV lithography apparatus (1), comprising:
at least one mirror (9, 10, 11, 13, 14) according to any of Claims 10 to 14,
which is arranged in a residual gas atmosphere (19) of the EUV lithography apparatus (1).

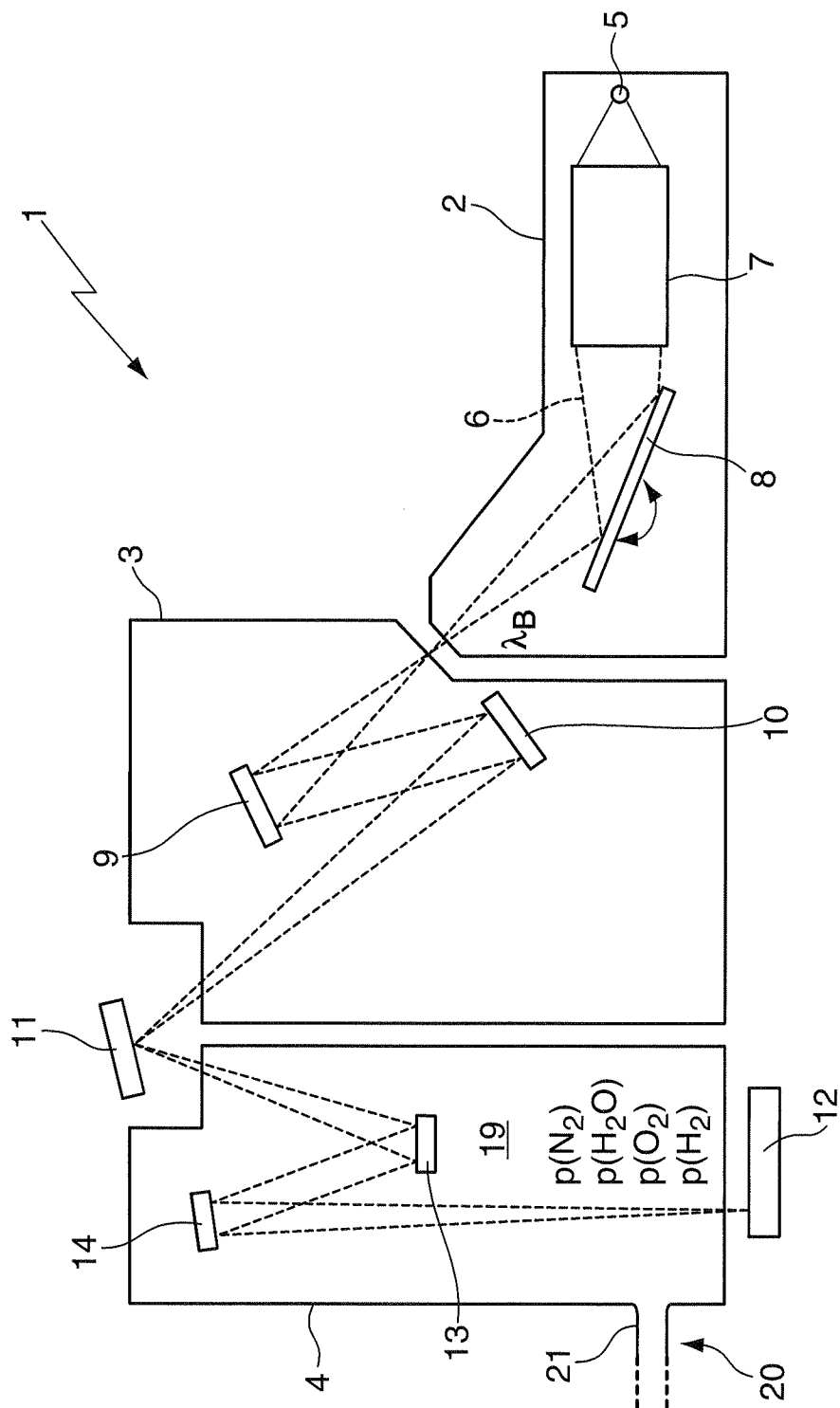


Fig. 1

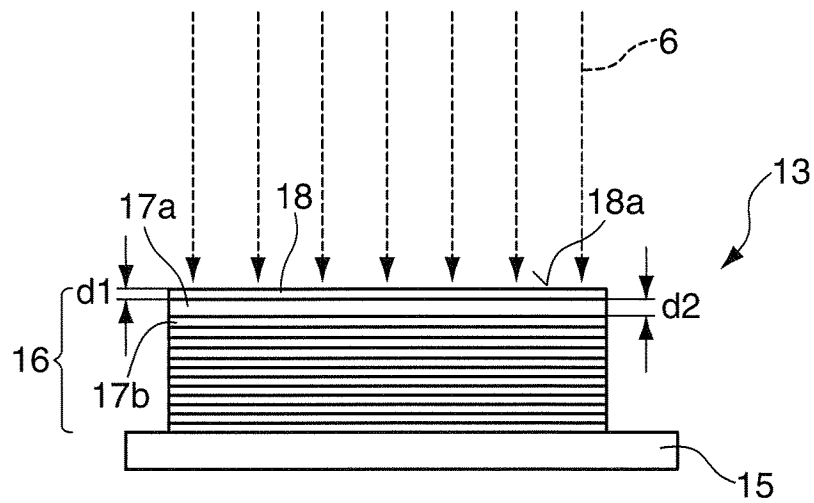


Fig. 2

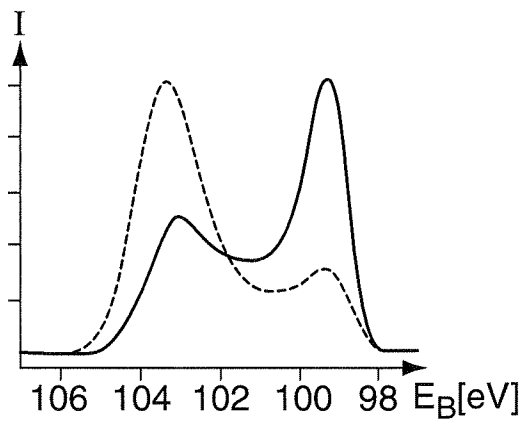


Fig. 3a

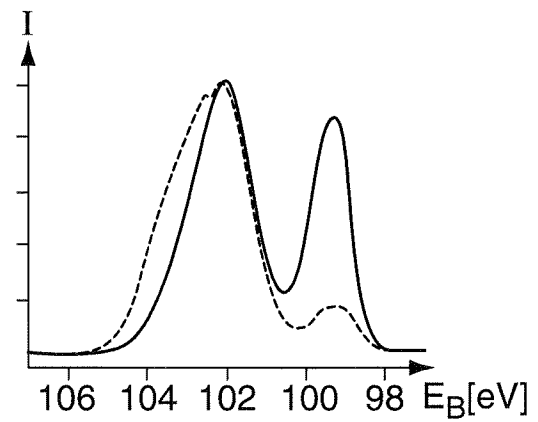


Fig. 3b

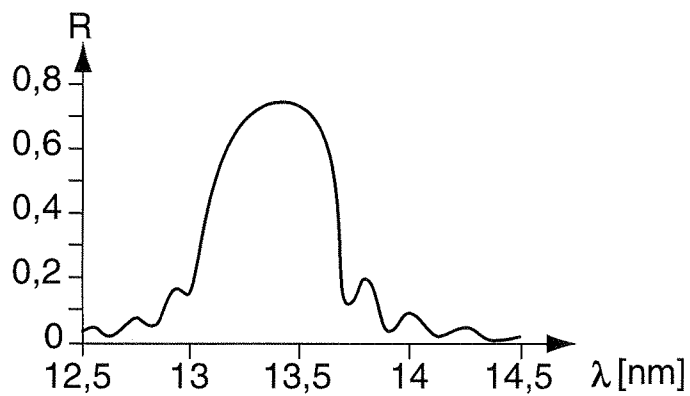


Fig. 4a

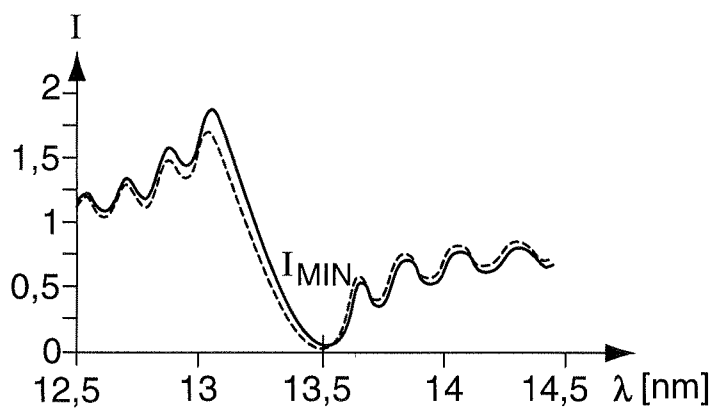


Fig. 4b

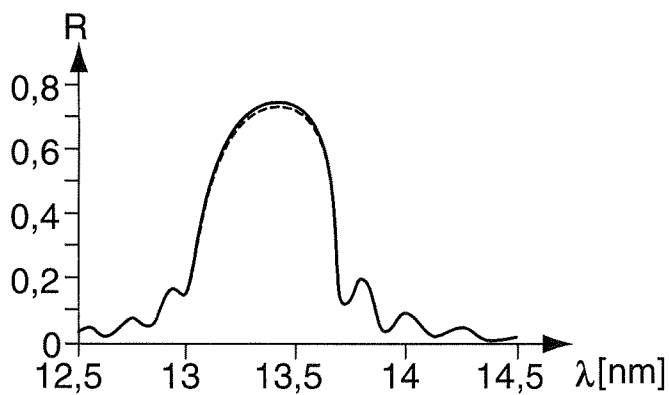


Fig. 5a

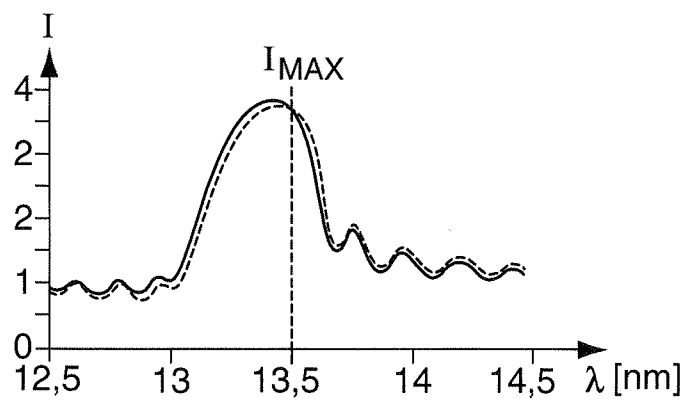


Fig. 5b

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/068319

A. CLASSIFICATION OF SUBJECT MATTER INV. G02B5/08 G21K1/06 G03F7/20 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) G03F G02B G21K		
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, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2010/190113 A1 (MURAKAMI KATSUHIKO [JP] ET AL) 29 July 2010 (2010-07-29) cited in the application	10,11, 13-15
A	paragraph [0030] - paragraph [0033]; figure 2 paragraph [0043] paragraph [0059]	1-9

X	US 2006/066940 A1 (TRENKLER JOHANN [DE] ET AL) 30 March 2006 (2006-03-30) cited in the application	10,12
A	paragraph [0020]	1-9

X	US 2010/216062 A1 (LEE DONG-GUN [KR] ET AL) 26 August 2010 (2010-08-26)	10
A	paragraph [0051]; figure 3D	1-9

-/-		
☒ 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 "E" earlier application or patent but published on or after the international filing date "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) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "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 "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 "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 "&" document member of the same patent family		
Date of the actual completion of the international search 18 February 2013	Date of mailing of the international search report 05/03/2013	
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 van Toledo, Wiebo	

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2012/068319

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 065 568 A2 (ASM LITHOGRAPHY BV [NL] ASML NETHERLANDS BV [NL]) 3 January 2001 (2001-01-03) cited in the application paragraph [0063] -----	1

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Information on patent family members

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