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INT CL **C03C, G02B, G03F**
Other: **Online**

(54) Abstract Title: **Protective coating with windows for protection of optical element that is soluble in immersion liquid.**

(57) Optical element (301) to be used in an immersion lithography projection objective (311), where the outer surface (319) of the last optical element is covered with a protective layer. The lens element is calcium fluoride (CaF2) or barium fluoride (BaF2), and the optical element is soluble in the immersion liquid (317) which is water. The protective layer is made of metal, metal fluorides, refractory metal mixtures, W/Ti, yttrium aluminium garnet (YAG) or lutetium aluminium garnet. A number of protective layers are placed in a stack, and the protection layer system contains diffusion barrier layers and adhesion layers. The protective cover layer only occupies a limited surface (319) of the optical element (301). A thin plate of SiO2 (321) is attached, by wringing, to the optical element. The system is used for illuminating UV-light sensitive photo resist with a pattern on top of a wafer (318) during semiconductor manufacture.

Fig. 3

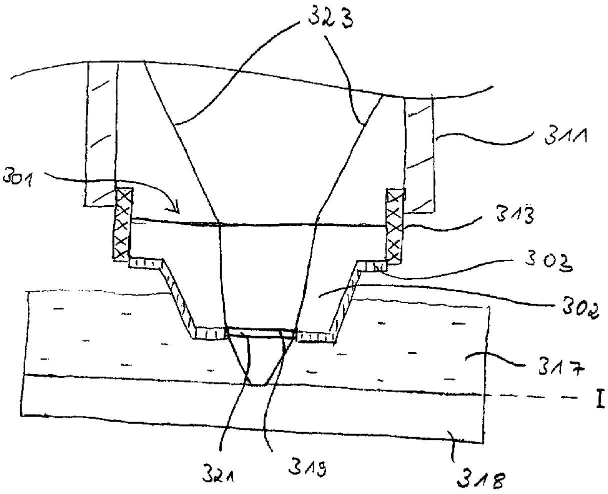

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Fig. 1

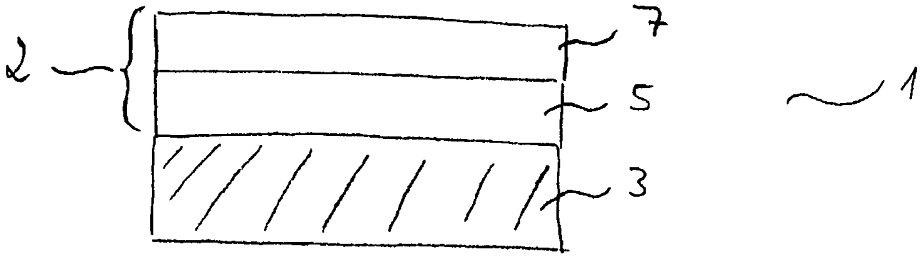


Fig. 2

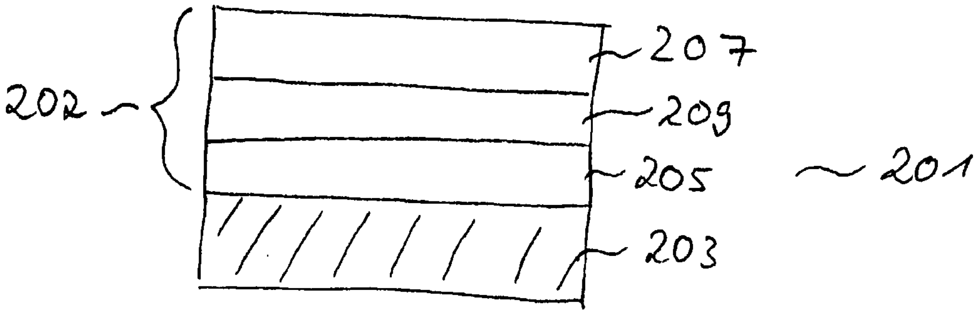


Fig. 3

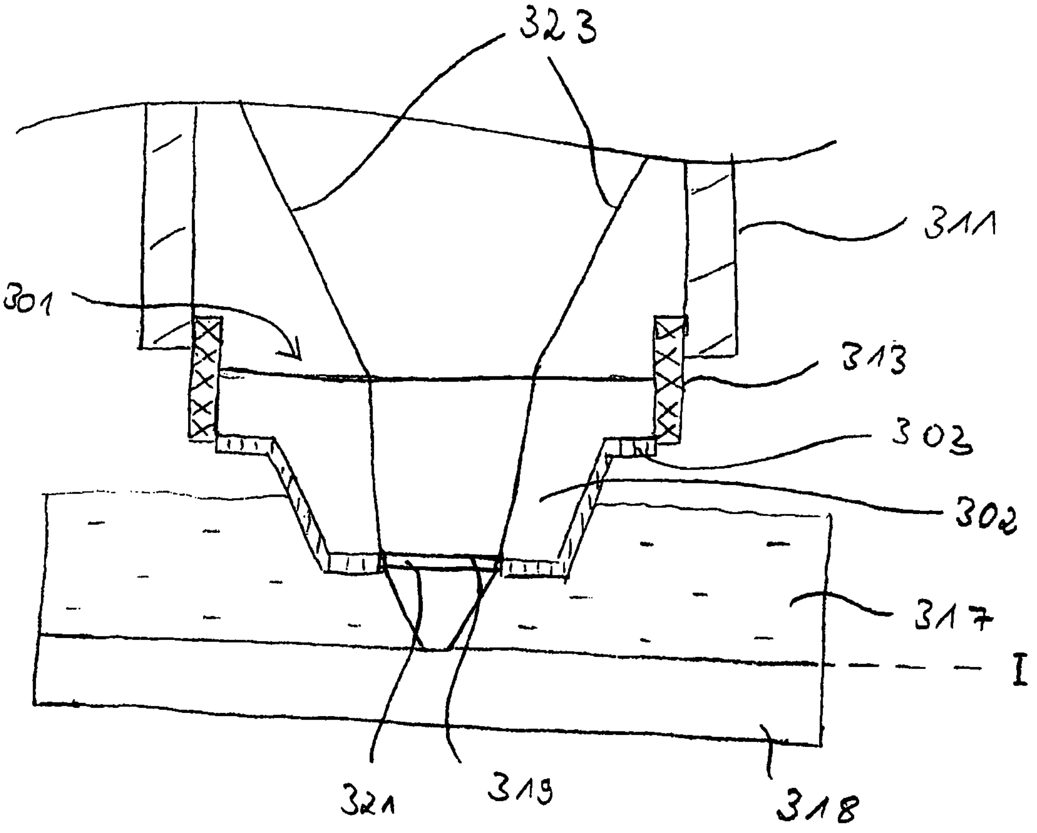
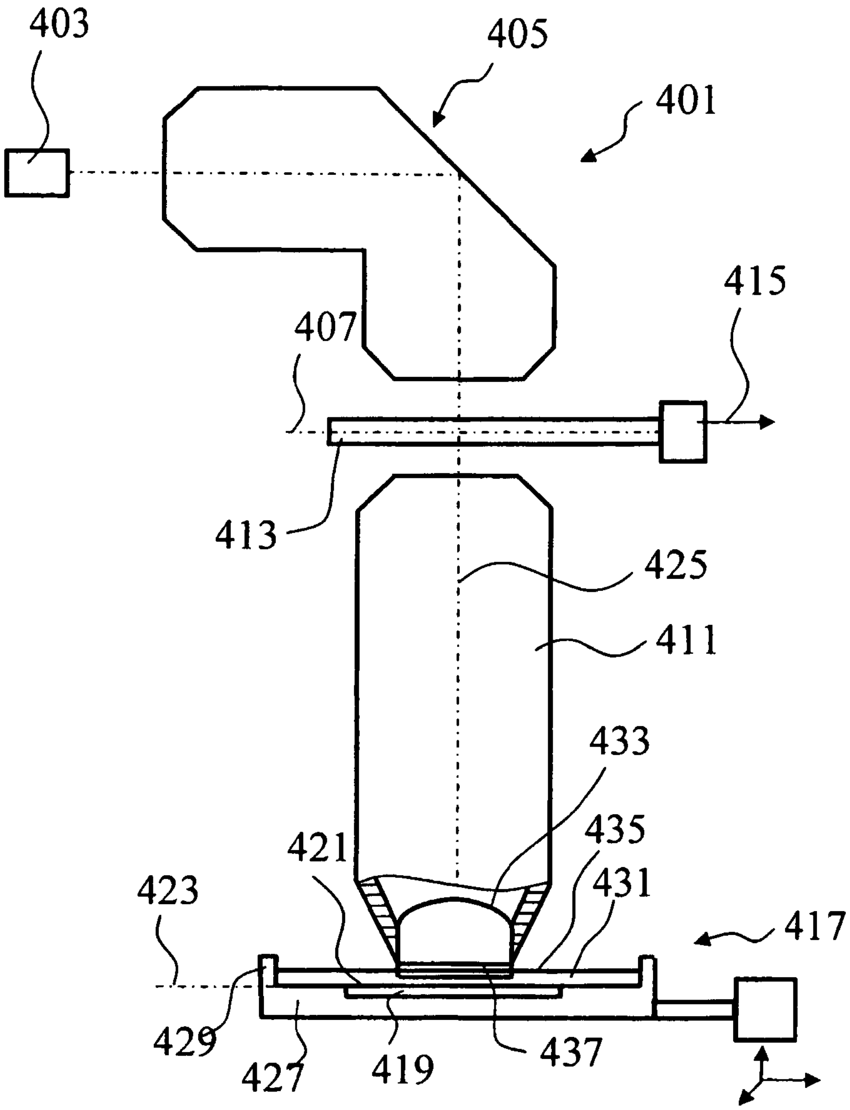


FIG.4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Optical element in a projection objective adapted for immersion lithography

Background of the Invention

The invention relates to an optical element in a projection objective adapted for immersion lithography.

A projection objective adapted for microlithography projects a structure arranged in an object plane, often called a reticle, into an image plane of the projection objective, where a light-sensitive substrate, for example a silicon wafer which is coated with a photosensitive resist, is arranged. Such a projection objective is part of a projection exposure apparatus for microlithography. In addition to the projection objective, the reticle and a device for carrying and positioning the light sensitive substrate, a projection exposure apparatus comprises a light source and an illumination system for illuminating the reticle. Structures from which to produce an image can also include micro-mirror arrays or LCD arrays. Projection exposure apparatus of this kind are used for the production of semiconductor components and other finely structured components.

One of the concepts for increasing the resolving power of a projection objective is based on the idea of bringing an immersion medium, in particular an immersion liquid, into the interstitial space that remains between a last lens element on the image side of the projection objective and the photo-sensitive resist or another light-sensitive layer that is to be exposed. This technique is referred to as immersion lithography. Projection objectives that are designed to be operated with immersion are therefore also called immersion objectives.

The advantages of immersion lithography are due to the fact that with the higher refractive index of the immersion liquid relative to vacuum, the illumination wavelength is reduced to an effective illumination wavelength. This goes together with an increase in resolution and in the depth of focus. Furthermore, by choosing appropriate materials for the objective lens elements and the immersion liquids it is possible to increase the numerical aperture of such an immersion objective up to a value of the order of 1.3 or even higher.

As immersion liquids a lot of different kinds of substances are known in the state of the art. In order to achieve a significantly higher resolution or numerical aperture, respectively, in comparison to a projection objective without an immersion liquid, it is important, that an immersion liquid has a refractive index as high as possible. However, it is further of significance in immersion objectives to use an immersion liquid which has an adequate transmission for light of the operating wavelength. Other desirable features of an immersion liquid are a good availability, environmental compatibility, and the possibility to reprocess already used liquid with reasonable effort. Taking all these demands into account, liquids like ultra pure water, aqueous solutions of inorganic salts, hydrocarbons with 1 to 10 carbon atoms and aqueous acids like H_2SO_4 or H_3PO_4 seem to be promising immersion liquids.

When an immersion liquid is used in a projection exposure apparatus, it has to be taken into account that the immersion liquid might undergo chemical reactions with the last lens element of the projection objective, in particular when the lens material is soluble in the immersion liquid. For example, if the last lens element of a projection objective is made of CaF_2 (calcium fluoride) and ultra pure water or any other liquid containing water is used as an immersion liquid, at least a part of the CaF_2-element will be dissolved in the immersion liquid. This will lead not only to a degradation of the optically active surface but also to an increase of the concentration of fluoride ions (F^-) in the liquid. These fluoride ions can chemically attack the wafer, which will lead to a general decrease of the performance of the complete projection exposure system.

In order to prevent chemical interactions between the immersion liquid and the last lens element of the projection objective, it has been proposed to provide a thin protective layer on the last lens element, which is chemically inert with respect to the immersion liquid. For example, for the protection of CaF_2 against water, a protective single layer of a lanthanide fluoride, like LaF_3 or NdF_3 or an oxide, like SiO_2 or Al_2O_3 can be used. The protective layer can be applied to the lens surface by the usual methods used for preparation of optical coatings, such as for example sputtering.

Summary of the invention

It is an object of the invention to make available a protective layer system for protecting the surface of an optical lens element in an immersion projection objective being in contact with the immersion liquid from dissolution or any chemical reactions with the immersion liquid.

A solution meeting this objective is offered in an optical element according to claim 1, and a production method for an optical element according to claim 27.

Further advantageous embodiments of the invention are defined by the features of the dependent claims.

The inventors have recognized, that a single layer of, for example, SiO_2 , which is known in the state of the art, will lose its adhesive strength and peel away from the lens substrate after being several days in contact with the immersion liquid or even with humid air.

The inventors have further recognized, that the adhesion of a protective coating can be significantly improved by providing a protective coating comprising a suitable adhesion layer. Suitable materials for adhesion layers are made of metal, metal alloy, metal oxide or metal fluoride. In particular, the metals Ta (tantalum), Ti (titanium), Nb (niobium), W (tungsten), Mo (molybdenum), and Al (aluminium), the metal mixture W/Ti, the metal oxides Al_2O_3 (aluminium oxide), TiO_2 (titanium dioxide), Ta_2O_5 (tantalum pentoxide) and TiO (titanium oxide) and the metal fluorides MgF_2 (magnesium fluoride), LaF_3 (lanthanum fluoride), GdF_3 (gadolinium fluoride), NdF_3 (neodymium fluoride), YF_3, (yttrium fluoride), YbF_3 (ytterbium fluoride), and ErF_3 (erbium fluoride) can be used.

In a particularly advantageous embodiment of the invention, the protective layer system consists solely of the adhesion layer. However, some of the materials named in the preceding paragraph might be subject to chemical attack when in contact with the immersion liquid for a long time. Therefore, it is another advantageous embodiment of the invention to provide in addition at least one further layer, which is chemically inert with respect to the immersion liquid, and which protects the underlying transparent substrate as well as the adhesion layer from dissolution or chemical attack. Suitable materials for this chemically inert layer are the metals Al, Cr (chromium), Ni (nickel), Ta, W, Mo, and Ti, the metal mixture W/Ti, the metal oxides Al_2O_3, TiO_2, Ta_2O_5, TiO, and SiO_2 (silicon dioxide).

In another advantageous embodiment of the invention, the protective layer system comprises at least one diffusion barrier layer, which is arranged between the adhesion layer and the further layer, which is chemically inert with respect to the immersion liquid. A diffusion barrier layer prevents water molecules or other contaminants from diffusion through the chemically inert layer towards the adhesion layer. If, for instance, water molecules would diffuse towards the adhesion layer, this might lead to peeling off of the adhesion layer and consequently to peeling off of the complete protective coating.

Preferably the thickness of all these layers made of metal, metal mixtures, oxides and fluorides should be at least 5 nm, in order to assure, that the layers are completely closed and that there are no surface areas of the underlying substrate remaining, which are still exposed directly to the immersion liquid. In order to save production time and cost it is recommendable to keep the layer thickness below 5000 nm, preferably below 2000 nm.

In another embodiment of the invention only a part of the surface of the transparent substrate is covered by the protective coating. The remaining part of the surface can be protected in a different manner, for example by a protective plate, which is directly connected to the substrate surface. This protective plate can be, for example, made of SiO_2. In a further development of this embodiment a part of the substrate surface comprising the clear aperture of the optical element in the projection objective is protected by such a protective plate, whereas the remaining part of the surface is protected by a protective coating according to the previous description. The term "clear aperture" means the optically active surface area of the optical element, or in different words, the surface area of the optical element which transmits the operating radiation, when the projection objective is used in a projection exposure apparatus for the production of microscopic structures.

In a production method for an optical element in an immersion objective which is in contact with an immersion liquid, a transparent substrate is provided and a protective layer system comprising an adhesion layer is applied to the surface of this transparent substrate. It is advantageous to use a PVD (physical vapour deposition) method for applying the coating, which means that the coating is applied from a solid phase material, because these methods lead to layers of a very high purity. However, CVD (chemical vapour deposition) methods, which means that the coating is applied from a gaseous precursor, can be used as well.

In order to produce an optical element which comprises two surface areas, that are protected in different ways from an immersion liquid, for example by a protective layer system comprising an adhesion layer and a protective plate directly connected to the substrate surface, it is of advantage to proceed in the following manner: In a first step the protective plate is connected to the surface, for example by wringing or bonding. After connecting the protective plate to the substrate it is possible to process the surface of the protective plate by conventional surface processing methods like for example abrading, polishing, ion beam figuring in order to decrease the thickness of the protective plate further. In a next step, the protective layer system comprising an adhesion layer is applied to the second surface area of the substrate, e. g. by PVD. In order to prevent deposition of material on top of the protective plate or the first surface area of the substrate, respectively, it is shielded by using a removable masking.

Further aspects and embodiments of the invention will become apparent from the dependent claims and the following description which refers to the appended figures. All combinations of the features disclosed, whether explicitly recited in the claims or not, are within the scope of the invention.

Brief Description of the Drawings

The invention will be explained in more detail hereinafter with reference to the drawings, wherein

Fig. 1 shows a protective layer system with an adhesive layer and a chemically inert layer;
Fig. 2 shows a protective layer system with an adhesive layer, a chemically inert layer and a diffusion barrier layer;
Fig. 3 shows a schematical drawing of an optical element in a projection objective adapted for immersion lithography; and
Figure 4 represents a projection exposure apparatus with a projection objective.

In Fig. 1 is shown schematically a general concept for a transmitting optical element 1 adapted for use in a projection objective, which can be used for immersion lithography by means of a protective layer system 2. On a transparent substrate 3 made of CaF_2 is provided an adhesion layer 5 made of Al, in order to improve the adhesion of the chemically inert layer 7, which is arranged directly on top of the adhesion layer 5. The chemically inert layer is made of SiO_2.

If the optical element 1 is used as last lens element in an immersion objective, which is operated with water as an immersion liquid, the protective layer system 2 will provide a complete protection of the CaF_2-substrate 3 from being dissolved or chemically attacked by the immersion fluid.

To make completely sure, that no water molecules will diffuse through the chemically inert layer 7 and attack the adhesion layer 5, one can provide a diffusion barrier layer between these two layers, like in the embodiment shown schematically in Fig. 2. The optical element 201 in this embodiment is a CaF_2-substrate 203 provided with a protective layer system 202, which in this case consists of three different layers. Adhesion layer 205 is positioned directly on top of the substrate 203 and the chemically inert layer 207 made of SiO_2 is arranged as outermost layer of the protective layer system. Layer 209 made of Al_2O_3 is arranged between layer 205 and layer 207 and prevents any diffusion of water molecules or other contaminating substances from the SiO_2-layer 207 to the adhesion layer 205.

Fig. 3 shows an optical element with a protective coating in a projection objective 311 adapted for immersion lithography. As the last lens element of projection objective 311, optical element 301 is fixed in a mount 313, which in turn is fixedly connected to the lens barrel of the projection objective 311. The optical element 301 is dipped into the immersion liquid, wherein its surface is at least partly wetted by the immersion liquid 317.

For performing immersion lithography the projection objective 311 is operated with laser light of a vacuum wavelength of for example 193 nm for imaging a pattern arranged in an object plane of the objective 311 into an image plane I. In the image plane I a light sensitive substrate 318, a so called wafer, is arranged. During exposure of the light sensitive substrate 318 exposure light 323 falls only on a part 319 of the surface of the last lens element. This region which is illuminated during exposure is called clear aperture 319. The size and shape of the clear aperture 319 depends on the optical design of the projection objective 311.

The substrate 302 of the optical element 301 is made of CaF_2. In order to protect the clear aperture from the immersion liquid a thin plate 321 made of SiO_2 has been wrung to the CaF_2 substrate 302. The remaining part of the surface of substrate 302 is provided with a protective layer system 303, even on those parts of the surface of substrate 302, that are not in contact with the immersion liquid 317. This is to make sure, that even when the level of the immersion liquid 317 increases, the complete CaF_2 substrate 303 is protected. The protective layer system can be chosen, for example, according to one of the figures 1 or 2.

Figure 4 schematically illustrates a projection exposure apparatus 401 designed for the production of highly integrated semiconductor elements by means of immersion lithography.

As a light source, the projection exposure apparatus 401 includes an excimer laser 403 with an operating wavelength of 248 nm. Alternatively, one could also use light sources with different operating wavelengths such as, e.g., 193 nm or 157 nm. An illumination system 405, arranged after the light source, produces at its exit plane or object plane 407 a large, sharply delimited illumination field of very homogeneous intensity, which is matched to the telecentricity requirements of the projection objective 411 that is arranged at a subsequent position in the apparatus. The illumination system 405 has devices for the control of the pupil illumination and for the selection of the illumination mode for setting a specified state of polarization of the illumination light.

A reticle stage, i.e., a device for holding and moving a mask 413, is arranged in the light path after the illumination system, so that the mask 413 lies in the object plane 407 of the projection objective 411 and can be moved in a travel direction 415 in this plane to perform a scan.

Behind the object plane 407, which is also referred to as mask plane, the reduction objective 411 follows next in series, projecting a reduced-scale image of the mask onto a substrate 419, for example a silicon wafer, that is coated with a photo-sensitive resist 421. The substrate 419 is arranged so that the planar substrate surface carrying the resist 421 substantially coincides with the image plane 423 of the projection objective 411. The substrate is held by a device 417 which includes a drive mechanism to move the substrate 419 in synchronism with and anti-parallel to the mask 413. The device 417 also includes manipulators for the purpose of advancing the substrate 419 in the z-direction, i.e., parallel to the optical axis 425 of the projection objective 411, as well as in the x- and y-directions perpendicular to the optical axis . A tilting device with at least one tilt axis running perpendicular to the optical axis 425 is integrated in the device 417.

The device 417 for holding the substrate 419 (the wafer stage) is designed for use in immersion lithography applications. It includes a receiving device 427 which has a base with a flat recess to receive the substrate 419 and which is movable by a scanner drive mechanism.

A border 429 around the perimeter forms a shallow liquid-tight receptacle that is open on top and serves to hold an immersion liquid 431. The height of the border is dimensioned so that when the immersion liquid 431 is in place, it can completely cover the substrate surface with the resist 421, and with the operating distance between the exit plane of the objective and the substrate surface correctly adjusted, the exit-end portion of the projection objective 411 can be submerged in the immersion liquid 431.

The projection objective 411 has an image-side numerical aperture NA of at least NA = 0.6, but preferably more than 0.8, and with special preference more than 0.95. Thus, it is specifically adapted for use with highly refractive immersion liquids 431.

The last optical element of the projection objective 411, closest to the image plane 423, is a planar-convex lens 433 whose exit surface 435 is the last optical surface of the projection objective 411. The last optical element can be also a planar-planar lens or have any other configuration which is suitable for this type of projection objectives.. When the projection exposure apparatus is in operation, the exit side of the last optical element is completely submerged in the immersion liquid 431 and is wetted by the latter. As described with Figure 3 a thin plate 437 is wrung to the exit surface 435 of the lens 433. Lens 433 has a protective coating outside the clear aperture of lens 433.

Claims:

1. An optical element for use in a projection objective adapted for immersion lithography using radiation at a wavelength λ, the optical element comprising:

a substrate formed from a first material that is substantially transparent at λ; and

a layer of a second material disposed on the substrate, the second material being different from the first material, and the second material being selected from a group consisting of a metal, a metal mixture, a metal oxide, and a metal fluoride,

wherein during operation of the projection objective a portion of the optical element including the layer of the second material is at least partly immersed in a liquid.

2. The optical element of claim 1 wherein the first material is soluble in the immersion liquid.

3. The optical element of claim 1 or 2, wherein the first material selected from the group that consists of CaF_2, BaF_2, MgF_2, $MgAl_2O_4$, yttrium aluminium garnet, and lutetium aluminium garnet.

4. The optical element of at least one of the claims 1 to 3 wherein the liquid comprises water.

5. The optical element of at least one of the claims 1 to 4 wherein the metal is selected from the group that consists of Ta, Ti, Nb, W, Mo, and Al.

6. The optical element of at least one of the claims 1 to 4 wherein the metal mixture is W/Ti.

7. The optical element of at least one of the claims 1 to 4 wherein the metal oxide is selected from the group that consists of Al_2O_3, TiO_2, Ta_2O_5, and TiO.

8. The optical element of at least one of the claims 1 to 4 wherein the metal fluoride is selected from the group that consists of MgF_2, LaF_3, GdF_3, NdF_3, YF_3, YbF_3, and ErF_3.

9. The optical element of at least one of the claims 1 to 8 wherein the layer of the second material has a thickness of about 5 nm or more.

10. The optical element of at least one of the claims 1 to 9 wherein the portion the optical element immersed in the liquid includes a region devoid of the layer of the second material.

11. The optical element of claim 10 further comprising a plate of a plate material substantially transparent at λ that covers the a region devoid of the layer of the second material.

12. The optical element of claim 11 wherein the plate material is SiO_2.

13. The optical element of at least one of the claims 10 to 12 wherein during operation of the projection objective the optical element transmits radiation at λ through the region devoid of the layer of the second material.

14. An optical element for use in a projection objective adapted for immersion lithography using radiation at a wavelength λ, the optical element comprising:

a substrate formed from a first material that is substantially transparent at λ; and

a layer of a second material disposed on the substrate, the second material being different from the first material; and

a layer of a third material disposed on the layer of the second material, the third material being different from the second material,

wherein during operation of the projection objective a portion of the optical element including the layer of the second material is at least partly immersed in a liquid.

15. The optical element of claim 14 wherein the first material is soluble in the immersion liquid.

16. The optical element of claim 14 or 15, wherein the first material selected from the group that consists of CaF_2, BaF_2, MgF_2, $MgAl_2O_4$, yttrium aluminium garnet, and lutetium aluminium garnet.

17. The optical element of at least one of the claims 14 to 16 wherein the liquid comprises water.

18. The optical element of at least one of the claims 14 to 17 wherein the second material being selected from a group consisting of a metal, a metal mixture, a metal oxide, and a metal fluoride.

19. The optical element of claim 18 wherein the metal is selected from the group that consists of Ta, Ti, Nb, W, Mo, and Al.

20. The optical element of claim 18 wherein the metal mixture is W/Ti.

21. The optical element of claim 18 wherein the metal oxide is selected from the group that consists of Al_2O_3, TiO_2, Ta_2O_5, and TiO.

22. The optical element of claim 18 wherein the metal fluoride is selected from the group that consists of MgF_2, LaF_3, GdF_3, NdF_3, YF_3, YbF_3, and ErF_3.

23. The optical element of at least one of the claims 14 to 22 wherein the layer of the second material has a thickness of about 5 nm or more.

24. The optical element of at least one of the claims 14 to 23 wherein the second material adheres the layer of the third material to a surface of the substrate.

25. The optical element of at least one of the claims 14 to 24 wherein the third material being selected from a group consisting of a metal, a metal mixture or an oxide.

26. The optical element of claim 25 wherein the metal is selected from the group that consists of Al, Cr, Ni, Ta, W, Mo, and Ti.

27. The optical element of claim 25 wherein the metal mixture is W/Ti.

28. The optical element of claim 25 wherein the oxide is selected from the group that consists of Al_2O_3, Ta_2O_5 , TiO_2, SiO_2, and TiO.

29. The optical element of at least one of the claims 14 to 28 wherein the layer of the third material has a thickness of about 5 nm or more.

30. The optical element of claim 14 to 29 wherein the third material is substantially chemically inert with respect to the liquid.

31. The optical element of claim 30 wherein a surface of the layer of the third material contacts the liquid when the portion of the optical element is at least partly immersed in the liquid.

32. The optical element of at least one of the claims 14 to 29 further comprising a layer of a fourth material disposed on the layer of the third material, the fourth material being different from the third material.

33. The optical element of claim 32 wherein the fourth material is substantially chemically inert with respect to the liquid.

34. The optical element of claim 32 or 33 wherein a surface of the layer of the fourth material contacts the liquid when the portion of the optical element is at least partly immersed in the liquid.

35. The optical element of at least one of the claims 32 to 34 wherein the fourth material being selected from a group consisting of a metal, a metal mixture or an oxide.

36. The optical element of claim 35 wherein the metal is selected from the group that consists of Al, Cr, Ni, Ta, W, Mo, and Ti.

37. The optical element of claim 35 wherein the metal mixture is W/Ti.

38. The optical element of claim 35 wherein the oxide is selected from the group that consists of Al_2O_3, Ta_2O_5 , TiO_2, SiO_2, and TiO.

39. The optical element of at least one of the claims 32 to 38 wherein the layer of the fourth material has a thickness of about 5 nm or more.

40. The optical element of claim 32 to 39 wherein during operation of the projection objective a portion of the optical element including the layer of the second material is at least partly immersed in a liquid and where the third layer substantially prevents diffusion of the liquid to the layer of the second material.

41. The optical element of at least one of the claims 14 to 40 wherein the portion the optical element immersed in the liquid includes a region devoid of the layer of the second material.

42. The optical element of claim 41 further comprising a plate of a plate material substantially transparent at λ that covers the a region devoid of the layer of the second material.

43. The optical element of claim 42 wherein the plate material is SiO_2.

44. The optical element of at least one of the claims 41 to 43 wherein during operation of the projection objective the optical element transmits radiation at λ through the region devoid of the layer of the second material.

45. An optical element for use in a projection objective adapted for immersion lithography using radiation at a wavelength λ, the optical element comprising:

a substrate formed from a first material that is substantially transparent at λ; and

a layer of a second material disposed on the substrate, the second material being different from the first material; and

a layer of a third material disposed on the layer of the second material, the third material being different from the second material,

wherein during operation of the projection objective a portion of the optical element including the layer of the second material is at least partly immersed in a liquid and where the second layer substantially prevents diffusion of the liquid to the substrate.

46. The optical element of claim 45 wherein the first material is soluble in the immersion liquid.

47. The optical element of claim 45 or 46, wherein the first material selected from the group that consists of CaF_2, BaF_2, MgF_2, $MgAl_2O_4$, yttrium aluminium garnet, and lutetium aluminium garnet.

48. The optical element of at least one of the claims 45 to 47 wherein the liquid comprises water.

49. The optical element of at least one of the claims 45 to 48 wherein the second material being selected from a group consisting of a metal, a metal mixture or an oxide.

50. The optical element of claim 49 wherein the metal is selected from the group that consists of Al, Cr, Ni, Ta, W, Mo, and Ti.

51. The optical element of claim 49 wherein the metal mixture is W/Ti.

52. The optical element of claim 49 wherein the oxide is selected from the group that consists of Al_2O_3, Ta_2O_5 , TiO_2, SiO_2, and TiO.

53. The optical element of at least one of the claims 45 to 52 wherein the layer of the second material has a thickness of about 5 nm or more.

54. The optical element of at least one of the claims 45 to 53 wherein the third material is substantially chemically inert with respect to the liquid.

55. The optical element of claim 45 or 54 wherein a surface of the layer of the third material contacts the liquid when the portion of the optical element is at least partly immersed in the liquid.

56. The optical element of at least one of the claims 45 to 55 wherein the third material being selected from a group consisting of a metal, a metal mixture or an oxide.

57. The optical element of claim 56 wherein the metal is selected from the group that consists of Al, Cr, Ni, Ta, W, Mo, and Ti.

58. The optical element of claim 56 wherein the metal mixture is W/Ti.

59. The optical element of claim 56 wherein the oxide is selected from the group that consists of Al_2O_3, Ta_2O_5, TiO_2, SiO_2, and TiO.

60. The optical element of at least one of the claims 45 to 59 wherein the layer of the third material has a thickness of about 5 nm or more.

61. A photolithography exposure system, comprising:

an illumination system;

a projection objective comprising the optical element of at least one of the claims 1 to 60,

wherein the photolithography exposure system is configured to expose a photosensitive substrate to radiation at λ from the illumination system through the projection objective.

62. Optical element in a projection objective adapted for immersion lithography, the optical element having a transparent substrate with a surface,

wherein at least part of the surface is protected against the immersion liquid with a protective layer system,

wherein the protective layer system comprises an adhesion layer.

63. Optical element according to claim 62, wherein the transparent substrate is made of a material which is soluble in the immersion liquid.

64. Optical element according to claim 62 or 63, wherein the transparent substrate is made of a material selected from the group that consists of CaF2, BaF2, MgF2, MgAl2O4, yttrium aluminium garnet, and lutetium aluminium garnet.

65. Optical element according to one of the claims 62 to 64, wherein the immersion liquid is ultra pure water.

66. Optical element according to one of the claims 62 to 65, wherein the adhesion layer is made of a metal, a metal mixture, a metal oxide or a metal fluoride.

67. Optical element according to claim 66, wherein the metal is selected from the group that consists of Ta, Ti, Nb, W, Mo, and Al.

68. Optical element according to claim 66, wherein the metal mixture is W/Ti.

69. Optical element according to claim 66, wherein the metal oxide is selected from the group that consists of Al_2O_3, TiO_2, Ta_2O_5, and TiO.

70. Optical element according to claim 66, wherein the metal fluoride is selected from the group that consists of MgF_2, LaF_3, GdF_3, NdF_3, YF_3, YbF_3, and ErF_3.

71. Optical element according to one of the claims 62 to 70, wherein the adhesion layer has a thickness of at least 5 nm.

72. Optical element according to one of the claims 62 to 71, wherein the protective layer system further comprises at least one further layer, which is chemically inert with respect to the immersion liquid.

73. Optical element according to claim 72, wherein the at least one further layer is made of a metal, a metal mixture or an oxide.

74. Optical element according to claim 73, wherein the metal is selected from the group that consists of Al, Cr, Ni, Ta, W, Mo, and Ti.

75. Optical element according to claim 73, wherein the metal mixture is W/Ti.

76. Optical element according to claim 73, wherein the oxide is selected from the group that consists of Al_2O_3, Ta_2O_5, TiO_2, SiO_2, and TiO.

77. Optical element according to one of the claims 72 to 76, wherein the at least one further layer has a thickness of about 5 nm or more.

78. Optical element according to one of the claims 72 to 76, wherein the protective layer system further comprises at least one diffusion barrier layer, which is arranged between the adhesion layer and the further layer, which is chemically inert with respect to the immersion liquid.

79. Optical element according to claim 78, wherein the diffusion barrier layer is made of a metal, a metal mixture or an oxide.

80. Optical element according to claim 79, wherein the metal is selected from the group that consists of Al, Cr, Ni, Ta, W, Mo, and Ti.

81. Optical element according to claim 79, wherein the metal mixture is W/Ti.

82. Optical element according to claim 79, wherein the oxide is selected from the group that consists of Al_2O_3, Ta_2O_5, TiO_2, SiO_2, and TiO.

83. Optical element according to one of the claims 78 to 82, wherein the diffusion barrier layer has a thickness of about 5 nm or more.

84. Optical element according to one of the claims 62 to 83, wherein only a first part of the surface of the optical element is provided with the protective layer system.

85. Optical element according to claim 84, wherein a second part of the surface of the optical element is protected against the immersion liquid with a protective plate which is directly connected to the substrate.

86. Optical element according to claim 85, wherein the surface of the optical element positioned in the projection objective has a clear aperture, and wherein the second part of the surface of the optical element comprises the clear aperture.

87. Optical element according to claim 85 or 86, wherein the protective plate is made of SiO_2.

88. Production method for an optical element according to one of the claims 62 to 87, comprising the steps of:

providing a transparent substrate for an optical element,

applying a protective layer system comprising an adhesion layer to the surface of the transparent substrate to produce a protected optical element.

89. Production method for an optical element according to claim 88, further comprising the step of:

connecting a protective plate directly to a first surface area of the transparent substrate.

90. Production method for an optical element according to claim 89, wherein the protective plate is connected to the transparent substrate by wringing or bonding.

91. Production method according to claim 89 or 90, comprising the further step of:

protecting a first surface area by a removable masking during applying the protective layer system to a second surface area.

92. Production method according to one of the claims 88 to 91, wherein the protective layer system is applied to the substrate by a PVD or CVD method.

93. Projection objective comprising an optical element according to one of the claims 62 to 87.

94. Projection exposure apparatus comprising a projection objective according to claim 93.

Application No: GB0618436.0 **Examiner:** Dr Thorkild Sørensen

Claims searched: 1-94 **Date of search:** 20 December 2006

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X,Y	X: 1, 2, 4, Y: 3, 18, 46, 47, 48, 49, 63	EP 1510871 A2 (ASML NETHERLANDS BV [NL]) See in particular the abstract and the passage [0009 - 25].
X,Y	X: 1, 14, 15, 16, 17, Y: 3, 7, 8, 18, 47	EP 1571700 A1 (NIPPON KOGAKU KK [JP]) See in particular the abstract, figure 8, and the passages [0007 - 0008], [0015 - 17] and [0021 - 0031].
X,Y	X: 1, 14, 15, 17, Y: 3, 18, 47	US 2003/0021015 A1 (MAIER et al.) See in particular the abstract and the passages [0004 - 0006], and [0038 - 56].
X,Y	X: 1, 14, 15, 16, 17, Y: 3, 5, 7, 18, 47, 65	US 2005/0100745 A1 (LIN et al.) See in particular the abstract, fig. 4, and the passages [0004 -0014, [0021-22], [0025], [0026], [0029 - 34], and [0037].
X,Y	X: 1, 6, 14, 15, 16, 17, Y: 3, 7, 8, 18, 47	US 2005/0225737 A1 (WEISSENRIEDER et al.) See in particular the abstract, figures 3 - 5, and the passages [0001 - 14] , [0022 - 21], [0026 - 28], and [0089 - 90].
X,Y	X: 45, 50, Y: 46, 47, 48, 49.	US 2004/0043331 A1 (KURT) See in particular the abstract and the passages [0017 - 25].
X,Y	X: 62, 64, 66, 67, 68, 69, Y: 63, 65	WO 2005/059618 A2 (ZEISS CARL SMT AG [DE]) See in particular the abstract and the passages a) page 7, line 32 - page 8, line 11, b) page 11, lines 1 - 7, c) page 14, line 26 - page 15, line 25, as well as claims 1 and 68.
X,E	E, X: 1	EP 1677153 A1 (ASML NETHERLANDS BV [NL]) See in particular the abstract and the passages [0003 - 0008], and [0043 -

		0053].

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
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Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^X :

Worldwide search of patent documents classified in the following areas of the IPC

C03C; G02B; G03F

The following online and other databases have been used in the preparation of this search report

WPI, EPODOC.