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(54) Title: A METHOD FOR TREATING SUBSTRATES WITH AN AQUEOUS LIQUID MEDIUM EXPOSED TO UV-RADIATION

(57) Abstract: Methods for treating substrates are described. The methods comprise the steps of flowing an aqueous liquid medium through a flow channel and at least one outlet slit onto a substrate to be treated and exposing the aqueous liquid medium to UV-radiation of a specific wavelength at least in a portion of the flow channel immediately adjacent the at least one outlet slit and after the aqueous liquid medium has flown through the outlet opening towards the substrate and thus prior to and while applying the aqueous liquid medium to the surface of the substrate to be treated. In one method, the electrical conductance of the aqueous liquid medium is adjusted to be in the range of 20 to 2000µS, by the addition of an additive to the aqueous liquid medium, the aqueous liquid medium prior to the addition of the additive having an electrical conductivity below 20µS, prior to or while exposing the same to the UV-radiation. Additionally, the pH of the aqueous liquid medium may be adjusted to a range of 8 to 11 or 3 to 6 prior to or while exposing the same to the UV-radiation. The adjustments may lead to a shift in an equilibrium of reactive species generated in the aqueous liquid medium by the UV-radiation towards preferred species.

A method for treating substrates with an aqueous liquid medium exposed to UV-radiation

Technical Field

The present invention relates to methods for treating substrates, with an aqueous liquid medium exposed to UV-radiation.

Background art

In the field of manufacturing semiconductors, several processing steps are performed on a semiconductor substrate, typically called a wafer. One of these steps includes photolithography, in which a photomask is used to expose a photoresist on a wafer to a pattern of intense light. The exposure to light causes a chemical change that allows some of the photoresist to be removed by a special solution, in accordance with the pattern.

In the field of manufacturing semiconductors and in particular in photolithography it is important that all components, such as for example the wafer and the photomask are very clean and preferably do not have foreign particles thereon. Such requirements are also present in other technologies, where a surface preparation and/or the removal of contaminants, in particular organic contaminants such as a resist are important and therefore, even though specific reference is made to substrates such as photomasks used in photolithography, the invention is also applicable for other substrates such as semiconductor substrates, wafers, imprint templates, panels, in particular flat panel substrates and multi layer ceramic substrates.

Although the present application will focus mainly on the treatment of photomasks as a substrate to perform a treatment on, the principles described herein are also transferable to the wafer itself or other substrates, as pointed out above.

Different methods have been used in the past for removing of photoresist from a photomask. One such method as described in DE 10 2009 058 962 A1, which is assigned to the assignee of the present invention, uses an aqueous medium which is exposed to UV-radiation immediately prior to and while applying a film of said aqueous liquid medium to the surface of the substrate to be treated.

Such a removal process may be divided into several individual steps such as a surface preparation, a strip, and a final clean. In the surface preparation, the surface energy may be adjusted to for example achieve a hydrophilic surface. In the strip, a main portion of the photoresist is removed by radicals generated in the aqueous liquid medium. In the final clean, remaining resist and other particles are removed. In the final clean, care has to be taken not to change such as etch the surface of the substrate itself, but to remove the particles without changing the surface of the substrate. It should be noted that depending on the type of treatment and for example the initial surface condition, not all of the steps of the above sequence have to be used. For example, a surface preparation is not always necessary, in particular if the surface is sufficiently hydrophilic when entering a process. Also, a new mask not having a resist thereon or a mask coming out of a storage space, which had been stripped some time ago, will not need a strip but only a final clean (optionally preceded by a surface preparation). Depending on the application, only a strip (optionally preceded by a surface preparation) is necessary.

The disclosure in DE 10 2009 058 962 A1 already indicates these steps and describes a single tool which may be used for all steps with changing media and/or radiation. The disclosure, however, does not give specific details with respect to the composition of the aqueous liquid media used in the individual steps.

The inventors of the present invention have now found that certain parameters of the media used in the specific steps may benefit the respective process.

Summary of the invention

In accordance with the invention, a method as set forth in claim 1 or 8 is provided. Further embodiments are inter alia disclosed in the dependent claims.

In accordance with one aspect, a method for treating substrates, comprises flowing an aqueous liquid medium through a flow channel and at least one outlet slit onto a substrate to be treated, and exposing the aqueous liquid medium to UV-radiation of a specific wavelength at least in a portion of the flow channel immediately adjacent the at least one outlet slit and after the aqueous liquid medium has flown through the outlet opening towards the substrate and thus prior to and while applying the aqueous liquid medium to the surface of the substrate to be treated. The method further comprises the step of adjusting the electrical conductance of the aqueous liquid medium to be in the range of 20 to 2000 µS, by the addition of an additive to the aqueous liquid medium, prior to or while exposing the same to the UV-radiation, wherein prior to the addition of the additive the aqueous liquid medium has electrical conductance below 20 µS. Adjusting the electrical conductance influences the equilibrium of reactive species generated in the aqueous liquid medium by the UV-radiation, and thus the equilibrium may be shifted towards preferred species. In particular, the equilibrium may be shifted such that at the time the aqueous liquid medium flows through the outlet slits, a certain concentration/ratio of reactive species is present.

In one application, the additive is an additive, which does not substantially change the pH of the aqueous liquid medium, wherein the term not substantially is supposed to cause a pH shift of less than 0.5. Non-limiting examples of such additives which may be used are salts such as Sodium chloride or potassium chloride.

In another application, the method further comprises shifting the pH of the aqueous liquid medium to a range of 8 to 11 or 3 to 6 by the addition of the additive, wherein the aqueous liquid medium prior to the addition of the additive has a pH in the range of 6 to 8, and wherein the additive comprises a base or an acid. The shift in the pH also influences an equilibrium of reactive species, and thus a shift of the equilibrium of reactive species generated in the aqueous liquid medium by the UV-radiation towards preferred species may be achieved. Such a shift in the pH may speed up or slow down certain reactions within the liquid medium caused by the UV-radiation and may thus shift an equilibrium of reacted species in the aqueous liquid medium. In particular, the equilibrium may be shifted such that at the time the aqueous liquid medium flows through the outlet slits, a certain concentration/ratio of reactive species is present. As an example, in ozone water first hydroxyl radicals are produced and then further species, such as O^- with less oxidation strength and same capability for organic removal. Alkaline pH extends lifetime of radicals in aqueous liquid medium thereby a shift/stabilization of the equilibrium of species may be achieved. Furthermore, an alkaline medium changes the electrical potential of a metal surface which is thus less sensitive to oxidation. An acidic medium for example slows down decomposition of Ozone while an alkaline medium speeds up decomposition of Ozone and thus the generation of further species. The invention thus enables an adjustment of the concentration/ratio of species at the outlet slit by shifting the pH of the liquid medium. The process may thus be tailored to the specific application and requirement.

The aqueous liquid medium may in particular be adjusted to have a pH-value in the range of 8 to 11 and electrical conductance in the range of 20 to 500µS, wherein the additive comprises a base. The media electrical conductance indicates an advantageous low concentration of the base. Only by mixing the medium prior to inserting it into the flow channel such low concentrations may be used to achieve the desired effect.

In accordance with another aspect of the invention, the aqueous liquid medium is adjusted to have a pH-value in the range of 9.5 to 10.5 and electrical conductance in the range of 70 to 150 µS. When using a base to shift the pH, a preferred material is TMAH, which even at low concentrations may achieve the required shift and is furthermore a non-coordinating compound.

The base is preferably a non-coordinating compound, which does not have available external electrons capable of establishing a direct bond with a metal on the surface of the substrate, such as for example Tetramethylammonium Hydroxide (TMAH) or Potassium Hydroxide (KOH). The aqueous base medium preferably comprises DI-Water.

In accordance with one aspect, the aqueous liquid medium is a mixture of an aqueous liquid medium, which is in substance a non-absorbing medium for the UV-radiation at the specific wavelength, and 5 to 100ppm of a substantially absorbing medium at the specific wavelength. Thus only a small amount of the overall medium is absorbing the UV-radiation at the specific wavelength, thereby enabling good adjustment of the amount of reactive species. The substantially absorbing medium may be the additive for adjusting the electrical conductance, but it is also possible that the absorbing medium is a different medium.

In one application, the method relates to a final clean of a substrate having an exposed metal layer, such as a EUV mask. Such a final clean may for example be performed after a photoresist strip.

The method may further comprise the step of adjusting the time the liquid medium is exposed to the UV-radiation in the flow channel before exiting the at least one exit slit, which may further enable the equilibrium of species to be shifted. In this context, at least one of the electrical conductance and the pH may be adjusted in accordance with the amount of time the aqueous liquid medium is exposed to the UV-radiation within the flow channel before exiting the at least one exit slit.

The above methods may further comprise the step of exposing the aqueous liquid medium to UV-radiation of a specific other wavelength as used in the step of exposing the aqueous liquid medium to UV-radiation of a specific wavelength immediately prior to and while applying a film of said aqueous liquid medium to the surface of the substrate to be treated, prior to said step. This may for enable prepare the aqueous liquid for specific radical generation and may further allow decomposing certain components in the liquid which are not supposed to reach the substrate, such as O_3.

The aqueous liquid medium may be adjusted to have an electrical conductance in the range of 70 to 150 μS and may also be adjusted to have a temperature in the range of 20 to 70°C, in particular in the range of 20 to 40°C.

In accordance with a preferred embodiment, the aqueous liquid medium is irradiated with UV-radiation at an intensity of 25 to 340 mW/cm^2. The distance of a source of UV-radiation and the surface of the substrate to be treated may be adjusted to be in the range of 1 to 5mm, in particular 1 to 2mm. The aqueous liquid medium may be exposed to UV-radiation of a wavelength in the range of 185 to 600nm, in particular 185 to 300nm. In the step of exposing the aqueous liquid medium to UV-radiation of a specific wavelength immediately prior to and while applying a film of said aqueous liquid medium to the surface of the substrate to be treated, the specific wavelength is preferably in the range of 200 to 300nm, preferably at about 254nm for generating radicals. The specific other wavelength may be below 200nm, preferably at about 185nm, which may be better suited for preparation/decomposing the liquid.

The method may specifically relate to a photo-resist strip from the substrate, wherein the composition of the aqueous liquid medium is adjusted to have an electrical conductance in the range of 20 to 500μS, in particular in the range of 70 to 150μS, and wherein the aqueous liquid medium is a mixture of an aqueous liquid medium, which is in substance a non-absorbing medium for the UV-radiation at the specific wavelength, and 5 to 100ppm of a substantially absorbing medium at the specific wavelength. In this application, the at least one absorbing medium may for example be selected from the group comprising O_3, H_2O_2 and TMAH.

The method may in one instance relate to an adjustment of the surface energy of the substrate, wherein the composition of the aqueous liquid medium is adjusted to have an electrical conductance in the range of 70 to 150μS, and wherein the aqueous liquid medium is a mixture of an aqueous liquid medium, which is in substance a non-absorbing medium for the UV-radiation at the specific wavelength, and 5 to 10ppm of a substantially absorbing medium at the specific wavelength The steps of the method may be repeated several times on the same substrate to achieve a desired effect, wherein different absorbing media may be used in different repeat cycles. Preferably, at least one absorbing medium is selected from O_3 and TMAH.

The method may specifically relate to a photo-resist strip from the substrate, wherein the composition of the aqueous liquid medium is adjusted to have an electrical conductance in the range of 20 to 500μS, in particular in the range of 70 to 150μS, and wherein the aqueous liquid medium is a mixture of an aqueous liquid medium, which is in substance a non-absorbing medium for the UV-radiation at the specific wavelength, and 5 to 100ppm of a substantially absorbing medium at the specific wavelength. In this application, the at least one absorbing medium may for example be selected from the group comprising O_3, H_2O_2 and TMAH.

In one application at least two of the above methods related to the adjustment of the surface energy, photo-resist strip and final clean are performed in the above order.

Brief description of the drawings

The invention will be explained in more detail herein below with reference to the drawings. In the drawings:

FIG. 1 is a schematic top view of a treatment apparatus which may be used in the method of the present invention;

FIG. 2 is a schematic sectional view of the apparatus of FIG. 1 along line I-I;

FIG. 3 is a schematic sectional view similar to FIG. 2 according to an alternative embodiment of the apparatus;

FIGs. 4a and 4b are graphs showing the influence of applying UV radiation to a specific liquid on contact angle values;

FIG. 5 is a diagram showing a summary of results of strip rates (normalized) for different process parameters;

FIG. 6 is a diagram showing a summary of results of strip rates (normalized) for different wavelength;

Fig. 7 is an AFM image of an EUV mask having a Ruthenium capping layer after 100X cleaning with DI-CO_2 water in combination with UV-radiation;

Fig. 8 shows AFM images of an EUV mask having a Ruthenium capping layer after 100X cleaning with TMAH in DI water in combination with UV-radiation.

Detailed description of the embodiments.

Any directional references used in the following description, such as above, below, left or right refers to the drawings and are not to be construed as limiting the application, even though they may refer to a preferred arrangement. Although the present invention is directed to a method, an exemplary apparatus for performing such method will initially be described. The apparatus and method will be described in combination with a photomask, in particular an EUV mask, but principles of the invention may also be applied to other substrates, in particular to semiconductor substrates during the processing thereof, wafers, imprint templates, panels, in particular flat panel substrates and multi layer ceramic substrates.

FIG. 1 shows a schematic top view onto an apparatus 1 for treating substrates 2, while FIG. 2 shows a schematic sectional view of the apparatus 1 along the line I-I.

The apparatus 1 basically consists of a receiver for the substrate, which will be called a substrate holder for an application unit 6. The substrate holder 4 and the application unit 6 may be arranged in a pressure chamber, which is not shown, in which a positive pressure or a negative pressure may be generated by appropriate means.

The substrate holder 4 is, as may be seen in the drawings, a flat rectangular plate for receiving the also rectangular substrate 2. The substrate holder 4 may have other shapes, which may be matched to the shape of the substrate 2 to be treated. The substrate holder 4 has a drainage, which is not shown, for liquids, which may be applied via the application unit 6 onto the substrate 2.

The application unit 6 consists of a main part 8 and a support part 10, which supports the main part 8 in a movable manner, as is shown by the double-headed arrows A and B. In particular, the support part 10 has a support arm 12, which is connected on one end to the main part 8. The other end of the support arm 12 is connected to a drive mechanism, which is not shown. As is shown by the double-headed arrows A and B, the drive mechanism may for example provide a pivotal movement of the support arm 10 and thus the main part 8 and/or a linear movement. In this manner, the main part 8 may be moved across a substrate 2, which is received on said substrate holder 4, in order to enable treatment of partial areas or the complete surface of the substrate 2. Furthermore, it is also possible that the support arm 10 provides a lift movement in order to adjust a distance between the main part 8 and the surface of a substrate 2 received on the substrate holder 4.

Alternatively, or additionally it is also possible to provide a moving mechanism for the substrate holder, in order to provide relative movement between the substrate 2 and the main part 8.

The main part 8 has a housing 14, liquid ports 16 and a radiation source 18. The housing 14 has an elongated cuboid shaped body 20, which defines in its longitudinal extension a flow chamber 22, which in substance extends across the complete lengths of the body 20. The flow chamber 22 has a lengthwise extension, which is larger than a width extension of the substrate 2, in order to be able to apply a liquid to the substrate across the complete width thereof, as will be explained in more detail herein below. It is, however, also possible that the flow chamber has a smaller dimension. An inner surface 23 of the flow chamber 22 may be designed to have a high reflectivity in particular with respect to UV radiation, while IR radiation may be substantially absorbed.

The flow chamber 22 has a substantially round cross-sectional shape. The flow chamber 22 is open towards the bottom side of the body 20, such that the body defines an outlet opening 21 directed towards the substrate 2 to be treated. In an upper portion of the flow chamber 22, a conduit 24 is provided in the body 20, which extends in substance parallel to the flow chamber 22. The conduit 24 is fluidly connected to the liquid ports 16. The conduit 24 is also fluidly connected to the flow chamber 22, via a plurality of conduits or bores 25 at a plurality of locations. It is thud possible to conduct fluids into the flow chamber 22 via the liquid ports 16, the conduit 24 and the plurality of conduits 25. In this respect it is noted that the conduit 24 in combination with the conduits 25 is capable of conducting fluids into the flow chamber 22 substantially over the complete length thereof.

The liquid ports 16 are each connected to an external conduit, not shown, via which one or more fluids may be conducted to the liquid ports 16. It is possible, that a plurality of fluids may be simultaneously or sequentially conducted to the liquid port via this external conduit. It is also possible to provide a plurality of external conduits, via which e.g. different fluids may be conducted to the liquid port. As fluids, e.g. liquids may be taken into consideration, but it is also possible to conduct gases to the liquid ports 16, which may e.g. be mixed with a liquid in the liquid ports 16 and the conduit 24, before they are conducted to the flow chamber 22. In FIG. 2 arrows are shown, which indicate the flow of a liquid from the liquid ports 16 via the conduit 24, into the flow chamber 22 and out of the housing 14. Although three liquid ports 16 are shown, it should be noted that more or less liquid ports 16 may be provided and that they may connect the same or different fluid sources to the conduit 24. Selected liquid ports 16 may also directly be connected to the flow chamber 22 or indirectly via a second conduit (not shown), similar to conduit 24.

Such arrangements may enable different possibilities of bringing different fluids into the flow chamber 22, as the skilled person will realize. In particular, such arrangements allow mixing different fluids prior to injecting them into the flow chamber 22, either upstream of the liquid port(s) 16 or downstream thereof in the conduit 24. Another possibility is to bring the different fluids separately via separate liquid ports 16 (and optionally separate conduits 24) into the flow chamber 22, such that they are admixed within the flow chamber 22.

The radiation source 18 has a longitudinally extending shape and extends along the complete flow chamber 22, substantially in the middle thereof. The radiation source 18 has a rod shaped lamp 30, which is surrounded by a cover 32, which is substantially transparent to the radiation of a lamp 30. The rod shaped lamp is of the type, which emits at least UV radiation in a predetermined range of wave lengths. It is also possible that the rod shaped lamp 30 emits radiation across a broad spectrum of wave lengths and in particular emits UV radiation and IR radiation.

The cover 32, which may consist for example of quartz glass surrounds the rod shaped lamp 30 completely within the flow chamber 22 and isolates the same with respect to fluids in the flow chamber 22. The cover 32 may for example extend through an end wall of the flow chamber 22 out of the body 20. This would enable access to the rod shaped lamp 30, for example for replacement or maintenance purposes, without having to access the flow chamber 22. Due to its arrangement in the flow chamber 22, the cover 32 together with the inner walls of the flow chamber 22 form a flow path for fluids conducted into the flow chamber 22 via the conduit 24 or a separate inlet (not shown). The flow path is split into two branches (left and right in Fig. 2) and at the outlet opening 21 of the body 20, outlet slits 37 are formed between the body 20 and the cover 32. The middle of the cover 32 is offset downwards with respect to the middle of the flow chamber 22, such that the branches of the flow path are narrowing towards the outlet slits 37. Such a narrowing intends to achieve a homogenization of a fluid flow in the flow chamber 22.

Such fluids flow around the cover 32 and thus as a whole around the radiation source 18. Radiation emitted by the rod shaped lamp 30 is thus introduced into any liquid flowing along the flow path. Furthermore, the cover 32 extends beyond the bottom surface of the body 20 and partially extends into and beyond the outlet opening 21 of the body 20. Thus it is possible that radiation emitted from the rod shaped lamp also exits the flow chamber 22 towards the substrate holder 4 or onto a substrate 2 placed thereon. In particular, the radiation may be introduced into a liquid film on the substrate 2, which is for example formed by a liquid, which flows through the flow chamber 22 and out of the outlet slits 37 onto the substrate. Although not shown, a partial cover may be provided for example on or in the cover 32 to shade certain regions of the flow path 22, with respect to UV radiation. In particular an entrance region for the liquid into the flow path may be shaded as the flow here may be turbulent and thus irradiation of the liquid may not be homogeneous or UV radiation may not yet be desired. Such a shading cover may be provided stationary or may be provided moveable, such that the shading of the flow channel may be changed. For Example, moveable shutters may be provided which in a first position let UV-radiation pass and in a second position block the UV-radiation. By providing such shading, the time of exposure to UV-radiation of fluid flowing though the flow channel may be adjusted. Such time may for example also at least partially be adjusted via the flow velocity of the fluid flowing through the flow channel.

FIG. 3 shows a schematic side view similar to FIG. 2 of an alternative embodiment of the apparatus 1 for treating substrates 2. When describing this embodiment, the same reference signs are used as previously inasmuch as the same or similar elements are provided.

The apparatus 1 again substantially consists of a substrate holder 4 for receiving a substrate and an application unit 6. The substrate holder may be designed in the same manner as described before with respect to FIGS. 1 and 2.

The application unit 6 again has a main part 8 and a support part, which is not shown in FIG. 3, which may, however, have the same design as previously described with respect to FIGS. 1 and 2. The main part 8 again substantially consists of a housing 14, liquid ports 16 and a radiation source 18, wherein the housing 14 and the liquid ports 16 may have the same design as previously described with respect to FIGS. 1 and 2.

The radiation source 18 again has an elongated shape and extends substantially in the middle through the flow chamber 22. The radiation source 18 in this embodiment has rod shaped lamps 30, 30’, which are surrounded by a cover 32, which is substantially transparent to the radiation of the rod shaped lamps 30, 30’ and arranged in the same manner as previously described. The rod shaped lamps 30, 30’ are shown above each other in FIG. 3, but they may also be arranged in a different manner within the cover 32 or more than two lamps may be provided. The rod shaped lamps may be of the same or of different types, wherein at least one of them emits UV radiation in a predetermined range of wave lengths. In particular, it is possible that both rod shaped lamps 30, 30’ emit UV radiation in different ranges of wave lengths. The upper rod shaped lamp 30’ may for example at least partially or primarily emit UV radiation in a wave length range below 200nm, preferably at about 185nm, while the lower rod shaped lamp 30 at least partially or primarily emits UV radiation in the wave length range of 200 to 300nm, preferably at about 254 nm. One or both of the rod shaped lamps 30, 30' may also emit an amount of IR radiation or other radiation. Although not shown a radiation guide element, such as a mirror may be placed between the rod shaped lamps, to guide the respective radiation of the lamps, such that the radiation of the upper lamp is primarily emitted into the flow chamber 22 and the radiation of the lower lamp is primarily emitted outside of the housing 14, although also a portion of the radiation of the lower lamp is also emitted into an end region of the flow path 22, adjacent to an exit opening thereof.

The cover 32 surrounds the rod shaped lamps 30, 30' completely within the flow chamber 22 and isolates the same with respect to fluids in said flow chamber 22. In this respect, the cover 32 may have the same design as the cover previously described with respect to FIGS. 1 and 2. Furthermore, it is also possible that further rod shaped lamps are received within the cover 32, which may each emit different radiation or also the same radiation. By the arrangement and the choice of rod shaped lamps 30, 30' a desired radiation profile (with respect to emitted wave lengths and spatial distribution thereof) may be generated within the flow chamber 22 and beyond the same via the outlet opening of the body 20. Again, a (partial) cover for shading the flow chamber from UV-radiation may be provided.

In the following, general operation of the apparatus 1 will be described in more detail with respect to the Figures.

For the treatment of a surface of the substrate 2, the main part 8 of the application unit 6 will be moved over a substrate 2 on the substrate holder 4. If the complete surface of the substrate should be treated the main part 8 may be moved during the treatment described herein below across the substrate, unless the embodiment according to FIG. 5 is used, which may completely cover the substrate.

Then, a liquid is applied to at least the surfaces of the substrate to be treated via the liquid ports 16, the conduits 24, 25 and the flow chamber 22. Radiation is introduced into said liquid, at least immediately prior to and while applying a film of said liquid to the surface of the substrate to be treated, via the first radiation source 18. The radiation is chosen such that it directly acts on the substrate, in order to treat the same and/or to act on the liquid for changing the characteristics thereof, in order to conduct the desired treatment. In so doing, different treatment possibilities for the surface of the substrate are given, which may be locally limited or may be conducted on the complete surface of the substrate.

In the following, specific examples of such treatments, where the UV-radiation acts on the liquid and in particular with respect to specific compositions of the liquid are explained in more detail. The treatment of an EUV photo mask will be given as an example, abut as pointed out above, similar treatment process may also be performed on other substrates.

EXAMPLE 1:

In this example, the surface energy of the substrate will be adjusted inter alia using a small amount of absorbing medium in an otherwise non-absorbing medium and switching between the same. Previously, as described in DE 10 2009 058 962, an in-situ UV exposure of the substrate through a non-absorbing liquid, such as DI-Water was used to adjust the surface energy, to thereby achieve hydrophilic water contact angle values.

In this example an initial preparation step of an EUV photomask is described. This process step is performed to adjust surface energy for optimal media distribution (surface conditioning); the process step may lead to water contact angles of <10° after treatment.

Surface conditioning is often performed in CO2-water. In the case of 254nm emission, this is a non-absorbing media. The inventors of the present invention have now found that choosing an absorbing media at low concentration (such as Ozone-water) is leading to a better and faster surface conditioning step, and the introduction of an alkaline media may preserve the surface integrity. Therefore a multi-media approach was designed, which leads to better performances in terms of surface energy adjustment.

Introduction:

As indicated above, in-situ UV exposure can be used to adjust the surface energy to hydrophilic water contact angle values. However, this process step was found to lead to unsatisfactory results when using a 254nm emitting UV-light source in combination with non-absorbing media (such as DI-CO_2 water). Fig. 4a shows how repeated exposure of the surface to DI-CO_2 water + UV-light at 254nm leads to an improvement of contact angle values to about 30°, which however are not satisfactory for all applications. In particular improvement to contact angles of <10° may be desired.

It was found that small additions of an absorbing medium to the otherwise non-absorbing medium lead to better results. In particular, a method was tested, where different absorbing media were alternately used in a treatment. As a first medium TMAH in DI-water at a concentration, which lead to about 150µS electrical conductance and a pH of

10.2 was selected as an absorbing medium. The low electrical conductance here indicates the low concentration of the TMAH used, which helps to preserve the surface from damage due to caustic nature of this compound (strong base). Secondly O_3-DI-water at 20ppm concentration was selected as an absorbing medium.

Several oscillations (UV apparatus dispenses the respective medium onto photomask while exposing the same to UV radiation as described above.) were performed for the media. In particular several oscillations (here 5) were performed for Tetramethylammonium Hydroxide TMAH in DI-water, followed by one oscillation of O_3-DI-water, and followed by several oscillations for TMAH in DI-water. Several of such cycles may be used as required and as shown in Fig. 4b, after a first cycle (or run) contact angles of <20° were achieved and after a second cycle contact angles of <10° were achieved.

In this case the several media are used, ie, TMAH which is preserving the surface against damage from Ozone or other species generated therefrom and thus a 20ppm concentration of Ozone can be used.

Switching from a non-absorbing medium to an absorbing medium significantly improved the contact angles. Using the alkaline medium, was considered to beneficial in preserving the surface integrity of the substrate. Although in the example given above, specific media and specific oscillations were described, the skilled person will realize that other absorbing media and other oscillations may be used.

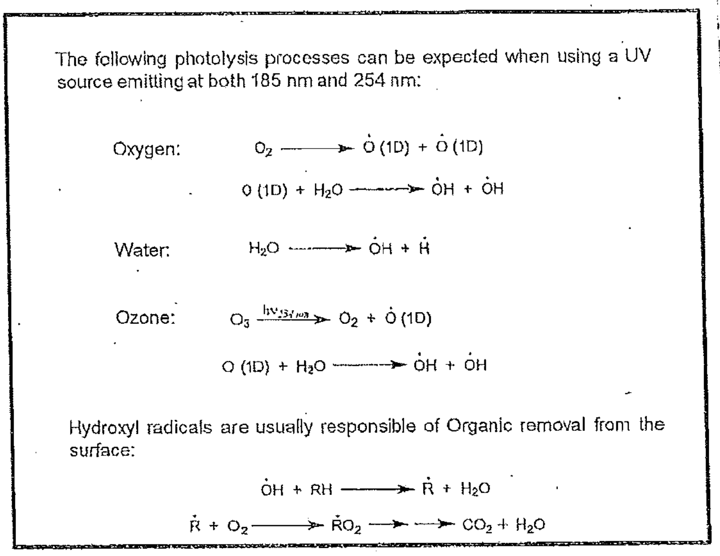
EXAMPLE 2:

Photoresist strip improvement by means of using different absorbing media concentration, and optionally at least one of different distances between light-source and surface and different emission wavelength

Introduction:

Photoresist strip has been performed over the past years by means of SPM (Sulphuric Acid + Hydrogen Peroxide mix); despite its decent cleaning capability, this mix has several drawbacks due to high amount of residual ions left on the surface.

SPM resist strip has been replaced by an In-situ UV process such as the one described in above referenced DE 10 2009 058 962. In a typical procedure, an absorbing media is treated with UV-light with generation of photo-products (mostly radicals) which in turn react with the organic layer (resist) on the surface: Used absorbing media can be Ozonated water at different concentrations, solubilized Oxygen or water itself (which is for example absorbing at 185nm). In the following some of the photolysis processes are given as examples:



The following photolysis processes can be expected when using a UV source emitting at both 185 nm and 254 nm:

Oxygen: $O_2 \longrightarrow \dot{O}\,(1D) + \dot{O}\,(1D)$

$O\,(1D) + H_2O \longrightarrow \dot{O}H + \dot{O}H$

Water: $H_2O \longrightarrow \dot{O}H + \dot{H}$

Ozone: $O_3 \xrightarrow{h\nu_{254\,nm}} O_2 + \dot{O}\,(1D)$

$O\,(1D) + H_2O \longrightarrow \dot{O}H + \dot{O}H$

Hydroxyl radicals are usually responsible of Organic removal from the surface:

$\dot{O}H + RH \longrightarrow \dot{R} + H_2O$

$\dot{R} + O_2 \longrightarrow \dot{R}O_2 \longrightarrow \longrightarrow CO_2 + H_2O$

The inventors have run several experiments to demonstrate that strip rates can be adjusted by means of different absorbing media concentrations, by heating one or more media during the process and distance between light-source and substrate. Fig. 5 summarizes the results and conditions used.

In particular, Fig. 5 shows that by adjusting Ozone concentration to high values (60ppm) leads to good ratio between scanned and non-scanned areas of the mask as well as good strip rates. Adjustment of the distance between light-source and substrate could further improve the performances (conditions 11 and 12).

Emission wavelength also has an impact on the strip rate performances and Fig. 6 shows experimental results upon introduction of 185nm emitting wavelength into the liquid medium. In particular, Fig. 6 shows that about three times higher strip rates can be achieved in the case of introduction of 185nm emission wavelength into the liquid medium compared to a 254nm wavelength.

In this context, the electrical conductance of the medium was found to influence the equilibrium of reactive species generated by the UV radiation. In particular, an increased electrical conductance of at least 20µS, caused by adding an additive to the liquid medium was found to be beneficial. In the case of using an additive which causes a combination of a pH shift and a shift in the electrical conductance, an electrical conductance in the range of 20 to 500μS was found to be beneficial. In case of an additive which is in substance neutral with respect to the pH, an even higher electrical conductance up to 2000μS may be beneficial. Suitable additives which do not substantially alter the pH, i.e. less than by a value of 0.5 are for example sodium chloride and potassium chloride. Although a lower limit of at least 20μS is given for the electrical conductance, a lower limit of at least 50μS, or even at least 70μS is preferred for most applications.

In this example it is shown how photoresist strip rates can be optimized by changing of the concentration of absorbing medium, change of distance between light-source and substrate and change in the emission wavelength of light-source.

EXAMPLE 3:

Final clean improvements using pH and electrical conductance adjustments in absorbing and non-absorbing media, wherein the pH and electrical conductance adjustments may lead to surface preservation.

In this example we describe improvements in the final clean of EUV photomasks. This process step is usually performed after photoresist strip to eliminate any residual organic (or inorganic) impurities and particles from the photomask surface.

Final clean is often performed in CO_2-water. We here show how the shift in pH to alkaline values (>8.5) leads to surface preservation.

Introduction:

The EUV photomask surface is composed by an absorber, usually made by Tantalum Boron Nitride TaBN and a metallic Ruthenium capping layer; the Ruthenium capping layer can be degraded during a wet cleaning step; the major root-causes for this damage are direct or indirect metal oxidation:

Ru (metallic) + UV-light + oxidizing agent === Ru (oxidized)

When Ruthenium is fully oxidized (oxidation state = +8) it forms a volatile compound with resulting peeling off of the metal layer.

Oxidizing agents are usually created upon exposure of water and Oxygen to UV-light:

Oxygen + UV-light: $O_2 \rightarrow O^{\bullet}\,(1D) + O^{\bullet}\,(1D)$

$O^{\bullet}\,(1D) + H_2O \rightarrow HO^{\bullet} + HO^{\bullet}$.

Water + Uv-light: $H_2O \rightarrow H^{\bullet} + HO^{\bullet}$

$O^{\bullet}$ and $OH^{\bullet}$ are typical oxidizing agents.

A second root-cause for metal damage is oxygen inter-diffusion into under-laying Mo/Si bilayers, which may lead to silicon dioxide formation, as is for example reported in Y. Jang, A. John, F. Goodwin, S. Y. Lee, S. S. Kim "Understanding the mechanism of capping layer damage and development of a robust capping material for 16 nm HP EUV mask", 2013 International Symposium on Extreme Ultraviolet Lithography, Toyama, Japan 6-10 October 2013. The formation of amorphous silicon dioxide is leading to a volume increase which in turn breaks the metal layer leading to peel-off.

It was found that the electrochemistry shows the following Ruthenium and media properties:

1) The oxidation potential of metallic Ruthenium as well as stable Ruthenium oxides is decreasing with increasing pH.

2) In alkaline environment $OH^{\bullet}$ radicals have less oxidizing power and more reducing capability; $OH^{\bullet}$ radicals are converted into O^- at alkaline pH; O^- can give similar reactions with hydrocarbons, but has lower oxidation strength than $OH^{\bullet}$.

3) In alkaline media, RuO_4 is easily reduced into RuO_4^- and RuO_4^{2-}

4) O_3, at alkaline pH, is converted into OH radicals; thus, the risk of not decomposed Ozone occurring, which is reported to degrade metal surfaces, is further minimized at this pH range.

Furthermore, the use of an organic strong base whose molecular dimensions are much bigger compared to Si-O-Si dimension such as Tethramethylammonium Hydroxide (TMAH) could lead to lesser inter-diffusion through the surface material layers.

In Fig. 7 typical damage results obtained in conventional used media such as DI-CO_2 are shown. Figure 7 shows AFM images of a Ruthenium layer of an EUV mask after 100X times clean in slightly acid media such as CO_2 water solution (measured pH= 5.5). Experiments done in DI-water (pH = 6.0) gave similar results.

This same experiments was conducted in a diluted solution of TMAH base; the dilution was such that the final electrical conductance of the solution was about 50µS and the resulting measured pH was 10,2. Similar AFM images, as shown in Fig. 8 show no damage after 100X times clean.

Thus, it can be shown how a pH shift to alkaline values positively impacts surface integrity of EUV photomasks during an In-situ UV strip or final clean.

The above examples show how the use of absorbing media in a non-absorbing media and a shift to alkaline values in an aqueous liquid medium may influence the results in an In-situ UV wet treatment of substrates. In particular the following general parameter set was deduced for an in-situ wet treatment of a substrate from the experimental results performed by the inventors.

	Parameter	**Parameter range**	**Preferred parameter range**
1	Absorbing media concentration	5-100ppm	20-60ppm
2	Electrical conductance of media	20-500µS	70-150µS
3	Media pH	8-11	9.5-10.5
4	Media Temperature	20-70°C	20-40°C
5	Emission wavelength	185-600nm	185-300nm or 200-300nm
6	UV source Intensity	25-340mW/cm^2	35 to 310 mW/cm^2 depending on the application
7	Distance between light-source and substrate	1-5mm	1-2mm

Not all parameters have to be fulfilled for the different treatments such as surface preparation, strip and final clean. Rathermore, specific parameters are of more relevance than others in the different processes. In each of the processes an increase of the electrical conductance of the liquid medium is beneficial as it allows tailoring the equilibrium of reactive species generated. Furthermore, in the surface conditioning, the absorbing media concentration in the non-absorbing media concentration is important. In particular a low concentration of not more than 20ppm, preferably not more than 5ppm should be used. In the resist strip, the absorbing media concentration is again an important parameter. Here also the emission wavelength has been shown to have a significant influence on the result of the process. In the final clean, the pH-value in combination with the electrical conductance is important.

Although the invention was described with respect to the specific application of cleaning a EUV photomask, many of the above principles and also ranges given above will also apply to other substrates, where a high cleanliness of a substrate surface is required.

An important aspect of the invention is that the aqueous liquid medium is irradiated with UV-radiation immediately prior to applying the same to the surface of the substrate. In so doing, the medium will already be decomposed/radical species will be generated prior to application of the liquid to the substrate. Depending on the composition of the medium, a certain equilibrium of the reactive species may be present in the medium at the time of applying the medium on the substrate or in other words, when the medium exits through the outlet slits discussed above. Other factors may play into this equilibrium such as the duration (time) of exposure to the UV-radiation and the intensity of the radiation.

However, the inventors were the first to find out that by adjusting the electrical conductance, where the medium is exposed to UV-radiation prior to applying the same to a substrate to be treated, the equilibrium of reactive species may be shifted and a desired equilibrium may be adjusted. The electrical conductance ranges given indicate low concentrations of the respective additives, which are pushing the equilibrium of active species toward reagents or products. An additional effect may be the stabilization of certain radicals depending on the amount of charge. Such a shift in the equilibrium also occurs with an increase of the pH (to alkaline conditions) as well as a decrease of the pH (to acidic conditions). Both conditions may have certain other beneficial effects. For example, an alkaline medium may protect integrity of a metal layer on a photomask during a strip or final clean process, as discussed above.

For other applications, a shift of the pH to acid conditions may be preferable. For example, a CO_2-water clean (which is slightly acidic) in combination with UV-radiation has been demonstrated to be efficient cleaning media for optical photomask. Also, for specific applications in the field aqueous media, acidification of the media could be performed to for example preserve stable passivation oxides, such as Germanium Oxide, which would be damaged in alkaline media, while at the same time providing reactive species for example cleaning purposes. In such cases uses of low absorbing acids would be preferable. Germanium chemistry is widely used in the manufacture of ICs, and the use of an in-situ UV process as described above can be successfully applied to the wafer cleaning as well. Metallic germanium undergoes spontaneous oxidation to GeO_2 which acts as protective passivation layer.

With an alkaline medium this would be solubilized into $HGeO_3^-$.

$$GeO_2(s) + OH^- \rightarrow HGeO_3^-$$

Here, the shift to an acidic media would avoid this solubilization process thus impacting positively the surface integrity.

The invention thus not only considers an adjustment of the electrical conductance to a range of 20 to 2000μS but also of the pH to the range of 8 to 11 but also an adjustment of the pH to the range of 3 to 6, wherein a substantial shift from neutral is considered to be necessary to achieve a desired shift in the equilibrium of species when the medium is applied to a substrate (for example when it exits through the outlet slits of the device discussed above). Such a shift will also speed up/retard certain reactions caused by the UV-radiation. Other factors which may influence the equilibrium are the intensity of the UV-radiation and the duration of the exposure of the medium to the UV-radiation. Both of these may also be adjusted in accordance with the pH of the media or vice versa. In particular, the duration of exposure may be adjusted via the flow velocity of the medium, although certain minimum and maximum flows may be required for the process. Another option is to change the length (distance) of exposure to UV-radiation within the flow channel, for example by a shading cover, such as the shutters described above.

The invention was described here in above with respect to several embodiments, without being limited to the particular embodiments. In particular, the in-situ UV-wet treatments discussed above may also be used in combination with other substrates, in particular semiconductor wafers. Also, the different features as described and as claimed herein below may be combined in any suitable manner. Therefore, it is intended that the invention not be limited to the particular embodiments disclosed, but that the invention will include all embodiments falling within the scope and spirit of the following claims.

Claims

1. A method for treating substrates, comprising:
flowing an aqueous liquid medium through a flow channel and at least one outlet slit onto a substrate to be treated;
exposing the aqueous liquid medium to UV-radiation of a specific wavelength at least in a portion of the flow channel immediately adjacent the at least one outlet slit and after the aqueous liquid medium has flown through the outlet opening towards the substrate and thus prior to and while applying the aqueous liquid medium to the surface of the substrate to be treated; and
adjusting the electrical conductance of the aqueous liquid medium to be in the range of 20 to 2000μS, by the addition of an additive to the aqueous liquid medium, the aqueous liquid medium prior to the addition of the additive having an electrical conductance below 20μS prior to or while exposing the same to the UV-radiation.

2. The method of claim 1, wherein the additive does not substantially change the pH of the aqueous liquid medium.

3. The method of claim 1, further comprising shifting the pH of the aqueous liquid medium to a range of 8 to 11 or 3 to 6 by the addition of the additive to the aqueous liquid medium prior to or while exposing the same to the UV-radiation, the aqueous liquid medium prior to the addition of the additive having a pH in the range of 6 to 8, the additive comprising a base or an acid.

4. The method of claim 3, wherein the aqueous liquid medium is adjusted to have a pH-value in the range of 8 to 11 and an electrical conductance in the range of 20 to 500μS, wherein the additive comprises a base.

5. The method of claim 5, wherein the aqueous liquid medium is adjusted to have a pH-value in the range of 9.5 to 10.5 and an electrical conductance in the range of 70 to 150μS.

6. The method of claim 4, wherein the base is TMAH.

7. The method of claim 4, wherein the base is a non-coordinating compound, which does not have available external electrons capable of establishing a direct bond with a metal on the surface of the substrate.

8. The method of claim 1, wherein the aqueous liquid medium is a mixture of an aqueous liquid medium, which is in substance a non-absorbing medium for the UV-radiation at the specific wavelength, and 5 to 100ppm of a substantially absorbing medium at the specific wavelength.

9. The method of claim 8, wherein the substantially absorbing medium is the additive for adjusting the electrical conductance.

10. The method of claim 4, wherein the method relates to a final clean of a Substrate having an exposed metal layer.

11. The method of claim 10, wherein the substrate is a EUV mask.

12. The method of claim 1, comprising the step of adjusting the time the liquid medium is exposed to the UV-radiation in the flow channel before exiting the at least one exit slit.

13. The method of claim 1, wherein the electrical conductance is adjusted in accordance with the amount of time the aqueous liquid medium is exposed to the UV-radiation within the flow channel before exiting the at least one exit slit.

14. The method of claim 3, wherein the pH is adjusted in accordance with the amount of time the aqueous liquid medium is exposed to the UV-radiation within the flow channel before exiting the at least one exit slit.

15. The method of claim 1, further comprising the step of exposing the aqueous liquid medium to UV-radiation of a specific other wavelength as used in the step of exposing the aqueous liquid medium to UV-radiation of a specific wavelength immediately prior to and while applying a film of said aqueous liquid medium to the surface of the substrate to be treated, prior to said step.

16. The method of claim 1, wherein in the step of exposing the aqueous liquid medium to UV-radiation of a specific wavelength immediately prior to and while applying a film of said aqueous liquid medium to the surface of the substrate to be treated, the specific wavelength in the range of 200 to 300nm, preferably at about 254nm.

17. The method of claim 11, wherein the specific other wavelength is below 200nm, preferably at about 185nm.

18. The method of claim 1, wherein the aqueous liquid medium is irradiated with UV-radiation at an intensity of 25 to 340mW/cm^2.

19. The method of claim 1, wherein the distance of a source of UV-radiation and the surface of the substrate to be treated is in the range of 1 to 5mm, in particular 1 to 2mm.

20. The method of claim 1, wherein the treatment relates to an adjustment of the surface energy of the substrate, wherein the composition of the aqueous liquid medium is adjusted to have an electrical conductance in the range of 70 to 150µS, and wherein the aqueous liquid medium is a mixture of an aqueous liquid medium, which is in substance a non-absorbing medium for the UV-radiation at the specific wavelength, and 5 to 10ppm of a substantially absorbing medium at the specific wavelength.

21. The method of claim 20, wherein the steps of the method are repeated several times on the same substrate, and wherein different absorbing media are used in at least two different repeat cycles.

22. The method of claim 21, wherein at least one absorbing medium is selected from O_3 and TMAH.

23. The method of claim 1, wherein the treatment relates to a photo-resist strip from the substrate, wherein the composition of the aqueous liquid medium is adjusted to have an electrical conductance in the range of 20 to 500µS, and wherein the aqueous liquid medium is a mixture of an aqueous liquid medium, which is in substance a non-absorbing medium for the UV-radiation at the specific wavelength, and 5 to 100ppm of a substantially absorbing medium at the specific wavelength.

24. The method of claim 23, wherein at least one absorbing medium is selected from the group comprising O_3, H_2O_2 and TMAH.

Fig. 1

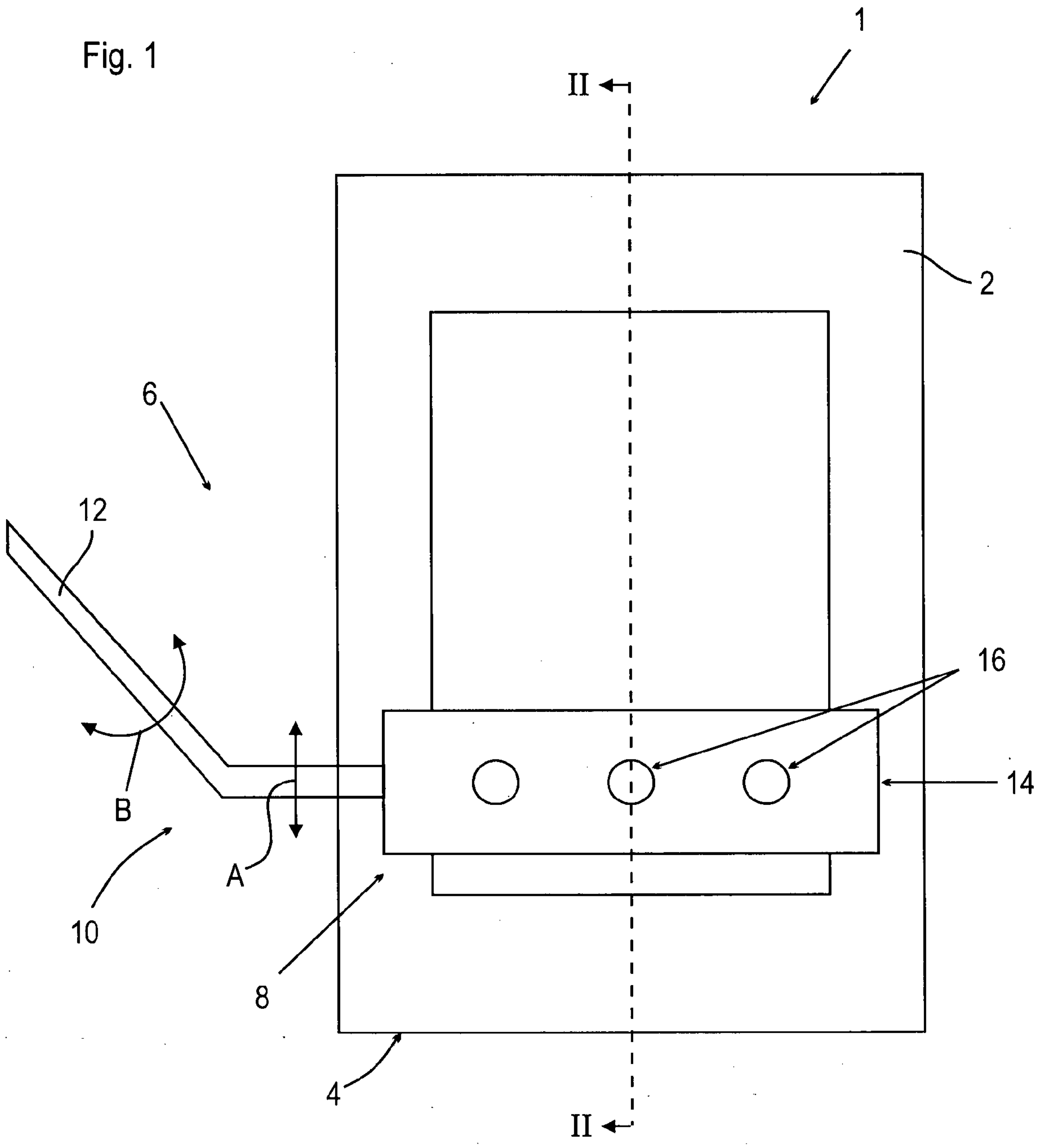


Fig. 2

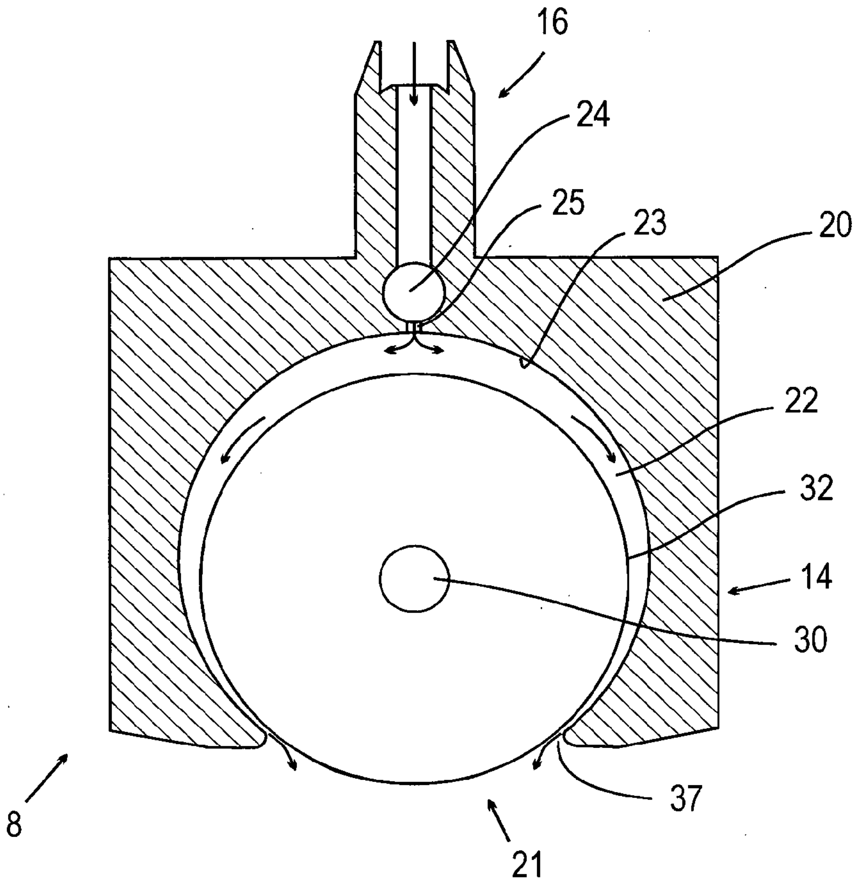


Fig. 3

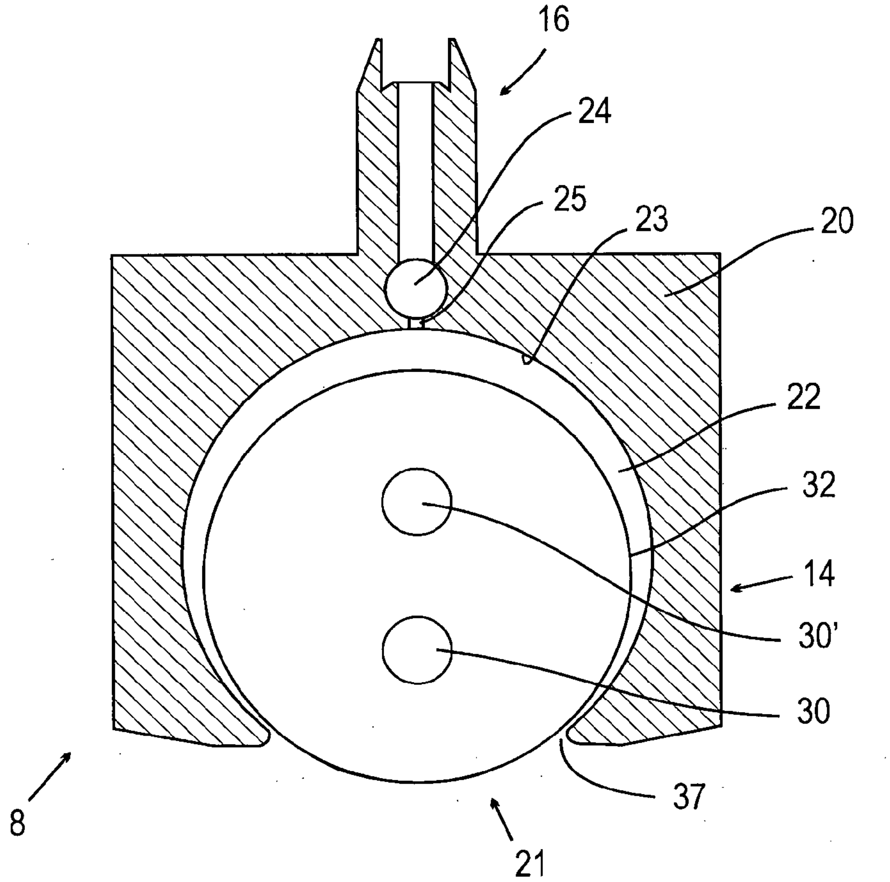


Fig. 4

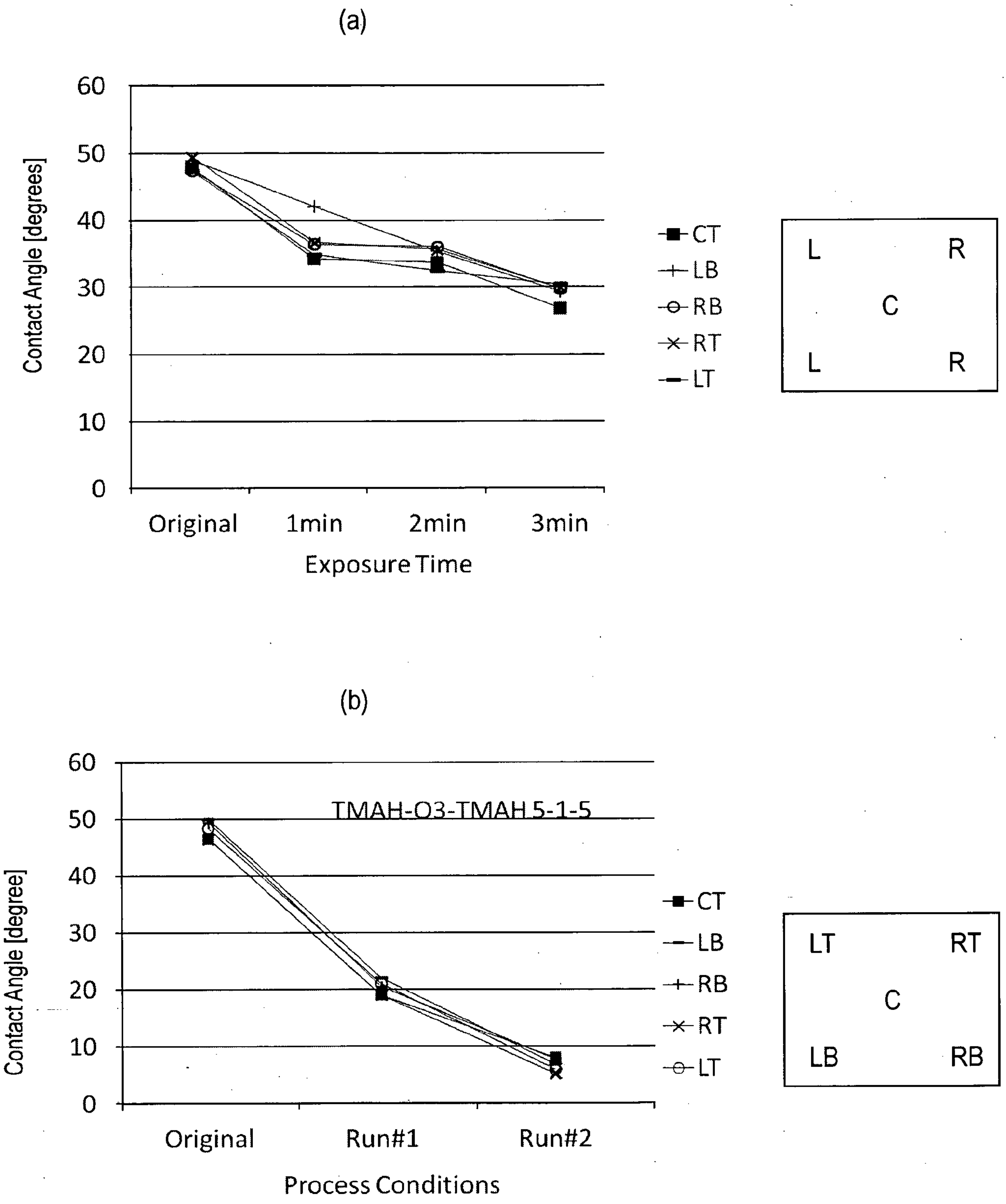

(a)
60
50
40
30
20
10
0
Contact Angle [degrees]
Original
1min
2min
3min
Exposure Time
CT
LB
RB
RT
LT
L
R
C
L
R
(b)
60
50
40
30
20
10
0
Contact Angle [degree]
TMAH-O3-TMAH 5-1-5
Original
Run#1
Run#2
Process Conditions
CT
LB
RB
RT
LT
LT
RT
C
LB
RB

Fig. 5

	Condition #	1	2	3	4	5	6	7	8	9	10	11	12
Condition	H2O-O3, ppm	low	low	low	low	medium	medium	medium	medium	medium	medium	high	high
	H2O-CO2, Heated	no	yes	yes	no	no	yes	no	yes	no	no	no	no
	UV power, %	60%	60%	60%	60%	60%	60%	60%	60%	60%	60%	60%	60%
	Lamp distance	medium	medium	medium	small	large	medium	medium	medium	medium	medium	medium	small
	Scan speed, mm/s	50	50	50	50	50	50	50	50	50	50	50	50
	Process time,s	360	360	360	360	360	360	360	360	360	360	360	360

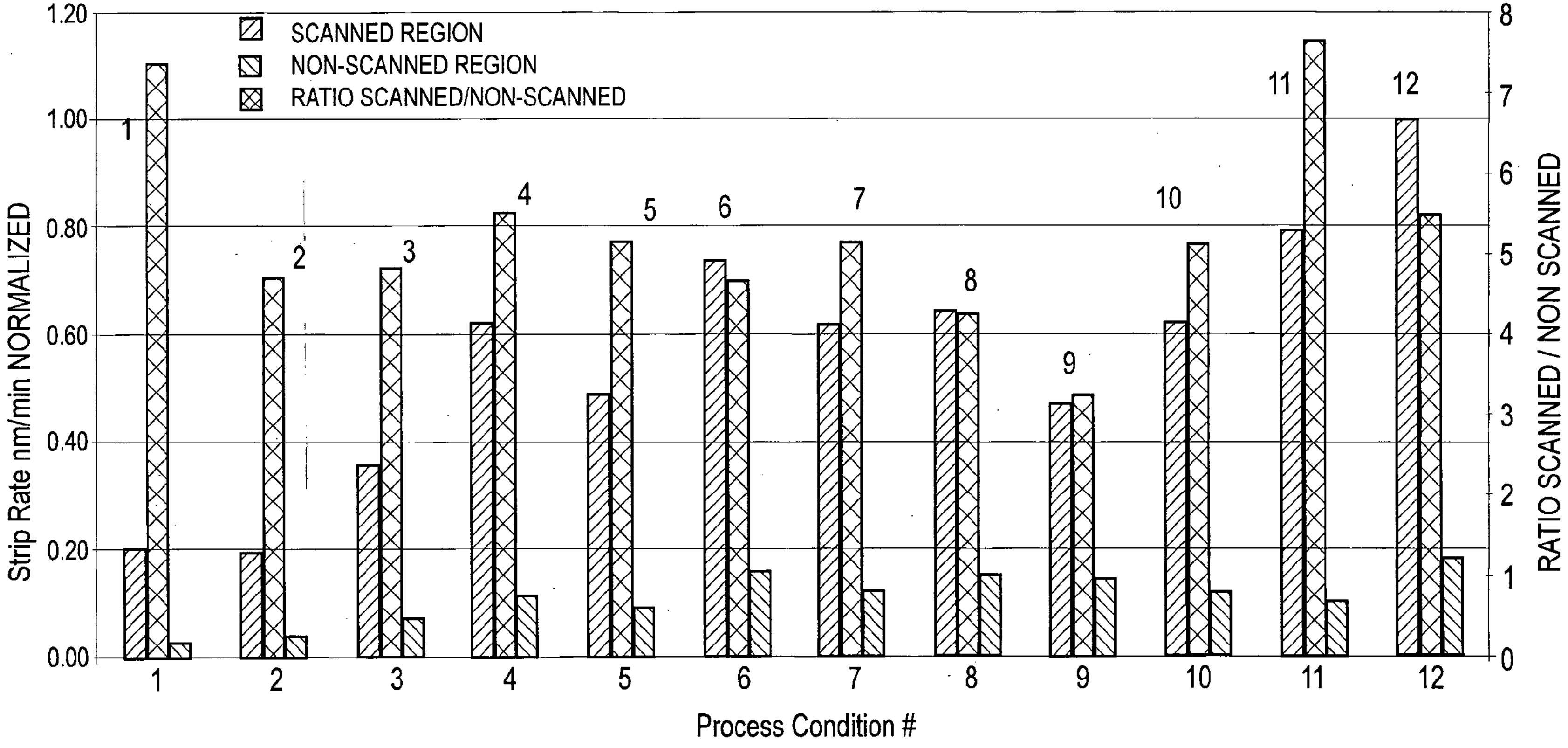


Fig. 6

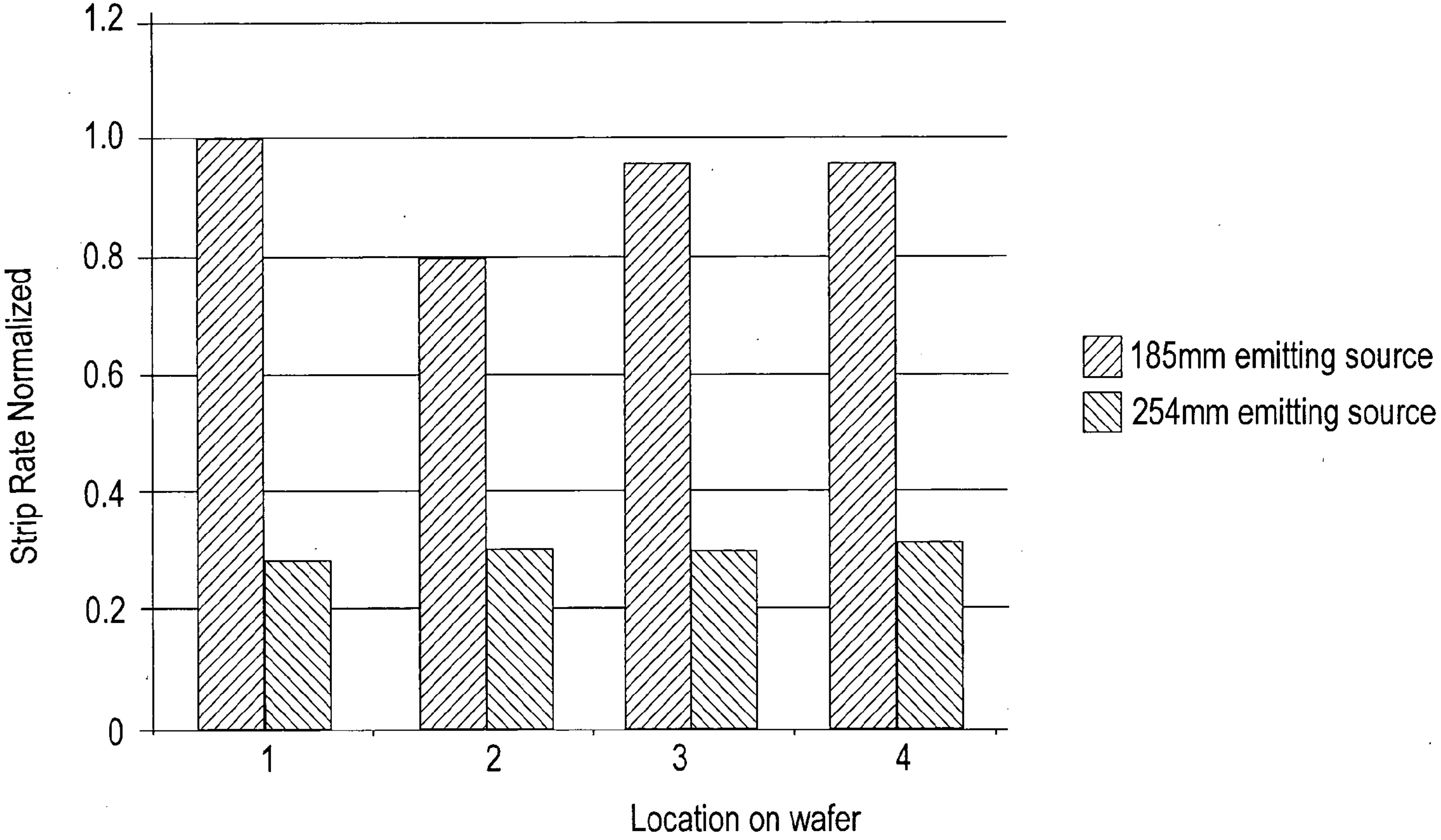

1.2
1.0
0.8
0.6
0.4
0.2
0
Strip Rate Normalized
1
2
3
4
Location on wafer
▨ 185mm emitting source
▧ 254mm emitting source

Fig. 7

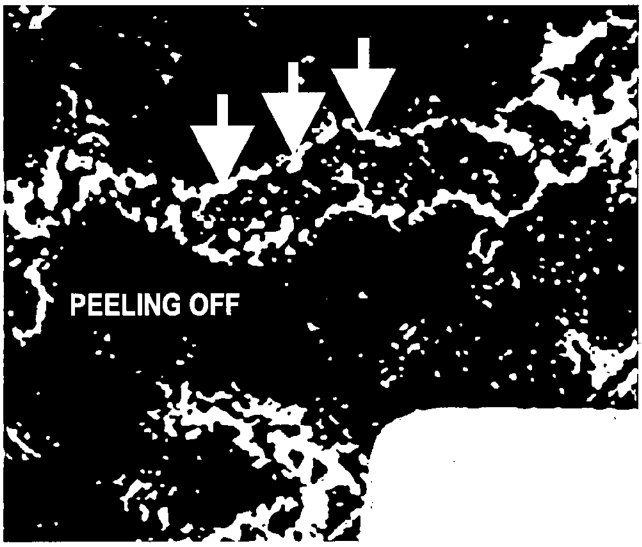
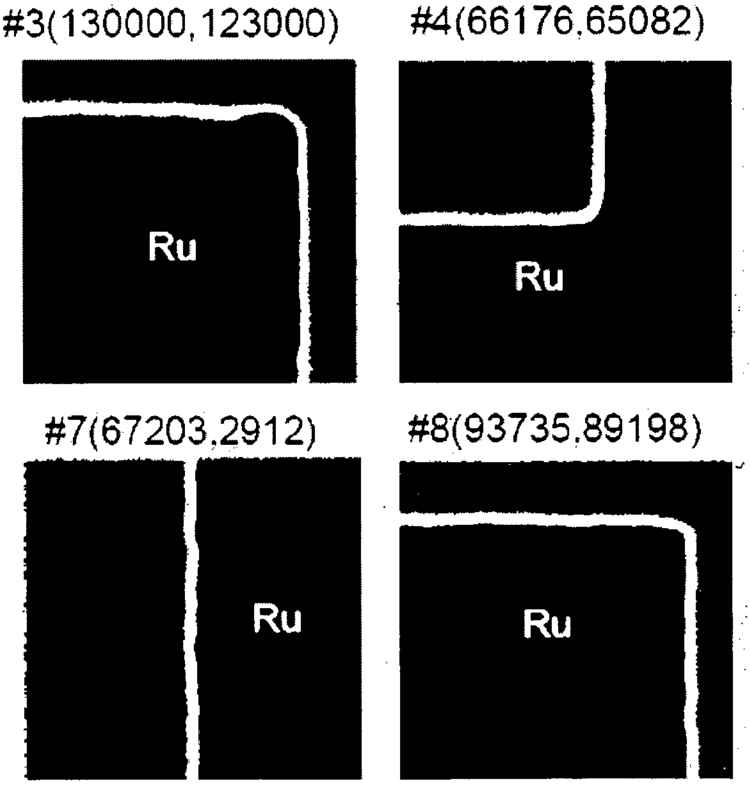


Fig. 8



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#8(93735,89198)

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. G03F7/20 B08B3/10 B08B7/00 G03F1/82 H01L21/67
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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 B08B H01L B05B

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.
A	JP 2004 241726 A (SHARP KK) 26 August 2004 (2004-08-26) abstract paragraph [0005]; figures 1-4 paragraph [0027] -----	1-24
A	DE 10 2009 058962 A1 (HAMA TECH APE GMBH & CO KG [DE]) 5 May 2011 (2011-05-05) cited in the application paragraphs [0038] - [0079]; figure 1 -----	1-24
A	US 2003/205240 A1 (BERGMAN ERIC J [US]) 6 November 2003 (2003-11-06) paragraphs [0097] - [0108]; figure 6 ----- -/--	1-24

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"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 13 December 2016	Date of mailing of the international search report 02/01/2017
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

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/072325

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	EP 1 793 276 A2 (ASML NETHERLANDS BV [NL]) 6 June 2007 (2007-06-06) paragraph [0053] -----	1

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Information on patent family members

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(87)PCT国际申请的公布数据
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(54)发明名称

用于利用暴露于UV-辐射的含水液体介质处理衬底的方法

(57)摘要

描述了用于处理衬底的方法。方法包括如下步骤:使含水液体介质流动通过流动通道和至少一个出口狭缝到待处理的衬底上,以及至少在流动通道的紧邻至少一个出口狭缝的一部分中以及在所述含水液体介质已经朝着衬底流动通过出口开口之后且因此在将含水液体介质施加至待处理的衬底的表面之前和在将含水液体介质施加至待处理的衬底的表面的时候,使所述含水液体介质暴露于特定波长的UV-辐射。在一个方法中,在将含水液体介质暴露于UV-辐射的时候或之前,通过将添加剂添加至含水液体介质,将含水液体介质的电导率调整至在20至2000μS的范围中,含水液体介质在添加所述添加剂之前具有低于20μS的电导率。额外地,在将含水液体介质暴露于UV-辐射的时候或者之前,含水液体介质的pH可以被调整到8至11或3至6的范围。调整可以导致通过UV-辐射在含水液体介质中生成的反应物质的平衡朝优选的物质移动。

1.一种用于处理衬底的方法,其包括:

使含水液体介质流动通过流动通道和至少一个出口狭缝到待处理的衬底上;

至少在所述流动通道的紧邻所述至少一个出口狭缝的一部分中以及在所述含水液体介质已经朝着所述衬底流动通过所述出口开口之后且因此在将所述含水液体介质施加至待处理的所述衬底的表面之前和在将所述含水液体介质施加至待处理的所述衬底的表面的时候,使所述含水液体介质暴露于特定波长的UV-辐射;以及

在将所述含水液体介质暴露于所述UV-辐射之前或在将所述含水液体介质暴露于所述UV-辐射的时候,通过将添加剂添加至所述含水液体介质,将所述含水液体介质的电导率调整为在20至2000 μS的范围中,所述含水液体介质在添加所述添加剂之前具有低于20 μS的电导率。

2.根据权利要求1所述的方法,其中,所述添加剂基本上不改变所述含水液体介质的pH。

3.根据权利要求1所述的方法,其还包括:在将所述含水液体介质暴露于所述UV-辐射之前或在将所述含水液体介质暴露于所述UV-辐射的时候,通过将所述添加剂添加至所述含水液体介质,将所述含水液体介质的pH改变至8至11或3至6的范围,所述含水液体介质在添加所述添加剂之前具有在6至8的范围中的pH,所述添加剂包括碱或酸。

4. 根据权利要求3所述的方法,其中,所述含水液体介质被调整为具有在8至11的范围中的pH-值和在20至500 μS的范围中的电导率,其中,所述添加剂包括碱。

5. 根据权利要求5所述的方法,其中,所述含水液体介质被调整为具有在9.5至10.5的范围中的pH-值和在70至150 μS的范围中的电导率。

6.根据权利要求4所述的方法,其中,所述碱是TMAH。

7.根据权利要求4所述的方法,其中,所述碱是非-配位复合物,其没有能够与在所述衬底的所述表面上的金属建立直接结合的可用外部电子。

8. 根据权利要求1所述的方法,其中,所述含水液体介质是含水液体介质,其对于在所述特定波长处的UV-辐射大体是非-吸收介质,和5至100 ppm的在所述特定波长处的基本上吸收介质的混合物。

9.根据权利要求8所述的方法,其中,所述基本上吸收介质是用于调整所述电导率的添加剂。

10.根据权利要求4所述的方法,其中,所述方法涉及具有暴露的金属层的衬底的最终清洁。

11.根据权利要求10所述的方法,其中,所述衬底是EUV掩模。

12.根据权利要求1所述的方法,其包括调整所述液体介质在离开所述至少一个离开狭缝之前在所述流动通道中暴露于所述UV-辐射的时间的步骤。

13.根据权利要求1所述的方法,其中,根据所述含水液体介质在离开所述至少一个离开狭缝之前在所述流动通道内暴露于所述UV-辐射的时间量来调整所述电导率。

14.根据权利要求3所述的方法,其中,根据所述含水液体介质在离开所述至少一个离开狭缝之前在所述流动通道内暴露于所述UV-辐射的时间量来调整所述pH。

15.根据权利要求1所述的方法,其还包括如下步骤:

使所述含水液体介质暴露于特定其他波长的UV-辐射,所述特定其他波长与在所述步

骤之前，在马上将所述含水液体介质的膜施加至待处理的所述衬底的表面之前和在将所述含水液体介质的膜施加至待处理的所述衬底的表面的时候使所述含水液体介质暴露于特定波长的UV-辐射的步骤中使用的波长不同。

16. 根据权利要求1所述的方法，其中，在马上将所述含水液体介质的膜施加至待处理的所述衬底的表面之前和在将所述含水液体介质的膜施加至待处理的所述衬底的表面的时候使所述含水液体介质暴露于特定波长的UV-辐射的步骤中，所述特定波长在200至300 nm的范围中，优选地在大约254 nm处。

17. 根据权利要求11所述的方法，其中，所述特定其他波长低于200 nm，优选地在大约185 nm处。

18. 根据权利要求1所述的方法，其中，以25至340 mW/cm^2的强度利用UV-辐射照射所述含水液体介质。

19. 根据权利要求1所述的方法，其中，UV-辐射的源和待处理的所述衬底的表面的距离在1至5 mm，尤其是1至2 mm的范围中。

20. 根据权利要求1所述的方法，其中，所述处理涉及所述衬底的表面能量的调整，其中，所述含水液体介质的组成被调整以具有在70至150 μS的范围中的电导率，以及其中，所述含水液体介质是含水液体介质，其对于特定波长处的UV-辐射大体是非-吸收介质，和5至10 ppm的在所述特定波长处的基本上吸收介质的混合物。

21.根据权利要求20所述的方法，其中，在同一衬底上重复若干次所述方法的步骤，以及其中，在至少两个不同的重复循环中使用不同的吸收介质。

22.根据权利要求21所述的方法，其中，从O_3和TMAH选择至少一个吸收介质。

23. 根据权利要求1所述的方法，其中，所述处理涉及从所述衬底的光致抗蚀剂去除，其中，所述含水液体介质的组成被调整以具有在20至500 μS的范围中的电导率，以及其中，所述含水液体介质是含水液体介质，其对于特定波长处的UV-辐射大体是非-吸收介质，和5至100 ppm的在所述特定波长处的基本上吸收介质的混合物。

24.根据权利要求23所述的方法，其中，从包括O_3、H_2O_2和TMAH的组中选择至少一个吸收介质。

用于利用暴露于UV-辐射的含水液体介质处理衬底的方法

技术领域

[0001] 本发明涉及用于利用暴露于UV-辐射的含水液体介质处理衬底的方法。

背景技术

[0002] 在制造半导体的领域中，在通常称为晶片的半导体衬底上执行若干处理步骤。这些步骤中的一个包括光刻法，在其中，光掩模用于使晶片上的光致抗蚀剂暴露于强光模式。暴露于光导致化学改变，其根据模式允许通过专门的溶液来移除一些光致抗蚀剂。

[0003] 在制造半导体的领域中且尤其是在光刻法中，重要的是，所有部件(诸如例如晶片和光掩模)非常干净，且优选地在其上不具有外来颗粒。在其中表面准备和/或尤其是诸如抗蚀剂的有机污染物的污染物的移除是重要的其他技术中也存在此类要求，且因此，即使具体参考衬底诸如在光刻法中使用的光掩模，本发明也适用于其他衬底，诸如半导体衬底、晶片、压印模板、面板、尤其是平板衬底和多层陶瓷衬底。

[0004] 尽管本申请将主要集中于光掩模的处理(光掩模作为衬底以对其执行处理)，本文中所述的原理也可转移至晶片本身或其他衬底，如上文中指出的。

[0005] 在过去，已经使用不同方法来从光掩模移除光致抗蚀剂。如在转让给本发明的受让人的DE 10 2009 058 962 A1中描述的一个此类方法使用含水介质，在马上将所述含水液体介质的膜施加至待处理的衬底的表面之前以及在将所述含水液体介质的膜施加至待处理的衬底的表面的时候，使所述含水介质暴露于UV-辐射。

[0006] 这种移除过程可以分成若干单独的步骤，诸如表面准备、去除和最终清洁。在表面准备中，可以调整表面能量，以例如实现亲水表面。在去除中，通过在含水液体介质中生成的自由基来移除光致抗蚀剂的主要部分。在最终清洁中，残余的抗蚀剂和其他颗粒被移除。在最终清洁中，必须小心谨慎以不改变诸如蚀刻衬底本身的表面，但是移除颗粒而不改变衬底的表面。应当注意，取决于处理的类型和例如初始表面状况，并非必须使用上述顺序的所有步骤。例如，表面准备不总是必需的，尤其如果当进入过程时表面是充分亲水的时。而且，在其上不具有抗蚀剂的新的掩模或者从存储空间出来的掩模(其之前已经被去除)将不需要去除，而是仅需要最终清洁(可选地之前有表面准备)。取决于应用，仅去除(可选地之前有表面准备)是必需的。

[0007] 在DE 10 2009 058 962 A1中的公开内容已经指示了这些步骤且描述了具有改变的介质和/或辐射的单个工具，其可用于所有步骤。然而，该公开未给出关于在单独的步骤中使用的含水液体介质的组成的具体细节。

[0008] 本发明的发明人现在已经发现，在具体步骤中使用的介质的特定参数可以有益于相应的过程。

发明内容

[0009] 根据本发明，提供如在权利要求1或8中陈述的方法。进一步的实施例尤其在从属权利要求中公开。

[0010] 根据一个方面，一种用于处理衬底的方法包括：使含水液体介质流动通过流动通道和至少一个出口狭缝到待处理的衬底上，以及至少在流动通道的紧邻至少一个出口狭缝的一部分中并且在所述含水液体介质已经朝衬底流动通过出口开口之后且因此在将所述含水液体介质施加至待处理的衬底的表面之前和在将所述含水液体介质施加至待处理的衬底的表面的时候，使所述含水液体介质暴露于特定波长的UV-辐射。所述方法还包括如下步骤：在将含水液体介质暴露于UV-辐射的时候或之前，通过将添加剂添加至含水液体介质，将含水液体介质的电导率调整到在20至2000 μS的范围中，其中，在添加添加剂之前，含水液体介质具有低于20 μS的电导率。调整电导率影响通过UV-辐射在含水液体介质中生成的反应物质的平衡，且因此平衡可以朝优选的物质移动。尤其，平衡可以移动成使得在含水液体介质流动通过出口狭缝的时候，存在特定浓度/比率的反应物质。

[0011] 在一个应用中，添加剂是基本上不改变含水液体介质的pH的添加剂，其中，术语“基本上不”被认为是引起小于0.5的pH改变。可以使用的此类添加剂的非-限制示例是盐，诸如氯化钠或氯化钾。

[0012] 在其他应用中，方法还包括通过添加添加剂使含水液体介质的pH改变到8至11或3至6的范围，其中，在添加添加剂之前，含水液体介质具有在6至8的范围中的pH，以及其中，添加剂包括碱或酸。pH的改变也影响反应物质的平衡，且因此，可以实现通过UV-辐射在含水液体介质中生成的反应物质的平衡朝优选物质的移动。pH的这种改变可以加速或减慢在液体介质内通过UV-辐射引起的特定反应，且可以因此使含水液体介质中的反应物质的平衡移动。尤其，平衡可以移动成使得在含水液体介质流动通过出口狭缝的时候，存在特定浓度/比率的反应物质。作为示例，在臭氧水中首先产生羟基自由基且然后是带有更少的氧化强度和相同的有机物移除能力的另外的物质，诸如O^-。碱性pH延长自由基在含水液体介质中的寿命，由此可以实现物质的平衡的移动/稳定。此外，碱性介质改变了金属表面的电势，其因此对氧化更不敏感。酸性介质例如减慢臭氧的分解，同时碱性介质加速臭氧的分解，且因此加速更多物质的生成。本发明因此能够通过改变液体介质的pH来实现对出口狭缝处的物质的浓度/比率的调整。可以因此针对具体应用和要求调整该过程。

[0013] 含水液体介质可以尤其被调整为具有在8至11的范围中的pH-值和在20至500 μS的范围中的电导率，其中，添加剂包括碱。介质电导率指示碱的有利的低浓度。仅通过在将介质插入到流动通道中之前混合介质，此类低浓度可以被用于实现期望的效果。

[0014] 根据本发明的另一方面，含水液体介质被调整为具有在9.5至10.5的范围中的pH-值和在70至150 μS的范围中的电导率。当使用碱来改变pH时，优选的材料是TMAH，其甚至以低浓度就可以实现所要求的改变，且此外是非配位复合物。

[0015] 碱优选地是非-配位复合物，其没有能够与衬底的表面上的金属建立直接结合的可用外部电子，诸如例如，四甲基氢氧化铵(TMAH)或氢氧化钾(KOH)。含水碱介质优选地包括DI-水。

[0016] 根据一个方面，含水液体介质是含水液体介质，其对于特定波长处的UV-辐射大体是非-吸收介质，和5至100 ppm的在特定波长处的基本上吸收介质的混合物。因此整体介质中仅小量吸收在特定波长处的UV-辐射，由此实现反应物质的量的良好调整。基本上吸收介质可以是用于调整电导率的添加剂，但是同样可能的是，吸收介质是不同的介质。

[0017] 在一个应用中，方法涉及对具有暴露的金属层(诸如EUV掩模)的衬底的最终清洁。

这种最终清洁可以例如在光致抗蚀剂去除之后执行。

[0018] 方法还可包括：调整所述液体介质在离开所述至少一个出口狭缝之前在所述流动通道中暴露于UV-辐射的时间的步骤，其可进一步使得物质的平衡能够移动。在该背景中，可以根据含水液体介质在离开至少一个出口狭缝之前在流动通道内暴露于UV-辐射的时间量来调整电导率和pH中的至少一个。

[0019] 上述方法还可包括如下步骤：使所述含水液体介质暴露于特定其他波长的UV-辐射，其与在所述步骤之前，在马上将所述含水液体介质的膜施加至待处理的所述衬底的表面之前和在将所述含水液体介质的膜施加至待处理的所述衬底的表面的时候使所述含水液体介质暴露于特定波长的UV-辐射的步骤中使用的波长不同。这可以实现针对特定自由基生成来准备含水液体，且还可允许在液体中分解不应当到达衬底的某些成分(诸如O_3)。

[0020] 含水液体介质可以被调整为具有在70至150 μS的范围中的电导率，且还可以被调整为具有在20至70℃范围中，尤其是在20至40℃范围中的温度。

[0021] 根据优选实施例，以25至340 mW/cm^2的强度利用UV-辐射照射含水液体介质。UV-辐射源和待处理的衬底的表面之间的距离可以被调整至在1至5 mm的范围中，尤其是在1至2 mm的范围中。含水液体介质可以被暴露于在185至600 nm的范围中，尤其是在185至300 nm的范围中的波长的UV-辐射。在将所述含水液体介质的膜施加至待处理的衬底的表面的时候和马上将所述含水液体介质的膜施加至待处理的衬底的表面之前使含水液体介质暴露于特定波长的UV-辐射的步骤中，所述特定波长优选地在200至300 nm的范围中，优选地在大约254 nm处用于生成自由基。特定其他波长可以低于200 nm，优选地在大约185 nm处，其可以更好地适用于准备/分解液体。

[0022] 方法可以具体地涉及从衬底去除光致抗蚀剂，其中，含水液体介质的组成被调整为具有在20至500 μS的范围中，尤其是在70至150 μS的范围中的电导率，以及其中，含水液体介质是含水液体介质，其对于在特定波长处的UV-辐射大体是非-吸收介质，和5至100 ppm的在特定波长处的基本上吸收介质的混合物。在本申请中，可以例如从包括O_3、H_2O_2和TMAH的组中选择至少一个吸收介质。

[0023] 方法可以在一个实例中涉及对衬底的表面能量的调整，其中，含水液体介质的组成被调整为具有在70至150 μS的范围中的电导率，以及其中，含水液体介质是含水液体介质，其对于在特定波长处的UV-辐射大体是大体是非-吸收介质，和5至10 ppm的在特定波长处的基本上吸收介质的混合物。可以在同一衬底上重复若干次方法步骤以达到期望的效果，其中，可以在不同的重复循环中使用不同的吸收介质。优选地，从O_3和TMAH选择至少一个吸收介质。

[0024] 方法可以具体地涉及从衬底去除光致抗蚀剂，其中，含水液体介质的组成被调整为具有在20至500 μS的范围中，尤其是在70至150 μS的范围中的电导率，以及其中，含水液体介质是含水液体介质，其对于在特定波长处的UV-辐射大体是非-吸收介质，和5至100 ppm的在特定波长处的基本上吸收介质的混合物。在本申请中，可以例如从包括O_3、H_2O_2和TMAH的组中选择至少一个吸收介质。

[0025] 在一个应用中，涉及表面能量的调整、光致抗蚀剂去除和最终清洁的上述方法中的至少两个以上述顺序执行。

附图说明

[0026] 下面将参考附图在本文中更详细地解释本发明。在附图中：

图1是可以在本发明的方法中使用的处理装置的示意顶视图；

图2是图1的装置沿着线I-I的示意截面视图；

图3是根据装置的替代实施例类似于图2的示意截面视图；

图4a和图4b是曲线图，其示出施加UV辐射至特定液体对接触角值的影响；

图5是图解，其示出对于不同过程参数，去除速率(标准化的)的结果的总结；

图6是图解，其示出对于不同波长，去除速率(标准化的)的结果的总结；

图7是在利用DI-CO_2水结合UV-辐射进行100X次清洁之后，具有钌覆盖层的EUV掩模的AFM图像；

图8示出在利用DI水中的TMAH结合UV-辐射进行100X次清洁之后，具有钌覆盖层的EUV掩模的AFM图像。

具体实施方式

[0027] 在以下描述中使用的任何方向参考，诸如上、下、左或右参照附图，且不应当解释为限制本申请，即使其可指的是优选布置。尽管本发明涉及方法，但是将首先描述用于执行此类方法的示例性装置。将结合光掩模，尤其是EUV掩模来描述装置和方法，但是本发明的原理还可以应用到其他衬底，尤其是在其处理期间的半导体衬底、晶片、压印模板、面板、尤其是平板衬底和多层陶瓷衬底。

[0028] 图1示出用于处理衬底2的装置1的示意顶视图，而图2示出装置1沿着线I-I的示意截面视图。

[0029] 装置1主要包括用于衬底的接收器，其将称为用于施加单元6的衬底保持器。衬底保持器4和施加单元6可以布置在未示出的压力腔室中，在其中，可以通过适当的器件生成正压或负压。

[0030] 如在附图中可见的，衬底保持器4是平坦矩形板，其用于接收也是矩形的衬底2。衬底保持器4可以具有其他形状，其可以匹配待处理的衬底2的形状。衬底保持器4具有用于液体的未示出的引流器，所述液体可以经由施加单元6施加到衬底2上。

[0031] 施加单元6由主要部分8和支撑部分10组成，如通过双头箭头A和B示出的，支撑部分10以可移动的方式支撑主要部分8。尤其，支撑部分10具有支撑臂12，其在一端上连接至主要部分8。支撑臂12的另一端连接到驱动机构，其未示出。如通过双头箭头A和B示出的，驱动机构可以例如提供支撑臂10且因此主要部分8的枢转运动和/或线性运动。以该方式，主要部分8可以跨被接收在所述衬底保持器4上的衬底2运动，以便实现对衬底2的部分面积或整个表面的处理。此外，还可能的是支撑臂10提供提升运动，以便调整在主要部分8和接收在衬底保持器4上的衬底2的表面之间的距离。

[0032] 替代地、或额外地，还能够提供用于衬底保持器的运动机构，以便在衬底2和主要部分8之间提供相对运动。

[0033] 主要部分8具有壳体14、液体端口16和辐射源18。壳体14具有细长立方体形主体20，其沿着其纵向延伸限定流动腔室22，其大体跨主体20的整个长度延伸。流动腔室22具有

纵向延伸，其大于衬底2的宽度延伸，以便能够跨其整个宽度将液体施加至衬底，如下面将在本文中更详细地解释的。然而，还可能的是流动腔室具有更小的尺寸。流动腔室22的内表面23可以被设计为具有高反射率，尤其是相对于UV辐射，而IR辐射可以基本上被吸收。

[0034] 流动腔室22具有基本上圆形的横截面形状。流动腔室22朝主体20的底侧打开，使得主体限定指向待处理的衬底2的出口开口21。在流动腔室22的上部部分中，在主体20中提供导管24，其大体平行于流动腔室22延伸。导管24流体连接到液体端口16。导管24也在多个位置处经由多个导管或孔25被流体连接到流动腔室22。因此，可能将流体经由液体端口16、导管24和多个导管25输送到流动腔室22中。在这方面，应当注意，导管24结合导管25能够基本上在流动腔室22的整个长度上将流体输送到流动腔室22中。

[0035] 液体端口16各自连接到未示出的外部导管，经由其，一个或多个流体可以被输送至液体端口16。可能的是多个流体可以经由该外部导管同时或者顺序地输送至液体端口。还能够提供多个外部导管，经由其，例如不同的流体可以被输送至液体端口。虽然可以考虑流体，例如液体，但是还能够输送气体至液体端口16，其可以例如在其被输送至流动腔室22之前，在液体端口16和导管24中与液体混合。在图2中示出箭头，其指示液体从液体端口16经由导管24到流动腔室22中和离开壳体14的流动。尽管示出三个液体端口16，但是应当注意，可以提供更多或更少的液体端口16，且其可以将相同或不同的流体源连接至导管24。选择的液体端口16还可以直接地连接到流动腔室22或间接地经由类似于导管24的第二导管(未示出)连接到流动腔室22。如本领域技术人员将认识到的，此类布置可以实现将不同的流体带入流动腔室22中的不同可能性。尤其，此类布置允许在将不同的流体喷射到流动腔室22中之前，在(多个)液体端口16的上游或其下游在导管24中混合所述不同的流体。另一种可能性是经由分离的液体端口16(和可选地分离的导管24)将不同的流体分离地带到流动腔室22中，使得其在流动腔室22内混合。

[0036] 辐射源18具有纵向延伸的形状且沿着整个流动腔室22基本上在其中间延伸。辐射源18具有杆形灯30，其被盖32环绕，盖32对灯30的辐射基本上透明。杆形灯属于如下类型，即，其至少以预定范围的波长发射UV辐射。还可能的是杆形灯30跨波长的广谱发射辐射，且尤其发射UV辐射和IR辐射。

[0037] 盖32，其可以例如由石英玻璃组成，在流动腔室22内完全环绕杆形灯30，且将其与流动腔室22中的流体隔离。盖32可以例如通过流动腔室22的端壁延伸出主体20。这将实现对杆形灯30的接近，例如用于替换或维护目的，而不必接近流动腔室22。由于其在流动腔室22中的布置，盖32连同流动腔室22的内壁形成流动路径，其用于被经由导管24或分离的入口(未示出)输送到流动腔室22中的流体。流动路径分成两个分支(在图2中，左和右)，且在主体20的出口开口21处，在主体20和盖32之间形成出口狭缝37。盖32的中间相对于流动腔室22的中间朝下偏移，使得流动路径的分支朝出口狭缝37变窄。这种变窄预期实现流体流动在流动腔室22中的均匀化。

[0038] 此类流体围绕盖32流动，且因此整体上围绕辐射源18流动。通过杆形灯30发射的辐射因此被引入到沿着流动路径流动的任何液体中。此外，盖32延伸超出主体20的底部表面，且部分地延伸到主体20的出口开口21中并超出出口开口21。因此，可能的是从杆形灯发射的辐射也朝着衬底保持器4离开流动腔室22或到置放在衬底保持器4上的衬底2上。尤其，辐射可以被引入到衬底2上的液膜(其例如通过液体形成)中，液体流动通过流动腔室22并

离开出口狭缝37流到衬底上。尽管未示出，但是可以例如在盖32上或在盖32中提供部分盖，以相对于UV辐射遮蔽流动路径22的某些区域。尤其，用于液体到流动路径中的入口区域可以被遮蔽，因为此处的流动可以是紊流且因此对液体的照射可能不均匀，或者可能还未期望UV辐射。这种遮蔽盖可以静止地提供或者可以可移动地提供，使得可以改变流动通道的遮蔽。例如，可以提供可移动挡板，其在第一位置中允许UV-辐射通过并且在第二位置中阻挡UV-辐射。通过提供此类遮蔽，流动通过流动通道的流体暴露于UV-辐射的时间可以被调整。此类时间可以例如也至少部分地经由流动通过流动通道的流体的流动速率被调整。

[0039] 图3示出用于处理衬底2的装置1的替代实施例的类似于图2的示意侧视图。当描述该实施例时，因为提供相同或类似的元件，所以与先前一样使用相同的附图标记。

[0040] 装置1再次基本上由用于接收衬底的衬底保持器4和施加单元6组成。衬底保持器可以以与先前关于图1和图2描述的相同方式设计。

[0041] 施加单元6再次具有主要部分8和支撑部分，支撑部分未在图3中示出，然而其可以具有与先前关于图1和图2描述的相同设计。主要部分8再次基本上由壳体14、液体端口16和辐射源18组成，其中，壳体14和液体端口16可以具有与先前关于图1和图2描述的相同设计。

[0042] 辐射源18再次具有细长形状且基本上在中间延伸通过流动腔室22。在该实施例中，辐射源18具有杆形灯30、30’，其通过盖32环绕，盖32对杆形灯30、30’的辐射基本上透明且以与先前描述的相同方式布置。杆形灯30、30’在图3中示出为在彼此之上，但是其还可以以不同方式布置在盖32内，或者可以提供多于两个灯。杆形灯可以是相同或不同的类型，其中，它们中的至少一个以预定范围的波长发射UV辐射。尤其，可能的是两个杆形灯30、30’都以不同范围的波长发射UV辐射。上部杆形灯30’可以例如至少部分地或主要在低于200 nm的波长范围内，优选地在大约185 nm处发射UV辐射，而下部杆形灯30至少部分地或主要在200至300 nm的波长范围内，优选地在大约254 nm处发射UV辐射。一个或两个杆形灯30、30’还可以发射一定量的IR辐射或其他辐射。尽管未示出，但是辐射引导元件，诸如镜子，可以被置放在杆形灯之间，以引导灯的相应辐射，使得上部灯的辐射主要被发射到流动腔室22中，且下部灯的辐射主要被发射到壳体14的外侧，但是同样下部灯的辐射的一部分也被发射到流动路径22的邻近于其离开开口的端部区域中。

[0043] 盖32在流动腔室22内完全环绕杆形灯30、30’且使杆形灯30、30’相对于所述流动腔室22中的流体隔离。在这方面，盖32可以具有与先前关于图1和图2描述的盖相同的设计。此外，还可能的是更多的杆形灯被接收在盖32内，其可以各自发射不同的辐射，或者也可以各自发射相同的辐射。通过布置和选择杆形灯30、30’，可以在流动腔室22内以及经由主体20的出口开口超出流动腔室22生成期望的辐射分布(相对于发射的波长及其空间分布)。再次，可以提供用于遮蔽流动腔室免于UV-辐射的(部分)盖。

[0044] 在下文中，将关于附图更详细地描述装置1的一般操作。

[0045] 为了处理衬底2的表面，施加单元6的主要部分8将在衬底保持器4上的衬底2上方运动。如果应当处理衬底的整个表面，则主要部分8可以在下面本文中所述的处理期间跨衬底运动，除非使用根据图5的实施例，其可以完全覆盖衬底。

[0046] 然后，经由液体端口16、导管24、25和流动腔室22，液体被施加到待处理的衬底的至少表面。至少在马上将所述液体的膜施加至待处理的衬底的表面之前和在将所述液体的膜施加至待处理的衬底的表面的时候，经由第一辐射源18将辐射引入到所述液体中。辐射

被选择成使得其直接作用在衬底上，以便处理衬底和/或作用在液体上以用于改变其特性，以便进行期望的处理。在这情况下，给出对于衬底的表面的不同处理的可能性，其可以是局部有限的，或者可以在衬底的整个表面上进行。

[0047] 在下文中，更详细地解释此类处理的具体示例，其中，UV-辐射作用于液体且尤其相对于液体的具体组成。作为示例给出对EUV光掩模的处理，但是如上文中指出的，也可以对其他衬底执行类似的处理过程。

[0048] 示例1：

在该示例中，尤其在原本非-吸收介质中使用小量的吸收介质及在其之间切换来调整衬底的表面能量。之前，如在DE 10 2009 058 962中描述的，衬底通过非-吸收液体(诸如DI-水)的原位UV暴露用于调整表面能量，以由此实现亲水的水接触角值。

[0049] 在该示例中，描述EUV光掩模的初始准备步骤。执行该过程步骤，以针对最优介质分布调整表面能量(表面整修)；在处理后，该过程步骤可以导致<10°的水接触角。

[0050] 通常在CO2-水中执行表面整修。在254 nm发射的情形中，这是非-吸收介质。本发明的发明人现在已经发现，选择低浓度的吸收介质(诸如臭氧-水)导致更好且更快的表面整修步骤，且碱性介质的引入可以保护表面完整性。因此设计多-介质方法，其导致在表面能量调整方面更好的性能。

[0051] 介绍：

如上文中指示的，原位UV暴露能够用于将表面能量调整为亲水的水接触角值。然而，发现当结合非-吸收介质(诸如去DI-CO_2水)使用254 nm发射UV-光源时，该过程步骤导致不令人满意的结果。图4a示出表面如何重复暴露于DI-CO_2水+254 nm处的UV-光导致接触角值至大约30°的改进，然而，其不是对于所有应用都是令人满意的。尤其，可能期望至<10°的接触角的改进。

[0052] 已经发现，吸收介质至原本非-吸收介质的小量添加导致更好的结果。尤其，测试了一种方法，其中，在处理中交替地使用不同的吸收介质。作为第一介质TMAH在DI-水中以导致大约150 µS电导率和10.2的pH的浓度被选择为吸收介质。此处，低电导率指示所使用的TMAH的低浓度，其帮助保护表面不受由于该复合物(强碱)的腐蚀性质引起的损坏。第二，处于20 ppm浓度的O_3-DI-水被选择为吸收介质。

[0053] 对介质执行几次振荡(oscillation)(UV装置将相应的介质分配到光掩模上，同时使其暴露于如上面所描述的UV辐射)。尤其对于在DI-水中的四甲基氢氧化铵TMAH执行几次振荡(此处是5次)，之后是O_3-DI-水的一次振荡，且之后是对于在DI-水中的TMAH的几次振荡。可以根据需要使用几次此类循环并且如在图4b中所示，在第一循环(或运行)之后，达到<20°的接触角，并且在第二循环之后，达到<10°的接触角。

[0054] 在该情形中，使用几个介质，即，TMAH，其保护表面不受臭氧或从其生成的其他物质的损坏，且因此能够使用20 ppm浓度的臭氧。

[0055] 从非-吸收介质切换至吸收介质显著地改进接触角。使用碱性介质被认为对于保护衬底的表面完整性是有益的。尽管在上文中给出的示例中，描述了具体介质和具体振荡，但是本领域技术人员将认识到可以使用其他吸收介质和其他振荡。

[0056] 示例2：

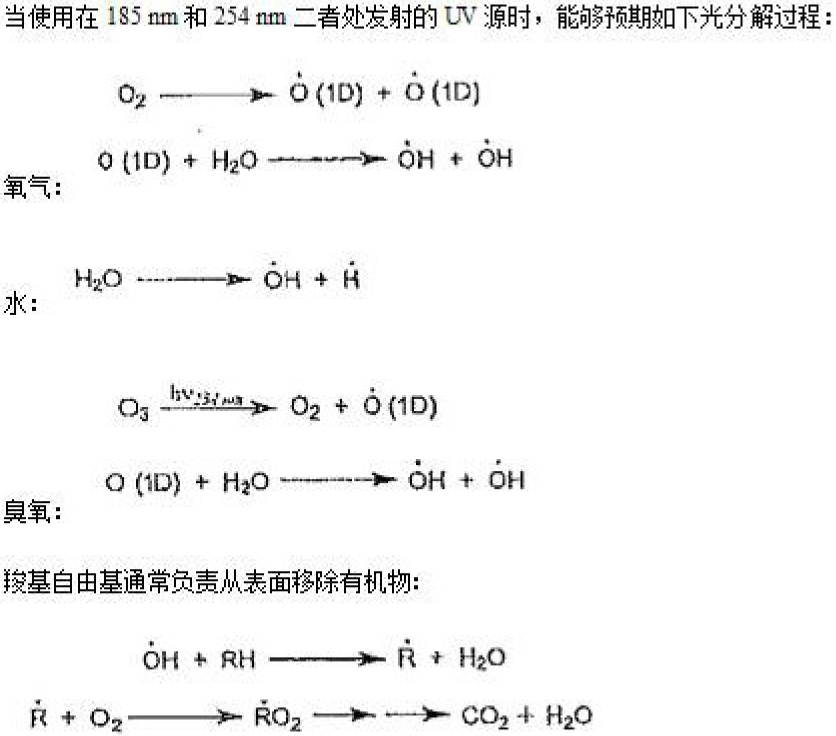
借助于使用不同的吸收介质浓度和可选地在光源和表面之间的不同距离和不同发射

波长中的至少一个的光致抗蚀剂去除改进

介绍：

在过去数年间，已经借助于SPM(硫酸+过氧化氢混合物)执行光致抗蚀剂去除；尽管其清洁能力相当好，但是由于留在表面上的高量的残留离子，所以该混合物具有若干缺点。

[0057] 已经通过诸如在上文引用的DE 10 2009 058 962中描述的一个的原位UV过程替代SPM抗蚀剂去除。在典型的程序中，利用UV-光处理吸收介质，其中，生成光产品(主要是自由基)，其继而与表面上的有机物层(抗蚀剂)反应：所使用的吸收介质能够是具有不同浓度的臭氧水、溶解的氧气或者水本身(其例如在185 nm处是吸收的)。在下文中，一些光分解过程作为示例给出：



当使用在185 nm和254 nm二者处发射的UV源时，能够预期如下光分解过程：

$$O_2 \longrightarrow \dot{O}\,(1D) + \dot{O}\,(1D)$$

$$O\,(1D) + H_2O \longrightarrow \dot{O}H + \dot{O}H$$

氧气：

$$H_2O \longrightarrow \dot{O}H + \dot{H}$$

水：

$$O_3 \xrightarrow{h\nu;254\,nm} O_2 + \dot{O}\,(1D)$$

$$O\,(1D) + H_2O \longrightarrow \dot{O}H + \dot{O}H$$

臭氧：

羧基自由基通常负责从表面移除有机物：

$$\dot{O}H + RH \longrightarrow \dot{R} + H_2O$$

$$\dot{R} + O_2 \longrightarrow \dot{R}O_2 \longrightarrow \cdots \longrightarrow CO_2 + H_2O$$

。

[0058] 本发明人已经进行若干实验，以展示去除速率能够借助于不同的吸收介质浓度、通过在过程期间加热一个或多个介质和在光源和衬底之间的距离来调整。图5总结了结果和所使用的条件。

[0059] 尤其，图5示出，通过将臭氧浓度调整至高值(60 ppm)导致在掩模的扫描区域和非扫描区域之间的良好比率以及良好的去除速率。对光源和衬底之间的距离的调整可进一步改善性能(条件11和12)。

[0060] 发射波长也对去除频率性能有影响，且图6示出在将185 nm发射波长引入到液体介质中时的实验结果。尤其，图6示出，与254 nm波长相比较，在将185 nm发射波长引入到液体介质中的情形中，能够实现大约三倍的去除速率。

[0061] 在该背景下，发现介质的电导率影响通过UV辐射生成的反应物质的平衡。尤其，发现通过添加添加剂至液体介质引起的电导率的至少20 μS的增加是有益的。在使用导致pH改变和电导率改变的组合的添加剂的情形中，发现在20至500 μS的范围中的电导率是有益的。在相对于pH是大体中性的添加剂的情形中，高达2000 μS的甚至更高的电导率可能是有益的。基本上不改变pH(即，改变小于0.5的值)的合适的添加剂例如是氯化钠和氯化钾。尽

管对于电导率给出至少20 μS的下限，但是对于大部分应用，至少50 μS，或者甚至至少70 μS的下限是优选的。

[0062] 在该示例中，示出如何能够通过改变吸收介质的浓度、改变在光源和衬底之间的距离以及改变光源的发射波长来优化光致抗蚀剂去除速率。

[0063] 示例3：

最终清洁改进在吸收和非吸收介质中使用pH和电导率调整，其中，pH和电导率调整可以导致表面保护。

[0064] 在该示例中，我们描述了对EUV光掩模的最终清洁的改进。通常在光致抗蚀剂去除之后执行该过程步骤，以消除来自光掩模表面的任何残留的有机(或者无机)杂质和颗粒。

[0065] 通常在CO_2-水中执行最终清洁。我们此处示出，pH至碱性值(>8.5)的改变如何导致表面保护。

[0066] 介绍：

EUV光掩模表面由吸收体，其通常由氮化钽硼(TaBN)制成和金属钌覆盖层构成；在湿法清洁步骤期间，钌覆盖层能够降解；该损坏的主要根本原因是直接或者间接的金属氧化；

Ru(金属)+UV-光+氧化剂===(氧化的)Ru。

[0067] 当钌完全氧化时(氧化状态=+8)，其形成易挥发复合物，结果导致金属层的脱层。

[0068] 通常一使水和氧气暴露于UV-光就形成氧化剂：

$$O_2 \rightarrow O^\bullet\,(1D) + O^\bullet\,(1D)$$

氧气+UV-光：

$$O^\bullet\,(1D) + H_2O \rightarrow HO^\bullet + HO^\bullet$$

水+UV-光：$H_2O \rightarrow H^\bullet + HO^\bullet$

$O^\bullet$和$OH^\bullet$是典型的氧化剂。

[0069] 金属损坏的第二根本原因是氧气到下层Mo/Si双层中的内部扩散，其可以导致二氧化硅形成，如例如在Y. Jang, A. John, F. Goodwin, S. Y. Lee, S. S. Kim的“理解覆盖层损坏的机理和用于16 nm HP EUV掩模的鲁棒覆盖材料的发展”(2013年十月6-10日日本富山，2013年关于远紫外线光刻的国际研讨会)中报告的。非晶形二氧化硅的形成导致体积增加，其继而使金属层破裂，从而导致脱层。

[0070] 已经发现电化学示出如下钌和介质性质：

1)金属钌以及稳定的钌氧化物的氧化电位随着pH增加而降低。

2)在碱性环境中，$OH^\bullet$自由基具有更小的氧化能力以及更大的还原能力；在碱性pH下，$OH^\bullet$自由基转变成O^-；O^-能够给出与烃类似的反应，但是相比$OH^\bullet$具有更小的氧化强度。

3)在碱性介质中，RuO_4容易被还原成RuO_4^-和RuO_4^{2-}

4)在碱性pH下，O_3被转变成OH自由基；因此，在该pH范围处进一步最小化出现不分解的臭氧(据报道其使金属表面降解)的风险。

[0071] 此外，诸如四甲基氢氧化铵(TMAH)的有机强碱(与Si-O-Si尺寸相比较，其分子尺寸大得多)的使用可导致通过表面材料层的更少的内部扩散。

[0072] 在图7中，示出在常规使用的介质(诸如DI-CO_2)中获得的典型损坏结果。图7示出在诸如CO_2水溶液(测量的pH=5.5)的微酸介质中清洁100X次之后，EUV掩模的钌层的AFM图

像。在DI-水(pH=6.0)中完成的实验给出类似的结果。

[0073] 在TMAH碱的稀释溶液中进行该相同实验;稀释使得溶液的最终电导率是大约50 μS,且所得到的测量的pH是10,2。如在图8中所示的类似的AFM图像示出在100X次清洁之后没有损坏。

[0074] 因此,其能够表明在原位UV去除或最终清洁期间,pH改变至碱性值如何积极地影响EUV光掩模的表面完整性。

[0075] 上述示例示出,吸收介质在非-吸收介质中的使用和在含水液体介质中至碱性值的改变可以如何影响衬底的原位UV湿法处理的结果。尤其,对于衬底的原位湿法处理,从由发明人进行的实验结果推断如下一般参数设置。

	参数	参数范围	优选的参数范围
1	吸收介质浓度	5-100 ppm	20-60 ppm
2	介质的电导率	20-500 μS	70-150 μS
3	介质pH	8-11	9.5-10.5
4	介质温度	20-70℃	20-40℃
5	发射波长	185-600 nm	185-300 nm或者200-300 nm
6	UV源强度	25-340 mW/cm^2	35-310 mW/cm^2,取决于应用
7	光源与衬底之间的距离	1-5 mm	1-2 mm

[0076] 对于诸如表面准备、去除和最终清洁的不同处理,并非所有的参数都必须满足。而是,在不同的过程中,特定参数将比其他参数更相关。在每个过程中,液体介质的电导率的增加是有益的,因为其允许调整所生成的反应物质的平衡。此外,在表面整修中,在非-吸收介质浓度中的吸收介质浓度是重要的。尤其应当使用不多于20 ppm,优选地不多于5 ppm的低浓度。在抗蚀剂去除中,吸收介质浓度再次是重要参数。此处,发射波长同样显示出对过程的结果有显著的影响。在最终清洁中,pH-值结合电导率是重要的。

[0077] 尽管关于清洁EUV光掩模的特定应用描述了本发明,但是上述原理以及上文中给出的范围中的许多也将适用于其他衬底,其中,要求基片表面的高度清洁。

[0078] 本发明的重要方面在于,在马上将含水液体介质施加到衬底的表面之前,利用UV-辐射照射含水液体介质。在这种情况下,在施加液体至衬底之前,介质将已经被分解/将生成自由基物质。取决于介质的组成,在衬底上施加介质的时刻或者换言之,当介质通过上文中讨论的出口狭缝离开时,在介质中可以存在反应物质的特定平衡。其他因素可以影响该平衡,诸如暴露于UV-辐射的持续时间(时间)和辐射的强度。

[0079] 然而,本发明人是第一个发现,通过调整电导率,其中在将介质施加到待处理的衬底之前介质被暴露于UV-辐射,反应物质的平衡可以移动,且可以调整期望的平衡。所给出的电导率范围指示低浓度的相应添加剂,其朝着试剂或产品推动活性物质的平衡。取决于电荷的量,额外效果可以是特定自由基的稳定。平衡的这种移动也随着pH的增加(至碱性条件)以及pH的降低(至酸性条件)发生。两个条件都可以具有特定其他有益的效果。例如,如上文所述,在去除或最终清洁过程期间,碱性介质可以保护在光掩模上的金属层的完整性。

[0080] 对于其他应用,pH至酸性条件的改变可以是优选的。例如,CO_2-水清洁(其是略微酸性的)结合UV-辐射已经展示出是用于光学光掩模的高效清洁介质。而且,对于现场含水介质中的特定应用,可以执行介质的酸化,以例如保护稳定的钝化氧化物,诸如氧化锗,其

将在碱性介质中被损坏，而同时提供反应物质例如用于清洁目的。在此类情形中，低吸收酸的使用将是优选的。锗化学物质在IC的制造中广泛使用，且如上面所描述的原位UV过程的使用也能够被成功地应用到晶片清洁。金属锗经历自发氧化成GeO_2，其充当保护性钝化层。

[0081] 利用碱性介质，其将被溶解成$HGeO_3^-$。

[0082] $GeO_2(s)+OH^-\rightarrow HGeO_3^-$。

[0083] 此处，至酸性介质的改变将避免该溶解过程，因此积极地影响表面完整性。

[0084] 本发明因此不仅考虑将电导率调整至20至2000 μS的范围，而且也考虑将pH调整至8至11的范围，而且也考虑将pH调整至3至6的范围，其中，从中性的显著改变被认为是必需的，以在介质被施加到衬底时(例如当其通过上文中讨论的设备的出口狭缝离开时)，实现物质的平衡的期望移动。这种移动也将加速/阻止由UV-辐射引起的某些反应。可以影响平衡的其他因素是UV-辐射的强度和介质暴露于UV-辐射的持续时间。这两者还可以根据介质的pH被调整，或者反之亦然。尤其，可以经由介质的流动速率来调整暴露的持续时间，虽然该过程可以要求特定的最小和最大流动。另一选项是改变在流动通道内暴露于UV-辐射的长度(距离)，例如通过遮蔽盖，诸如上文中描述的挡板。

[0085] 在不受限于特定实施例的情况下，此处在上文中关于若干实施例描述了本发明。尤其，上文中讨论的原位UV-湿法处理还可结合其他衬底，尤其是半导体晶片使用。而且，如所描述的和如下面在本文中要求保护的不同特征可以以任何适当方式组合。因此，预期本发明不受限于所公开的特定实施例，而是本发明将包括落入所附权利要求的范围和精神内的全部实施例。

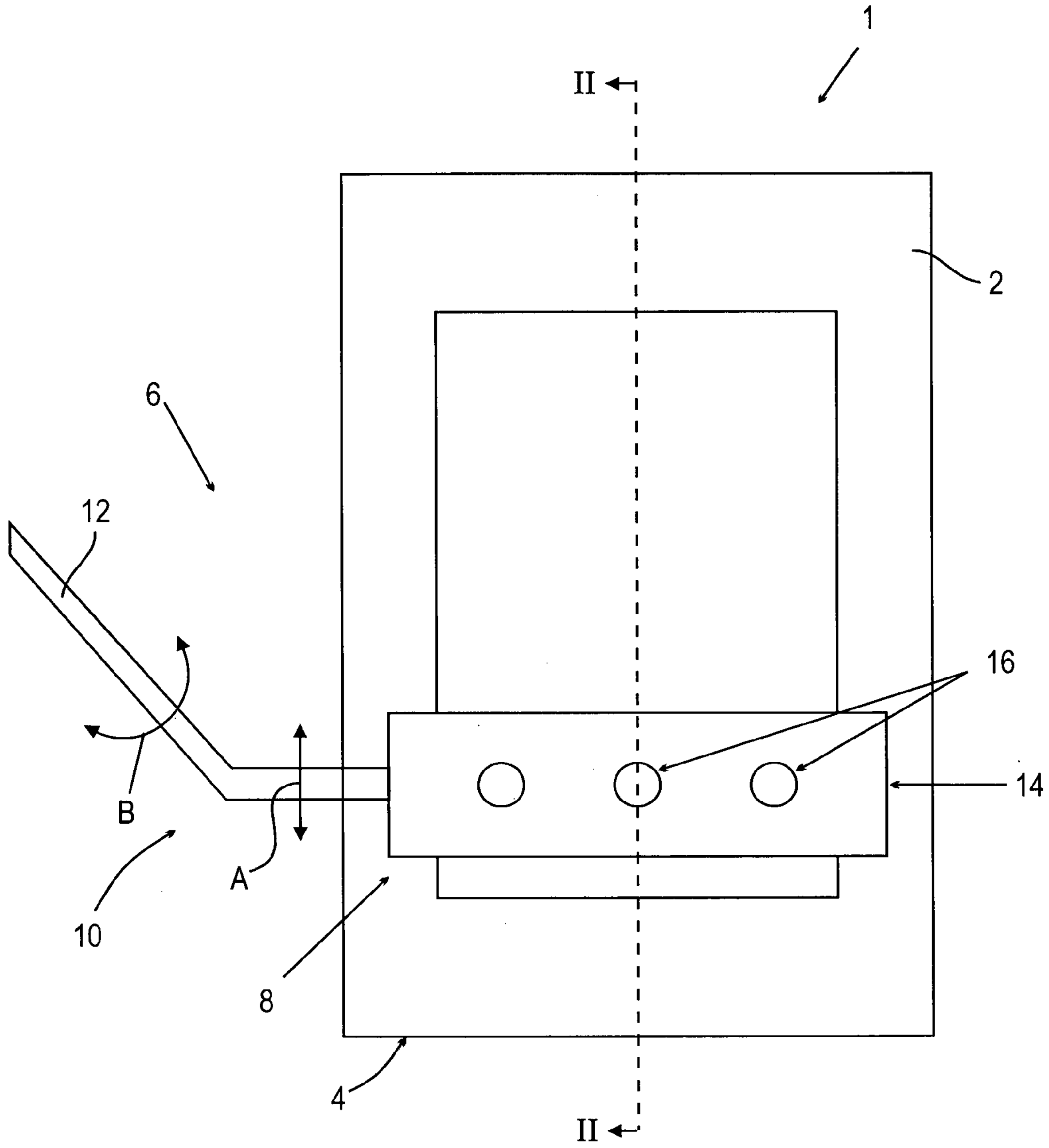


图 1

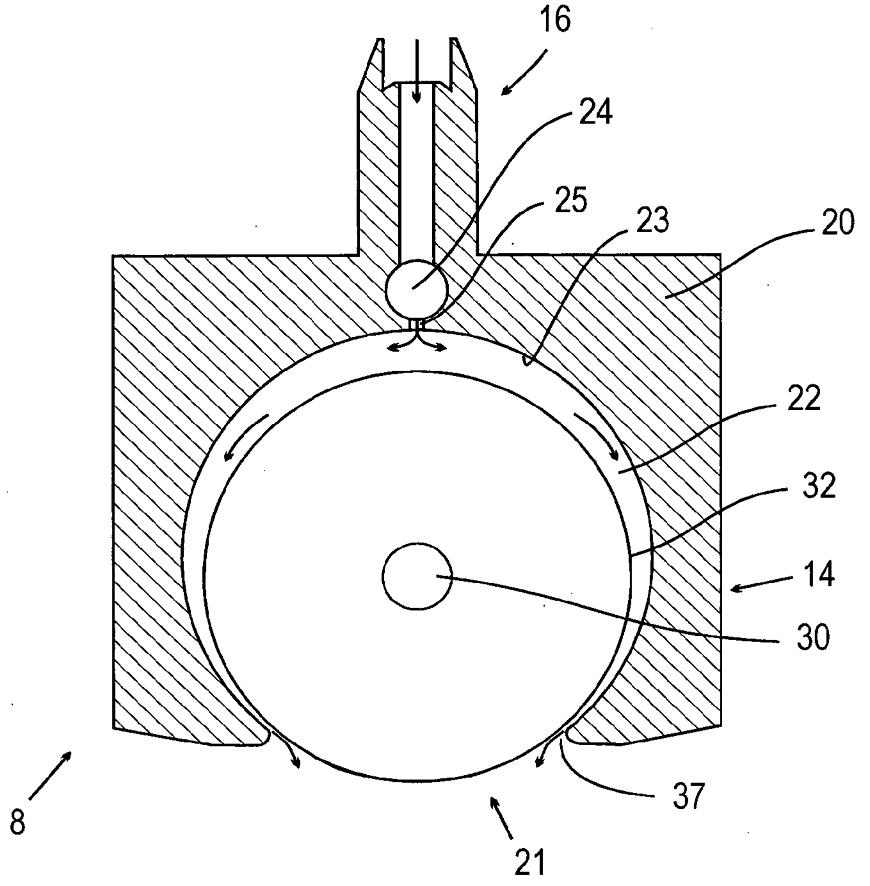


图 2

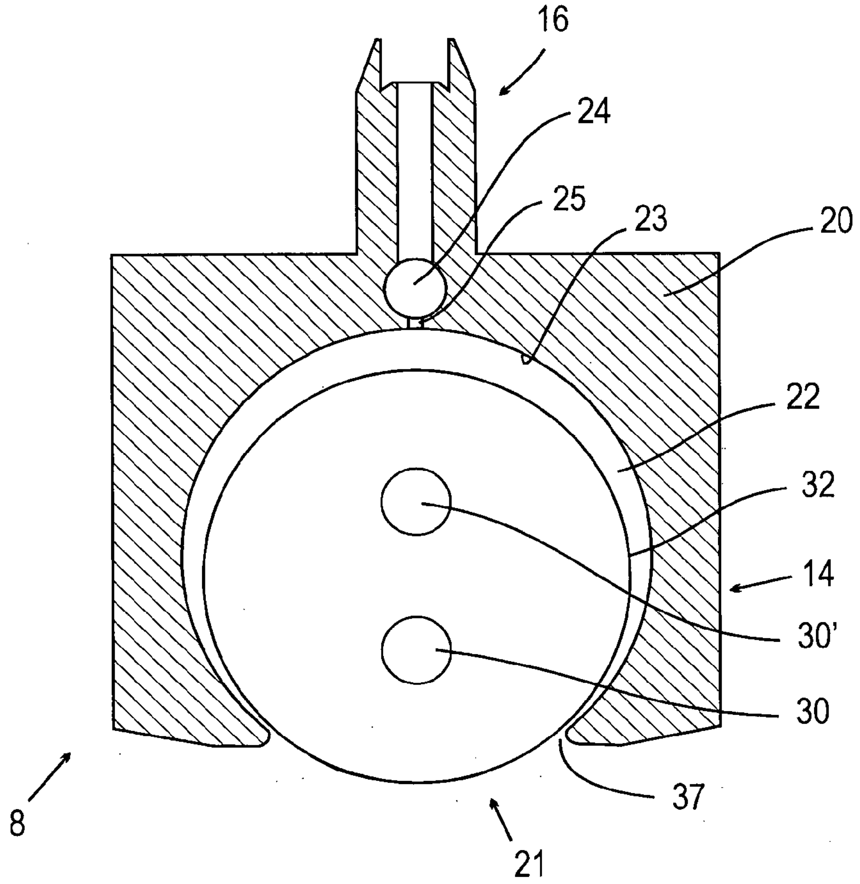


图 3

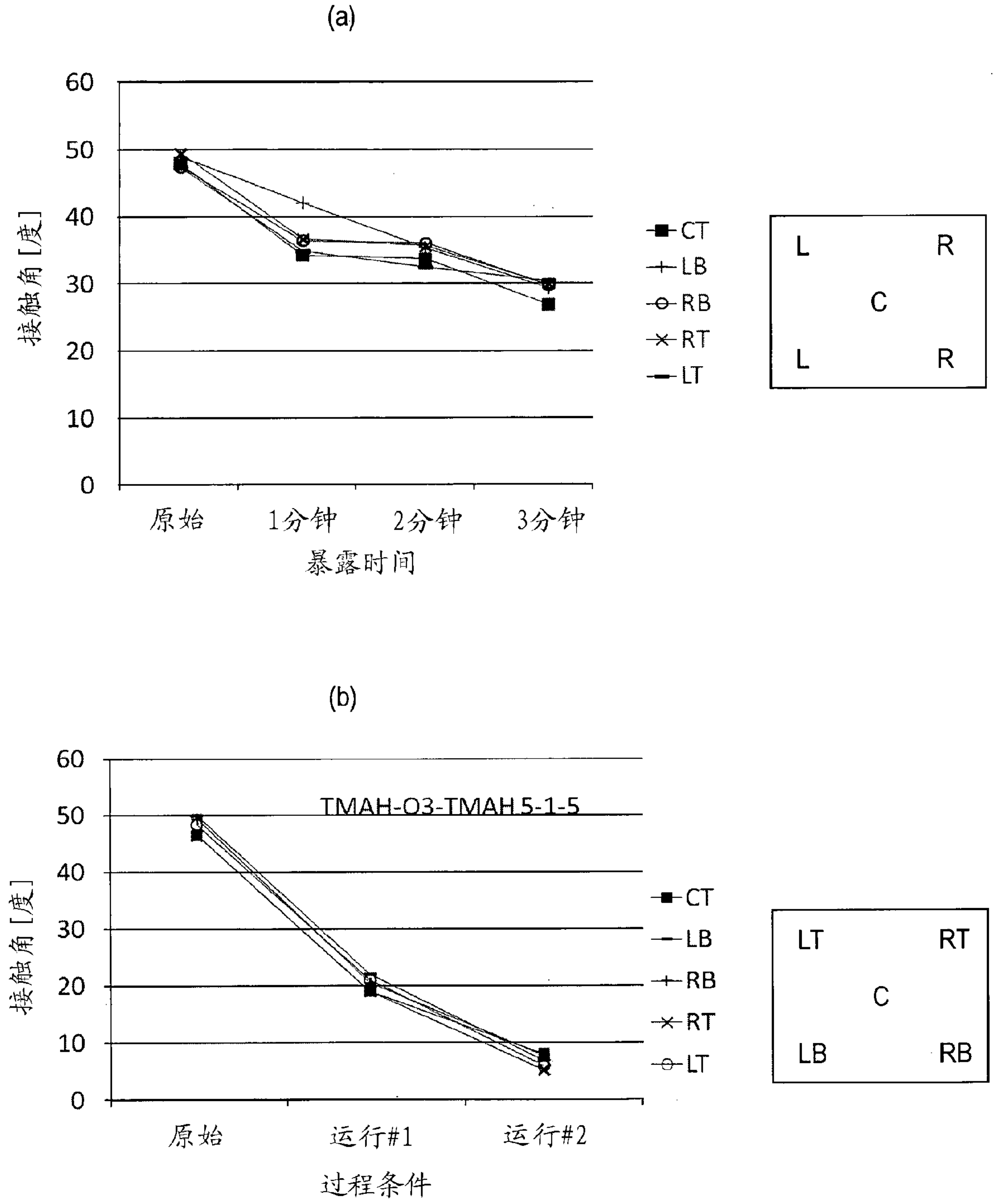

(a)
60
50
40
30
20
10
0
接触角[度]
原始
1分钟
2分钟
3分钟
暴露时间
CT
LB
RB
RT
LT
L
R
C
L
R
(b)
60
50
40
30
20
10
0
TMAH-O3-TMAH 5-1-5
接触角[度]
原始
运行#1
运行#2
过程条件
CT
LB
RB
RT
LT
LT
RT
C
LB
RB

图 4

	条件#	1	2	3	4	5	6	7	8	9	10	11	12
条件	H2O-O3, ppm	低	低	低	低	中	中	中	中	中	中	高	高
	H2O-CO2,被加热	否	是	是	否	否	是	否	是	否	否	否	否
	UV功率, %	60%	60%	60%	60%	60%	60%	60%	60%	60%	60%	60%	60%
	灯距离	中	中	中	小	大	中	中	中	中	中	中	小
	扫描速度, mm/s	50	50	50	50	50	50	50	50	50	50	50	50
	过程时间, s	360	360	360	360	360	360	360	360	360	360	360	360

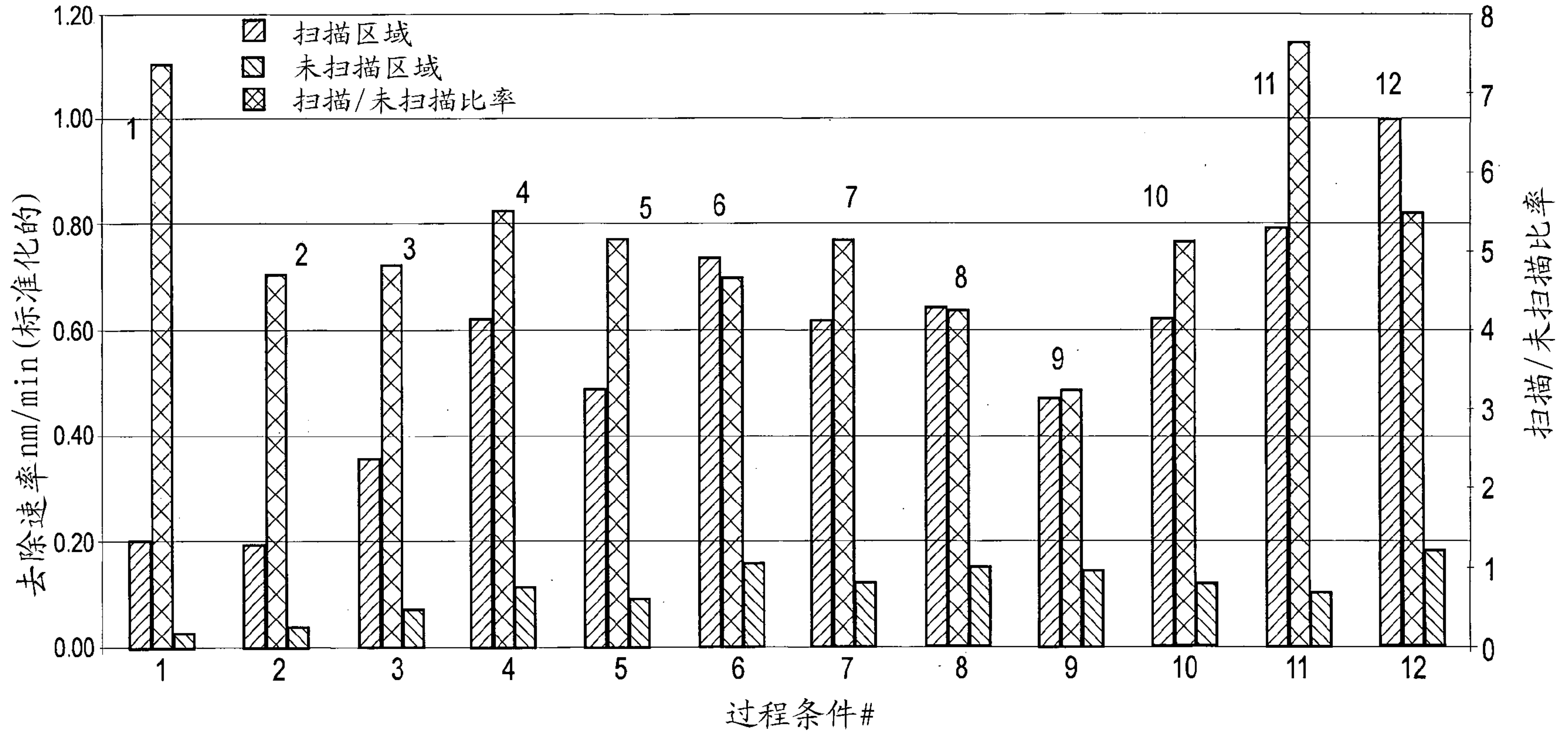


图 5

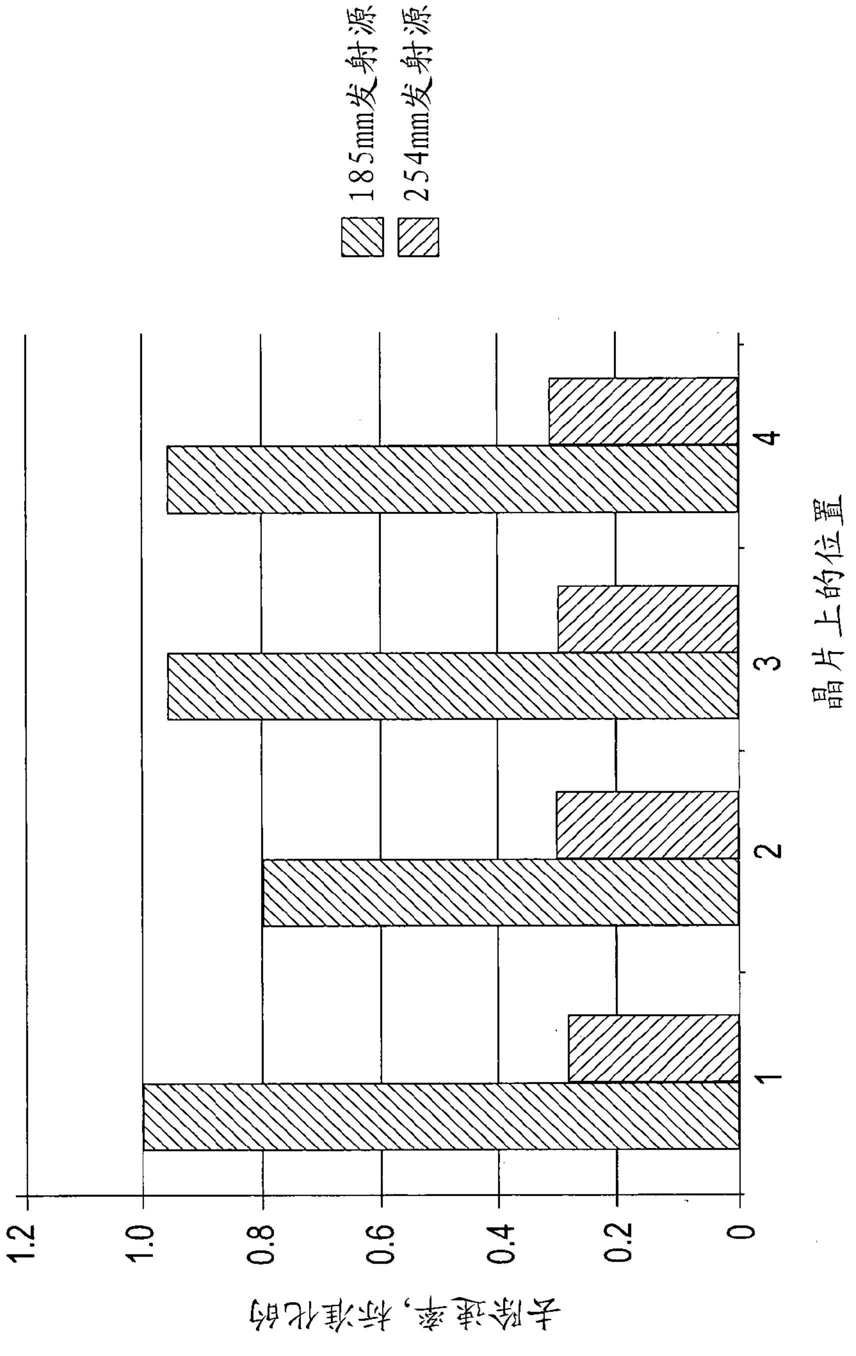


图 6

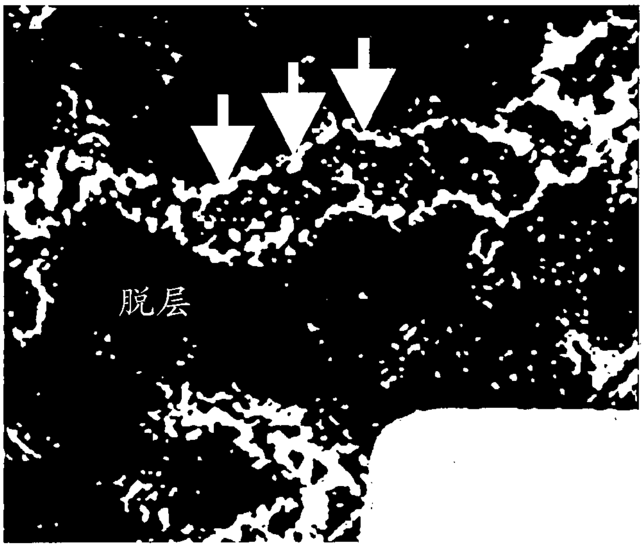
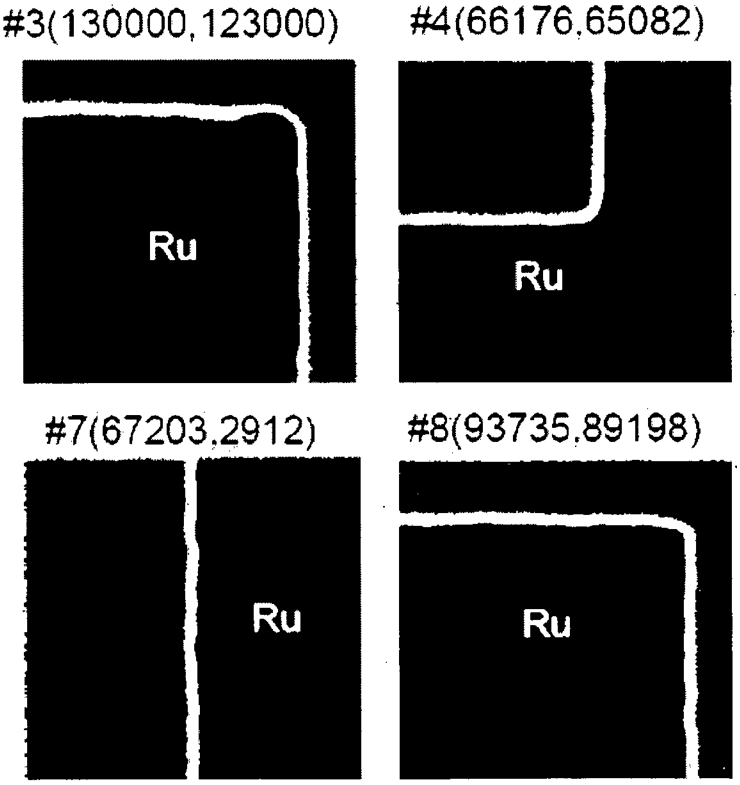

脱层

图 7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Ru
#7(67203,2912)
Ru
#8(93735,89198)
Ru

图 8