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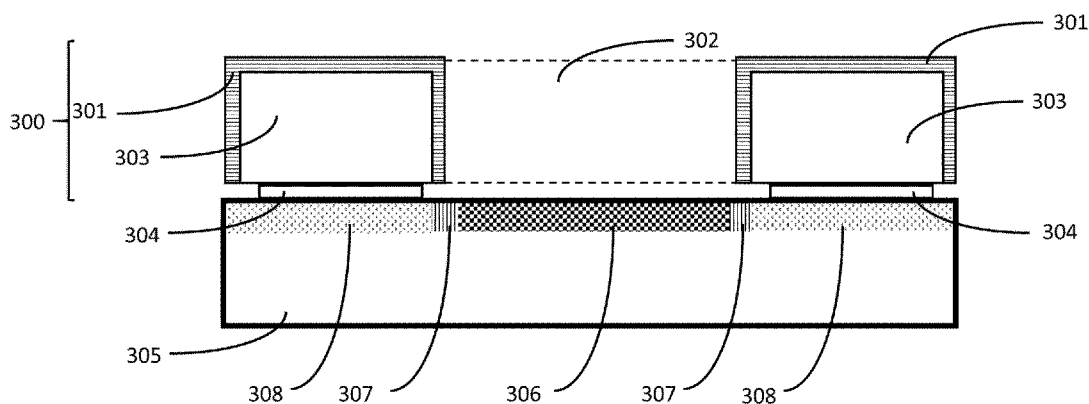
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(54) Title: REUSABLE ION IMPLANTATION MASK

FIG. 3



(57) Abstract: The present invention relates generally to a reusable ion implantation mask useful for repeatedly implanting selected areas of substrates with ions on a large scale. The present invention further relates to a method for partial ion implantation by means of a reusable ion implantation mask.

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DESCRIPTION

REUSABLE ION IMPLANTATION MASK

Technical Field

[0001] The present invention relates generally to a reusable ion implantation mask useful for repeatedly implanting selected areas of substrates with ions on a large scale, meaning implanting ions in substrates or areas of substrates larger than 5 cm² and up to several square meters. The ion implantation mask is being used for partial implantation of ions, that is for implanting ions in selected areas of a substrate and/or for protecting other selected areas of a substrate from the implantation of ions.

Background Art

[0002] The implantation of ions is known in the area of semi-conductors for manufacturing implanted materials with a very high precision. These methods generally are not useful for implanting ions on a larger scale, meaning implanting ions in substrates or areas of substrates larger than 1, 2 or 5 cm² and up to several square meters, because they are too slow for being economically feasible. Also the masking techniques known from the area of semi-conductors generally involve the deposition and patterning of a coating, which may then be etched after the implantation step, thereby involving numerous, costly steps. Furthermore these masks are inherently not reusable.

[0003] Electron cyclotron resonance (ECR) ion implantation sources are known that produce a large beam of several centimeters in diameter containing a single charge and multicharge ions of the gas being ionized. For the purposes of the present invention, these ion sources may be used to produce ions from gases such as for example O₂, N₂, Ar, Kr, He, Ne for example and are particular useful for large-scale use as the ion beam they form may have a diameter of at least 5 cm. The ions may be extracted from the ion source with an acceleration

voltage comprised in the range from 5 kV to 1000 kV, alternatively in the range from 10 kV to 100 kV. The ion dosage is typically comprised in the range from 10^{12} ions/cm² to 10^{18} ions/cm². For the efficient ion implantation in large areas it is necessary to use beams with ion currents of up to 2 mA, 4 mA, 6 mA, even up to 20 mA. The high currents and high dosages put a heavy strain on any masking material, in particular when a reusable masking material is sought. Such an ECR ion source is for example the Hardion+ ECR ion source from Ionics S.A. Under these implantation conditions there may also occur a significant amount of sputtering of the mask material when the ions hit the mask.

[0004] It is generally desirable to have a sharp distinction between implanted areas and non-implanted areas. For a reusable ion implantation mask that is used for covering selected areas of a substrate during ion implantation, it is desirable that the width of the transition zone, that separates the implanted area from the non-implanted area, i.e. masked, area, is as small as possible. For a sharp distinction the maximum width of the transition zone should be less than 300 μm , preferably less than 200 μm , more preferably less than 100 μm . Generally the maximum width of the transition zone is at least 1 μm . For a reusable ion implantation mask the maximum width of the transition zone should be obtained after using the implantation mask in an ion implantation process at least 4 times, at least 10 times, even at least 100 times.

[0005] Masks that are compatible with other high vacuum surface treatment techniques, such as magnetron sputtering or plasma enhanced chemical vapor deposition or semi-conductor ion implantation for example were found to be incompatible with large scale ion implantation. Masks of aluminum foil for instance are very heavily degraded and deformed by the (ECR) ion implantation sources described above. Polymers, such as for example poly(methyl methacrylate), polyurethane, or polypropylene undergo a chemical transformation under the ion beam that results in production of gases that pollute the process atmosphere and disturb the vacuum. This may also lead to the co-implantation of the pollutants in the substrate. Kapton, a polyimide film developed by DuPont, performs better than most other

polymers, but is deformed under the ECR ion beam and does not remain flat. Any degradation or deformation of the mask may also lead to a widening of the transition zone.

[0006] Thus, there remains a need in the art for an improved ion implantation mask, that can be used economically on a large scale with ion implantation sources, such as for example ECR ion sources, where for example the ions are extracted from the ion source with an acceleration voltage comprised in the range from 5 kV to 1000 kV, alternately in the range from 10 kV to 100 kV, where the ion dosage is typically comprised in the range from 10^{12} ions/cm² to 10^{18} ions/cm² and where the ion currents are higher than 0.1 mA, or higher than 0.5 mA, or higher than 1 mA and up to 2 mA, up to 4 mA, up to 6 mA, or even up to 20 mA.

Summary of invention

[0007] In one or more aspects of the invention, there is provided an ion implantation mask that, when exposed to the ion beam of an ion implantation source, is able to achieve a narrow transition zone between non-implanted areas and implanted areas. A narrow transition zone is achieved in particular when the an ion implantation source is a source where the ions are extracted from the ion source with an acceleration voltage comprised in the range from 5 kV to 1000 kV, where the ion dosage is typically comprised in the range from 10^{12} ions/cm² to 10^{18} ions/cm² and where the ion currents are higher than 0.1 mA and up to 2 mA, up to 4 mA, up to 6 mA, or even up to 20 mA. A narrow transition zone is achieved in particular when this ion implantation source is an electron cyclotron resonance (ECR) ion implantation source. A reduced transition zone is achieved in particular when this ion implantation source simultaneously provides a species' single charge ions and multicharge ions for implantation, such as for example N⁺, N²⁺, and N³⁺, or He⁺, and He²⁺. Single charge ions are ions carrying a single positive charge. Multicharge ions are ions carrying two or more positive charges.

[0008] In one or more other aspects of the invention, there is provided an ion

implantation mask, that is able to achieve low levels of pollution of the process atmosphere during ion implantation.

[0009] In one or more aspects of the invention, there is provided an ion implantation mask, that can be removed after implantation.

[0010] In one or more aspects of the invention, there is provided an ion implantation mask, that is reusable and that can thus be used multiple times in the ion implantation process.

[0011] In one or more other aspects of the invention, there is provided a mask comprising a mask bulk material and a sputtering reduction coating for reducing the amount of mask material that is sputtered by the impact of the ion beam and thus pollutes the process atmosphere. The sputtering reduction coating is provided at least on the mask bulk material's surface areas that will be or are exposed to the ion beam. The sputtering reduction coating may be provided on the entire surface of the mask bulk material.

[0012] In one or more aspects of the invention the implantation mask comprises a scratch avoidance film. The scratch avoidance film may be provided at least on parts of the mask bulk material's surface. In some embodiments the scratch avoidance film is applied on the bulk material's surface in areas that are in contact with the substrate.

[0013] In one or more other aspects of the invention, there is provided a method for implanting ions in selected areas of a substrate comprising covering selected areas of the substrate with an implantation mask and introducing the covered substrate in an ion beam. In certain aspects of the present invention the method for implanting ions into a substrate further comprises separating the implantation mask from the substrate.

[0014] In one or more other aspects of the invention, there is provided a method for implanting ions in selected areas of substrates comprising covering in sequence the following steps: covering selected areas of a first substrate with an implantation mask and introducing the covered first substrate in an ion beam, implanting ions in the substrates areas that are not covered by the implantation mask and that are exposed to the ion beam, separating the

implantation mask from the first substrate after the ion implantation, covering selected areas of a second substrate with the implantation mask and introducing the covered second substrate in an ion beam, implanting ions in the second substrate's areas that are not covered by the implantation mask and that are exposed to the ion beam, separating the implantation mask from the second substrate after the ion implantation. In certain aspects of the present invention the method for implanting ions into a substrate further comprises separating the implantation mask from the substrate.

[0015] In one or more aspects of the present of using a ion implantation mask utilizing a sputtering reduction coating for partial implantation of ions.

Brief description of drawings

[0016] **FIG. 1A** is a plan view of an implantation mask according to the present invention wherein the implantation mask is provided with an sputtering reduction coating. **FIG. 1B** is a cross-sectional view taken along line B-B in FIG. 1A

[0017] **FIG. 2A** is a plan view of an implantation mask according to the present invention wherein the implantation mask is provided with an scratch avoidance film. **FIG. 2B** is a cross-sectional view taken along line B-B in FIG. 2A.

[0018] **FIG. 3** shows a cross sectional view of a partially implanted substrate covered with an implantation mask according to the present invention.

[0019] **FIG. 4** shows a top surface view of a partially implanted substrate.

Description of embodiments

- [0020]** While the present invention may be embodied in many different forms, a number of illustrative embodiments are described herein with the understanding that the present disclosure is to be considered as providing examples of the principles of the invention and such examples are not intended to limit the invention to preferred embodiments described and/or illustrated herein. The various embodiments are disclosed with sufficient detail to enable those skilled in the art to practice the invention. It is to be understood that other embodiments may be employed, and that structural and logical changes may be made without departing from the spirit or scope of the present invention.
- [0021]** The sputtering reduction coatings of the instant invention are designed to have numerous advantageous properties that lead to a sharp distinction between non-implanted areas and fully implanted areas, reducing the width of the transition zone between these areas.
- [0022]** In an embodiment of the present invention the bulk material of the implantation mask is based on a metal or a metal alloy. In particular the bulk material of the implantation mask comprises at least 50 %, 60 %, 70 %, 80 %, or 90 % by weight of a metal or metal alloy. The bulk material of the implantation mask may be selected from the group consisting of the following metals Al, Cu, Zn, Mn, Ti, Ni, Fe, Mo, or of the alloys of one or more of the metals Al, Cu, Zn, Mn, Ti, Ni, Fe, Mo. The bulk material may also be based on highly oriented pyrolytic graphite (HOPG).or stainless steel, in particular the bulk material may comprise at least 50 %, 60 %, 70 %, 80 %, or 90 % by weight of at least 90 % by weight of graphite or stainless steel
- [0023]** In an embodiment of the present invention the thickness of the implantation mask of the present invention is at least 1.0 mm, at least 2.0 mm or at least 3.0 mm. With these minimum thicknesses particular small transition zones were observed. In particular when the an ion implantation source is a source where the ions are extracted from the ion source with an acceleration voltage comprised in the range from 5 kV to 1000 kV, where the ion dosage is typically

comprised in the range from 10^{12} ions/cm² to 10^{18} ions/cm² and where the ion currents are higher than 0.1 mA and up to 2 mA, 4 mA or even 6 mA, metal or metal-based foils, that is sheets of metal having a thickness of not more than 0.5mm have been found to be sometimes distorted by the thermal stress undergone in the ion implantation process. In particular thin metal foils, of less than 0.1mm thickness are strongly deformed and visibly degraded under these conditions. It is thought that when the thickness of the implantation mask according to the present invention was at least 1.0 mm, at least 2.0 mm or at least 3.0 mm, its ability to resist to the thermal stress without detrimental deformation was improved for these implantation conditions, where top surface temperatures of up to 200°C, up to 300°C or even 400°C can be reached.

[0024] In an embodiment of the present invention the implantation mask comprises a sputtering reduction coating. Such a sputtering reduction coating, when exposed to an ion beam, in particular in the implantation conditions mentioned hereinabove, is not easily sputtered by the impact of the implantation ions. Therefore the atmosphere is less polluted by the implantation mask and less material of the implantation mask is co-implanted in the substrate, in particular at the edge between the non-implanted area and the fully implanted area. In exemplary embodiments of the present invention, the sputtering reduction coatings have a low sputtering yield. Specifically, the sputter yield of the coatings is significantly below that of uncoated stainless steel. As a reference, the sputtering reduction coating is such that when exposed an inert Ar gas plasma, the sputter yield is preferably below 0.5 atoms per ion at 100 eV ion energies, and even more preferably below 0.2 atoms per ion at 100 eV ion energies.

[0025] Additionally, in exemplary embodiments of the present invention, the sputtering reduction coatings have a low chemical reaction rate with implantation ions. When ions of for example oxygen or nitrogen, contact the surface of uncoated ion implantation masks, the ions may chemically react with these surfaces to produce reaction products. The formation of such reaction products may interfere with mask durability and reusability. For

example, when stainless steel masks are exposed to oxygen ions, the oxygen reacts with the surface of the stainless steel, causing the formation of a thin, at least partly oxidized layer on the surface of the mask that reduces its surface conductivity and may lead to the build-up of surface charges that perturb the ion implantation process.

- [0026]** In exemplary embodiments of the present invention, the sputtering reduction coatings are conductive. In particular, the sputtering reduction coatings may have a low resistivity, in particular less than 5×10^7 ohm cm.
- [0027]** The inventors have found that selected materials used alone and/or in various combinations are capable of producing a sputtering reduction coating having one or more of the advantageous properties listed above, and may thus be used as sputtering reduction coatings on ion implantation masks.
- [0028]** In some embodiments, the sputtering reduction coatings may comprise a first material selected from the group consisting of boron, carbon, silicon, aluminum, or combinations thereof. For example, the coatings may comprise boron carbide, silicon carbide, or aluminum carbide. The coatings may further comprise a metallic second material, including tungsten, chromium, titanium, molybdenum, or zirconium. For example, the coatings may comprise tungsten carbide (WC) or chromium carbide (Cr_3C_2).
- [0029]** Additionally, in other embodiments, the sputtering reduction coatings may comprise selected metals or metal alloys. The coatings according to this embodiment may be selected from the group consisting of the metals cobalt, iron, nickel, chromium, or their alloys, or nickel-chromium alloys.
- [0030]** In further embodiments, the sputtering reduction coatings may comprise selected conductive ceramics. According to these embodiments, the coatings may comprise Ti, or Zr, or oxides or nitrides thereof.
- [0031]** In certain alternative embodiments, one or more of the materials listed above may be combined to form a sputtering reduction coating.
- [0032]** The sputtering reduction coatings of the instant invention may be deposited on ion implantation masks' bulk material using methods which are well-known

in the art, including spray coating, electroplating, chemical vapor deposition (CVD), and physical vapor deposition (PVD). Whether a particular coating technique is appropriate for coating an ion implantation mask for use in a particular application requires several considerations. First, the technique must be able to produce a coating with a desirable density and porosity for the particular application, but with minimal impurities, such as oxide or nitride impurities. The technique should also be able to produce a coating of an appropriate thickness that resists substantial peeling or cracking.

- [0033]** The sputtering reduction coatings of the instant invention may be deposited on ion implantation masks by thermal spray coating according to standard methods known to those of skill in the art. Thermal spray coating can be used to produce coatings with the desired composition, structure, morphology, and thickness. Several different thermal spray coating techniques exist, including plasma spraying, detonation spraying, wire arc spraying, flame spraying, high velocity oxygen-fuel spraying, warm spraying, and cold spraying. The coatings of the present invention are preferably deposited by plasma thermal spray coating. However, choice of a particular process will depend on the exact material to be deposited, the preferred equipment, and budget concerns.
- [0034]** In some embodiments of the instant invention, a binder is added to the sputtering reduction coating composition before deposition in order to increase adhesion and durability of the coating on the mask surface. The binder may comprise a single material, such as cobalt, nickel, or chromium. Alternatively, the binder may comprise a mixture of materials, such as a mixture of nickel and chromium or a mixture of nickel and cobalt. In some embodiments, the binder comprises about 5 to 30 weight percent of the final coating. More preferably, the binder comprises 10 to 15 weight percent of the final coating.
- [0035]** The sputtering reduction coatings of the instant invention are thick enough to protect the ion implantation mask's surfaces, but not too thick to peel or crack from thermal stress. However, the sputtering reduction coatings may have a wide range of thicknesses and still achieve the beneficial effects described herein. Preferably, the coatings have a thickness in the range of 100 μm to 500 μm . However, the coatings may have a thickness that is in the range of 1

µm to 100 µm.

[0036] The sputtering reduction coatings of the instant invention may be applied to a portion of an ion implantation mask, *i.e.* the portion or surface areas of the ion implantation mask that is exposed to an ion beam during the implantation process, such that the implantation mask is at least partially coated with the sputtering reduction coating. The sputtering reduction coatings of the instant invention may alternatively be applied to the entire implantation mask, such that the implantation mask is completely coated with the sputtering reduction coating.

[0037] **FIGS. 1A and 1B** show an ion implantation mask **100** with a sputtering reduction coating **101** in accordance with various embodiments of the invention. An aperture **102** is provided in the implantation mask through which a substrate may be exposed to an ion beam. As shown in **FIG. 1B**, the implantation mask's bulk material **103** is partially coated with the sputtering reduction coating **101**. In this exemplary embodiment, the top surface and the sides of the implantation mask are covered with the sputtering reduction coating, whereas the bottom side which will be oriented towards the substrate surface and thus not exposed to the ion beam is not coated with the sputtering reduction coating. In an alternative embodiment the implantation mask's complete surface may be coated with the sputtering reduction coating.

[0038] **FIGS. 2A and 2B** show an ion implantation mask **200** with an scratch avoidance film **204** in accordance with various embodiments of the invention. An aperture **202** is provided in the implantation mask through which a substrate may be exposed to an ion beam. As shown in **FIG. 3B**, the implantation mask's bulk material **203** is partially covered with an scratch avoidance film **204**. In this exemplary embodiment, the bottom side of the ion implantation mask, which is oriented towards the substrate, is covered with an scratch avoidance film. In this exemplary embodiment, the anti-scratch film covers the bottom side of the ion implantation mask up to a certain distance from the edge, so as to avoid the scratch avoidance film being exposed to the ion beam at the edges of the periphery or of the one or more apertures of the ion implantation mask. This distance may be at least 1 mm, at least 2 mm or

at least 3 mm. The scratch avoidance film may be continuous, or may be discontinuous and for instance cover the bottom side of the ion implantation mask in two or more distinct, non-contacting areas. In certain embodiments the scratch avoidance film may cover selected areas of the bottom side so as to avoid direct contact between the bulk implantation mask and the substrate. In certain embodiments of this invention the scratch avoidance film's material has a hardness that is lower than the hardness of the bulk material of the implantation mask, lower than the hardness of sputtering reduction coating's material (if present), and/or lower than the hardness of the substrate material. The hardness of these different materials can be evaluated by different tests, for instance by Vickers hardness tests. In certain exemplary embodiments the Vickers hardness of the scratch avoidance film is less than 1 GPa, in particular in the range from 0.01 to 0.5 GPa, in the range from 2.0×10^8 to 3×10^8 Pa, in particular in the range from 2.5×10^8 to 2.7×10^8 Pa. Vickers hardness of different materials may be measured according to standard ISO 6507-1:2005. For the present comparative purposes this standard method developed for metals may be applied in the same way to a non-metallic material of the scratch avoidance film or the substrate. The scratch avoidance film is in certain instances made of a polymer that is adapted for vacuum processes, for a pressure range of about 10^{-3} mbar to about 10^{-7} mbar. The scratch avoidance film is in certain instances made of a polymer that is adapted for continuous operating temperatures of at least 100°C, of at least 150°C, or even of at least 200°C, that it shows no visible degradation after at least 1000 hours at these temperatures. The scratch avoidance film may be directly coated on the implantation mask, glued by appropriate vacuum compatible glues onto the implantation mask. The material of the scratch avoidance film may be a thermoplastic and may comprise polymers selected from the group consisting of fluoropolymers, such as for example polytetrafluoroethylene, and polyimides. One exemplary scratch avoidance film material is Polyimide, for instance sold under the registered trademark Kapton. The scratch avoidance film may have a thickness of less than 500 μm , less than 250 μm or less than 100 μm . With lower film thickness the transition zone is decreased. In certain

embodiments the film thickness may be at least, 10 μm , at least 20 μm or at least 50 μm . It was found that for sensitive substrates and difficult handling conditions too low film thicknesses did not provide a sufficient anti-scratch effect or were difficult to handle and apply. The film thickness may be in the range from 10 μm to 500 μm , from 20 μm to 250 μm or from 50 to 100 μm .

[0039] **FIG. 3** shows the cross section of a substrate **305** that is covered by an implantation mask **300**. In this exemplary embodiment the implantation mask's bulk material **303** is provided with a sputter reduction coating **301** as well as an scratch avoidance film **304**. The substrate's **305** surface has been exposed to an ion beam (not shown) through the aperture **302** and shows a fully implanted area **306** and a transition zone **307** between the fully implanted area and the non-implanted area **308**. The non-implanted area has the same properties and composition as before the ion implantation step and is only identified on **FIG. 3** for illustrative purposes.

[0040] **FIG. 4** shows a partially implanted substrate **400** showing an implanted area **406**, a transition zone **407** and a non-implanted area **408**. The width of the transition zone **409** may be different at different locations. The transition zone may has properties that are different from the properties of both the fully implanted area and the non-implanted area. The properties that differ can be for example compositional, optical, structural and adapted measurement methods are chosen to determine the width of the transition zone. It may in some cases even be visible to the naked eye. Its width can be determined with the appropriate optical magnifying means. The transition zone may have different surface roughness properties that may be determined by atomic force microscopy (AFM) measurements for example. For compositional changes, surface composition measurements can for example be made by X-ray fluorescence spectroscopy or Electron probe micro-analysis (EPMA). In some cases the transition zone may comprise different sub-zones that have differing properties or It may present a property gradient over its width. As the width of the transition zone may vary on an implanted substrate in was decided to determine the maximum width of the transition zone. For a sharp distinction between non-implanted areas and fully implanted areas it was found that the

maximum width of the transition zone should be less than 300 μm , preferably less than 200 μm , more preferably less than 100 μm . For a reusable ion implantation mask the maximum width of the transition zone should be obtained after using the implantation mask in an ion implantation process at least 4 times, at least 10 times, even at least 100 times.

- [0041]** The implantation mask of the present invention covers only a part of the substrate, so as to expose a chosen area of the substrate's surface to the ion beam and so as to protect another chosen area of the substrate's surface from the ion beam. It may have one single aperture or more than one aperture where the substrate is not covered. The implantation mask may have no aperture, but cover only part of the substrate. Different shapes and arrangements are possible for the implantation masks. In particular the implantation mask's bottom surface is shaped so as to closely follow the shape of the substrate's surface it covers. The substrates may not be flat. For flat substrates, the bottom surface is preferably also flat. In particular the implantation mask is flat and sheet-like.
- [0042]** A single implantation mask may be used to partly cover a single substrate, or more than one substrate. More than one implantation mask may be provided for to partly cover a single substrate.
- [0043]** In certain embodiments, the implantation mask may cover the substrate and be in direct contact with the substrate. The mask's bulk material may thus be in direct contact with the substrate, or the mask's sputter reduction coating may be in direct contact with the substrate, or the mask's scratch avoidance film may be in direct contact with the substrate.
- [0044]** In certain embodiments, the implantation mask may cover the substrate without being in direct contact with the substrate. In this case it is preferable to minimize the distance between the mask and the substrate so as to minimize the transition zone between non-implanted areas and fully implanted areas on the substrate. For instance this distance should be less than 1 mm, less than 0.5 mm, less than 0.2 mm or even less than 0.1 mm.
- [0045]** In certain exemplary embodiments the implantation mask is temporarily fixed

by appropriate means, such as clamps for example, directly to the substrate, held by gravity on the substrate, or temporarily fixed to a substrate holder. The substrate may be covered with the implantation mask before entering the implantation chamber in which the implantation process takes place. For instance the substrate may be covered with the implantation mask at atmospheric pressure before entering the implantation device, and before being put under vacuum. The substrate may also be covered with the implantation mask within the vacuum atmosphere of the implantation device and the implantation mask may be removed from the substrate to be reused within the same device, without leaving the vacuum atmosphere.

[0046] Any kind of substrate that is adapted for ion implantation may be covered by the implantation mask of the present invention. The substrate may for example be chosen among glass, quartz, sapphire, metal, metal alloy, polymer, silicon, ceramic, graphite. The substrate may comprise a bulk material of these materials and further comprise a coating of a different material in which and/or through which the ions are implanted. In an embodiment of the present invention the surface area of the substrate is larger than 5 cm² and up to 1 x 1 m², and even up to one square meter, even up to several square meters, for example up to about 3.21 x 6 m².

[0047] In an embodiment of the present invention there is provided a method for repeatedly partially ion implanting substrates. In particular there is provided a method for partially implanting a first and a second substrate comprising covering selected areas of a first substrate with a reusable ion implantation mask according to any embodiment of the present invention, exposing the covered first substrate to an ion beam, separating the ion implantation mask from the first substrate, covering selected areas of the second substrate, exposing the covered second substrate to an ion beam, separating the ion implantation mask from the second substrate. With the ion implantation mask of the present invention the ion implantation step may be repeated at least 4 times, at least 10 times, even at least 100 times.

[0048] The following embodiments of the present invention are not intended to be limiting in any way. Those of skill in the art will recognize and appreciate how

to adapt the devices and methods described herein without departing from the spirit or scope of the present invention.

Examples

- [0049]** All examples below were implanted with a ECR ion source. N₂ was ionized by this ion source so as to provide a beam comprising a mixture of N⁺, N²⁺ and N³⁺. The acceleration voltage was set at 20 kV and the ion dosage was set at 9×10^{16} ions/cm². The current of the ion beam was set at 1.5 mA. The implantation was performed in a vacuum chamber at a pressure of $\sim 2 \times 10^{-5}$ mbar to $\sim 2 \times 10^{-6}$ mbar.
- [0050]** Regular clear soda-lime float glass of about 4mm thickness and of 10 cm x10 cm size was used as model substrate. The implantation parameters above lead to a reduction of the reflectance in the implanted area that is visible to the naked eye, particularly under diffuse lighting. The width of the transition zone was determined optically using a Leica DM2700 M microscope. The different masks were positioned so as to cover half of the substrate.
- [0051]** Comparative example C1 used as implantation mask aluminum foil of 0.02mm thickness in direct contact with the substrate. Comparative example C2 used as implantation mask a polyimide film, thickness 0.125 mm, of grade Kapton HN, in direct contact with the substrate. Comparative example C3 used as implantation mask a polytetrafluoroethylene (PTFE) film of 0.125 mm thickness, in direct contact with the substrate. All three comparative examples C1, C2, and C3 film showed strong deformation after implantation and the transition zones on the implanted substrates had maximum width of more than 1 mm.
- [0052]** Example 1 used as implantation mask an aluminum sheet of 2 mm thickness, in direct contact with the substrate. The implantation mask was reused 5 times under the same conditions. After implantation, the maximum transition zone width was determined to be in the range from 66 μ m to 200 μ m.
- [0053]** Example 2 used as implantation mask a highly oriented pyrolytic graphite (HOPG). The HOPG used here is, as defined by IUPAC, a pyrolytic

graphite with an angular spread of the c-axes of the crystallites of less than 1 degree. sheet of 1 mm thickness, in direct contact with the substrate. The implantation mask was reused 5 times under the same conditions. After implantation, the maximum transition zone width was in a similar range as for Example 1.

- [0054]** Other types of graphite (non highly oriented pyrolytic graphite, randomly oriented polycrystalline graphite for instance) were tested but were found to start crumbling under the present implantation conditions and are therefore not reusable. Probably this is due to the high currents that are higher than 0.1 mA.
- [0055]** Example 3 used the same implantation mask as example 1 which was held at a distance of 0.2 mm. After implantation, the maximum transition zone width was determined to be in the range from 75 μm to 240 μm .
- [0056]** Example 4 used the same implantation mask as example 1 which was provided on the bottom side with an scratch avoidance film of Polyimide tape of 0.125 mm thickness. The tape was kept at a distance of 2 mm from the edges of the mask. After implantation, the maximum transition zone width was similar as for example 3. No deterioration of the mask or the scratch avoidance film was observed after implantation.
- [0057]** Stainless steel masks were found to result in transition zone widths in the same range as aluminum masks.
- [0058]** Example 5 used a stainless steel mask with a sputtering reduction coating comprising tungsten carbide (WC) and a 12 % cobalt binder that was spray-coated onto all mask surfaces exposed to the ion beam. The thickness of the coating was approximately 100 μm . The maximum width of the transition zone was determined to be in the range from 20 μm to 50 μm .
- [0059]** While the present invention has been described with respect to specific embodiments, it is not confined to the specific details set forth, but includes various changes and modifications that may suggest themselves to those skilled in the art, all falling within the scope of the invention as defined by the following claims.

Claims

Claim 1. Reusable ion implantation mask for covering a selected area of a substrate surface during ion implantation, comprising :

a bulk mask material selected from the group consisting of the metals Al, Cu, Zn, Mn, Ti, Ni, Fe, Mo, and of the alloys of one or more of the metals Al, Cu, Zn, Mn, Ti, Ni, Fe, and Mo, and of highly oriented pyrolytic graphite and stainless steel,

wherein the ion implantation mask has a thickness of at least 1mm,

characterized in that the .

Claim 2. Reusable ion implantation mask according to claim 1 further comprising a sputtering reduction coating wherein the sputtering reduction coating comprises a material having a rate of sputtering when exposed to an argon plasma that is less than the rate of sputtering of the bulk mask material.

Claim 3. Reusable ion implantation mask according to claim 1 or 2, wherein the ion implantation mask comprises a sputtering reduction coating and wherein the rate of sputtering of the sputtering reduction coating when exposed to an argon plasma is less than 0.5 atoms per argon ion at 100 eV ion energies, preferably less than 0.2 atoms per ion at 100 eV ion energies.

Claim 4. Reusable ion implantation mask according to claims 2 or 3, wherein the sputtering reduction coating comprises a first material selected from the group consisting of boron, carbon, or silicon.

Claim 5. Reusable ion implantation mask according to claims 2 or 3, wherein the sputtering reduction coating comprises a metal selected from the group consisting of tungsten, chromium, titanium, molybdenum, and zirconium.

Claim 6. Reusable ion implantation mask according to claims 2 or 3, wherein the sputtering reduction coating comprises a carbide selected from the group

consisting of tungsten carbide, chromium carbide, boron carbide, and silicon carbide.

Claim 7. Reusable ion implantation mask according to claims 2 or 3, wherein the sputtering reduction coating comprises a metal alloy.

Claim 8. Reusable ion implantation mask according to claim 7, wherein the metal alloy is selected from the group consisting of alloys of cobalt, nickel, chromium, nickel-chromium.

Claim 9. Reusable ion implantation mask according to claims 2 or 3, wherein the coating comprises a conductive ceramic material.

Claim 10. Reusable ion implantation mask according 9, wherein the conductive ceramic material comprises an element selected from the group consisting of Ti and Zr, and an oxide or nitride thereof.

Claim 11. Reusable ion implantation mask according to any preceding claim further comprising an scratch avoidance film of a polymer adapted for use in vacuum processes in a pressure range of about 10^{-3} mbar to about 10^{-7} mbar.

Claim 12. Reusable ion implantation mask according to claim 11, wherein the scratch avoidance film has a thickness in the range from 10 to 500 μm .

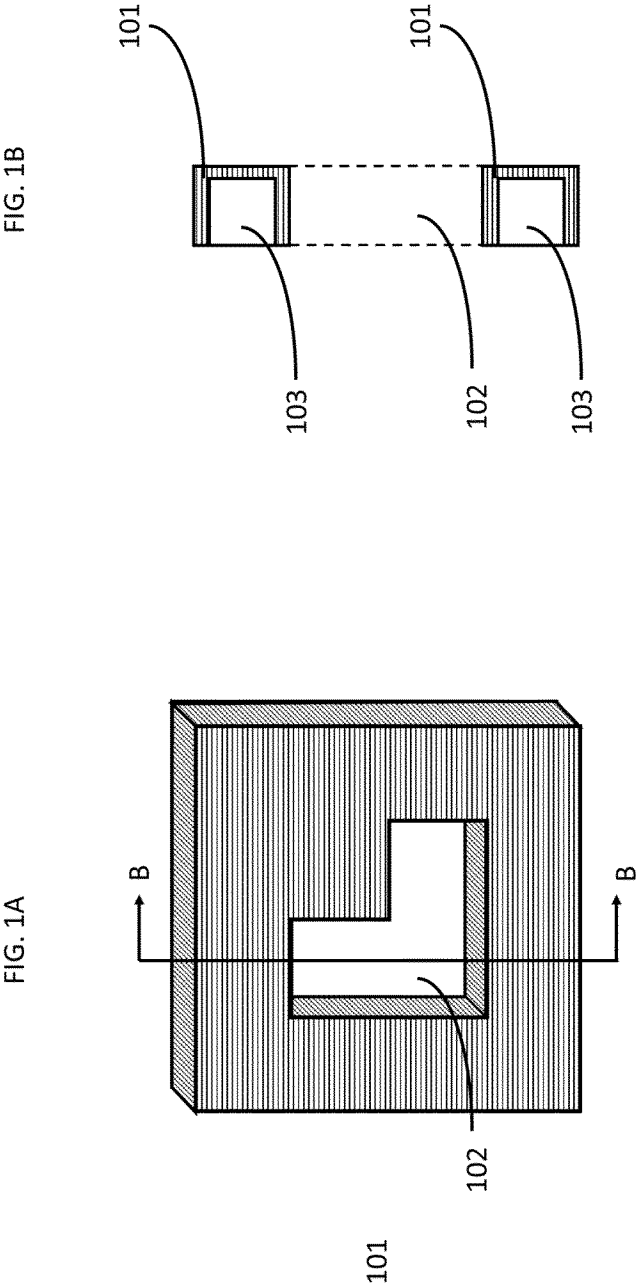
Claim 13. Reusable ion implantation mask according to claims 11 or 12, wherein the material of the scratch avoidance film has a Vickers hardness of less than 1 GPa.

Claim 14. Reusable ion implantation mask according to any one of claims 11 to 13, wherein the material of the scratch avoidance film is adapted for continuous operating temperatures of at least 100°C.

Claim 15. Partially ion implanted substrate, wherein the maximum width of the transition zone between a fully implanted surface area and a non-implanted surface area is less than 300 μm .

Claim 16. Method for partially ion implanting a first and a second substrate comprising covering selected areas of a first substrate with a reusable ion implantation mask according to any one of claims 1 to 14, exposing the covered first substrate to an ion beam, separating the ion implantation mask from the first substrate, covering selected areas of the second substrate, exposing the covered second substrate to an ion beam, separating the ion implantation mask from the second substrate.

Drawings



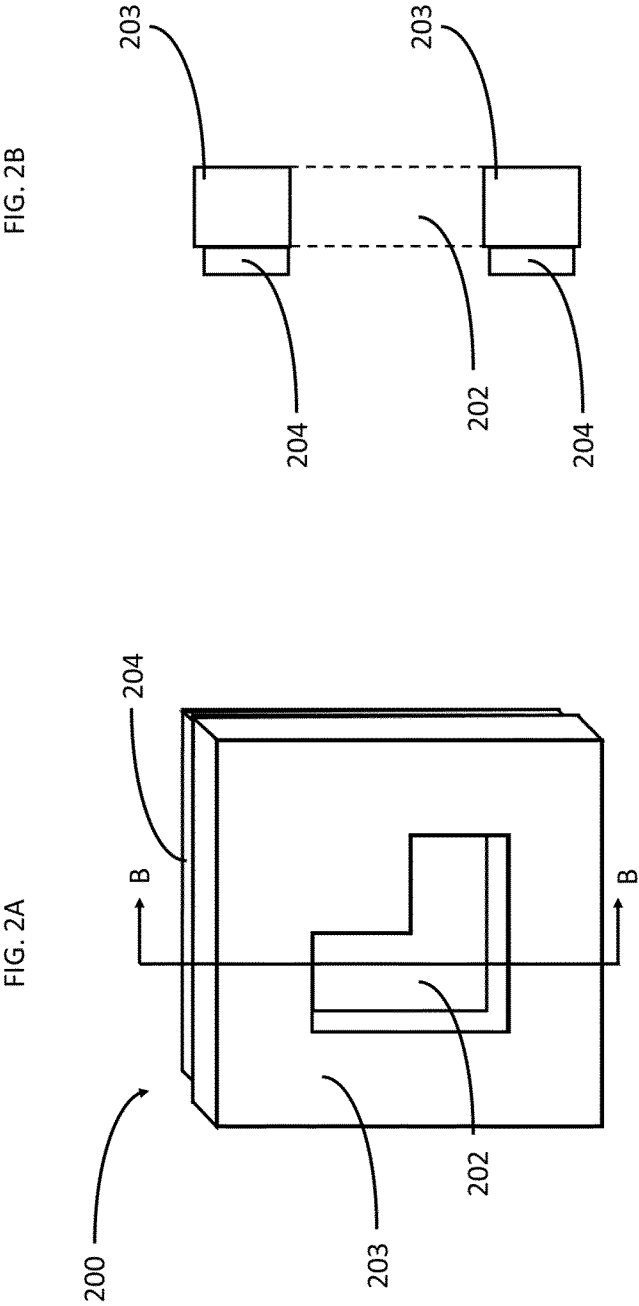


FIG. 3

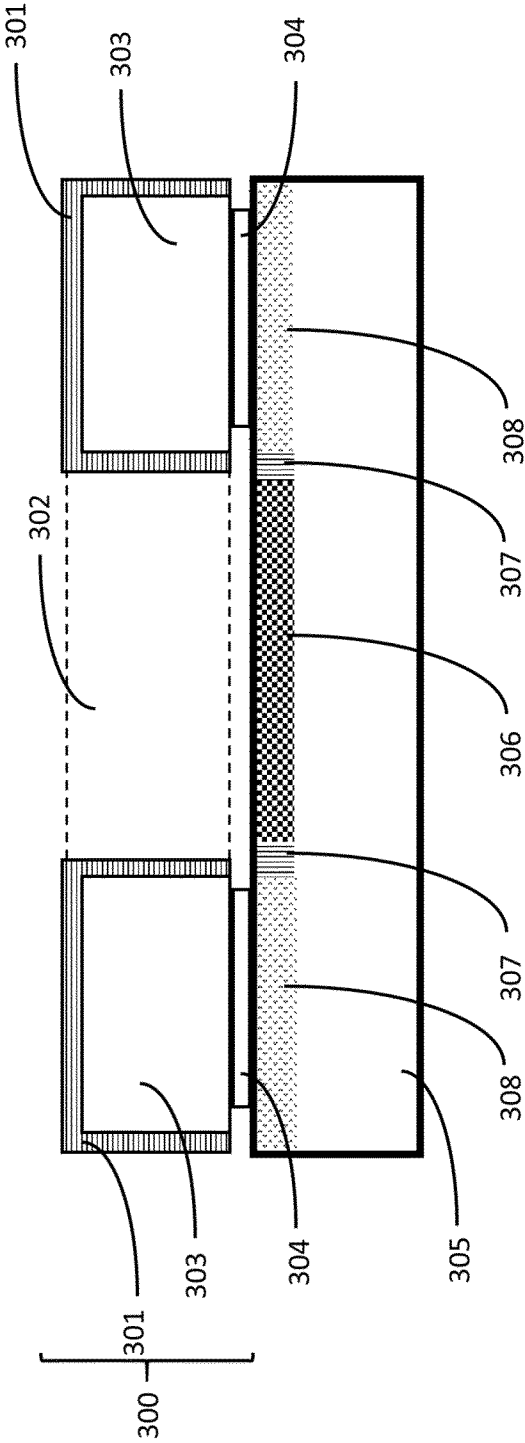
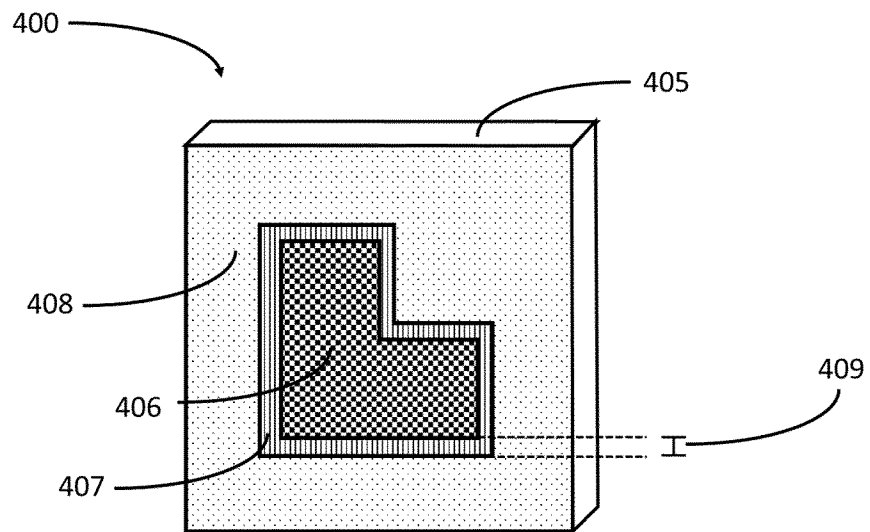


FIG. 4



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/052082

A. CLASSIFICATION OF SUBJECT MATTER INV. C23C14/04 C23C14/48 C23C16/04 H01J37/317 ADD. H01J37/32		
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) C23C G03F H01J H01L		
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.
Y	US 9 070 535 B2 (VARIAN SEMICONDUCTOR EQUIPMENT [US]) 30 June 2015 (2015-06-30) column 3, line 43 - line 55; figures 1, 11 column 4, line 41 - column 5, line 49 -----	1-14
X	US 6 656 614 B1 (LI XINWEI [US] ET AL) 2 December 2003 (2003-12-02) column 11, line 30 - line 53; figures 4(A), 4(B) -----	15
Y	US 2006/258128 A1 (NUNAN PETER [US] ET AL) 16 November 2006 (2006-11-16) paragraphs [0035], [0041] -----	1-14
X	EP 1 487 005 A1 (SHINETSU CHEMICAL CO [JP]) 15 December 2004 (2004-12-15) paragraphs [0055] - [0068] -----	1,16
Y	----- -/--	2-10
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 8 April 2019		Date of mailing of the international search report 15/04/2019
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 Schwake, Andree

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2019/052082

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2019/052082

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP H09 95762 A (SUMITOMO CHEMICAL CO) 8 April 1997 (1997-04-08) paragraphs [0007] - [0017]; figures 1,2 -----	11-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2019/052082

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 9070535	B2	30-06-2015	NONE
US 6656614	B1	02-12-2003	NONE
US 2006258128	A1	16-11-2006	JP 2008533721 A 21-08-2008
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		US 2006258128 A1 16-11-2006	
		WO 2006096818 A1 14-09-2006	
EP 1487005	A1	15-12-2004	EP 1487005 A1 15-12-2004
		KR 20040102319 A 04-12-2004	
		TW I284686 B 01-08-2007	
		US 2004238759 A1 02-12-2004	
JP H0995762	A	08-04-1997	NONE

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-16

Reusable ion implantation mask comprising a sputtering reduction coating.

Reusable ion implantation mask comprising a scratch avoidance film.

1.1. claims: 11-14

Reusable ion implantation mask comprising a scratch avoidance film.
