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(54) **HYDROPHOBIC PROPERTY ALTERATION USING ION IMPLANTATION**

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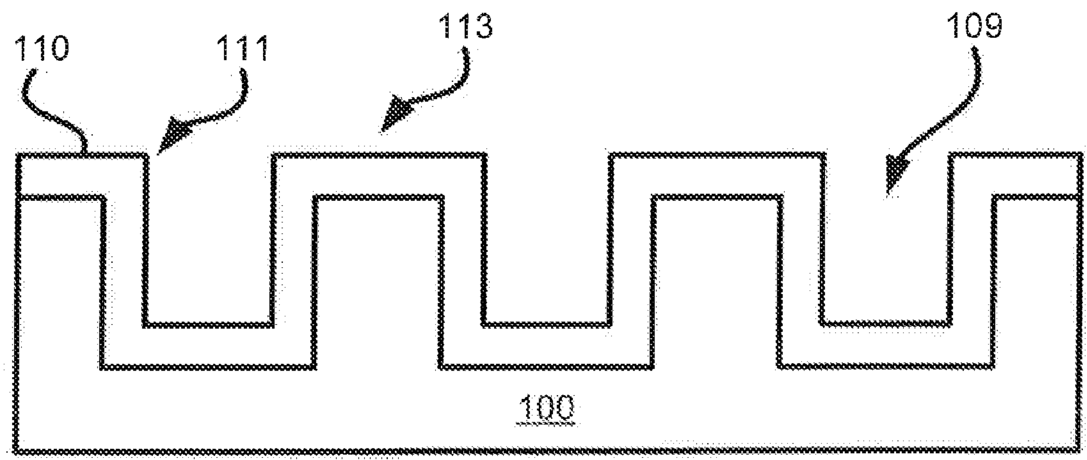
| ***C23C 14/48*** | (2006.01) |

(52) **U.S. Cl.** .......... **118/504**; 427/526; 438/45; 438/514; 427/2.11; 257/E33.001; 257/E21.473

(57) **ABSTRACT**

A template used for printing is implanted to change the properties of the materials it is composed of. This template may have multiple surfaces that define indentations. The ion species that is implanted may be C, N, H, F, He, Ar, B, As, P, Ge, Ga, Si, Zn, and Al and is configured to render the implanted regions hydrophobic in one instance. This will reduce adhesion of a polymer to the template during a printing process. The implant may be at a plurality of angles so all surfaces of the template are implanted. In other instances, a film on the surface of the template is knocked in or hardened using the ion species.



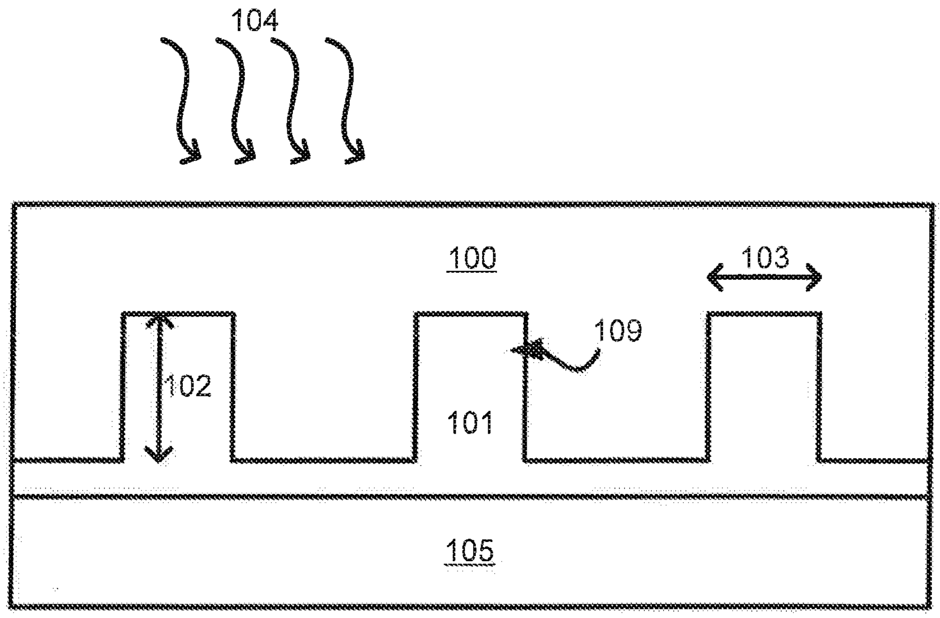



FIG. 1
(Prior Art)

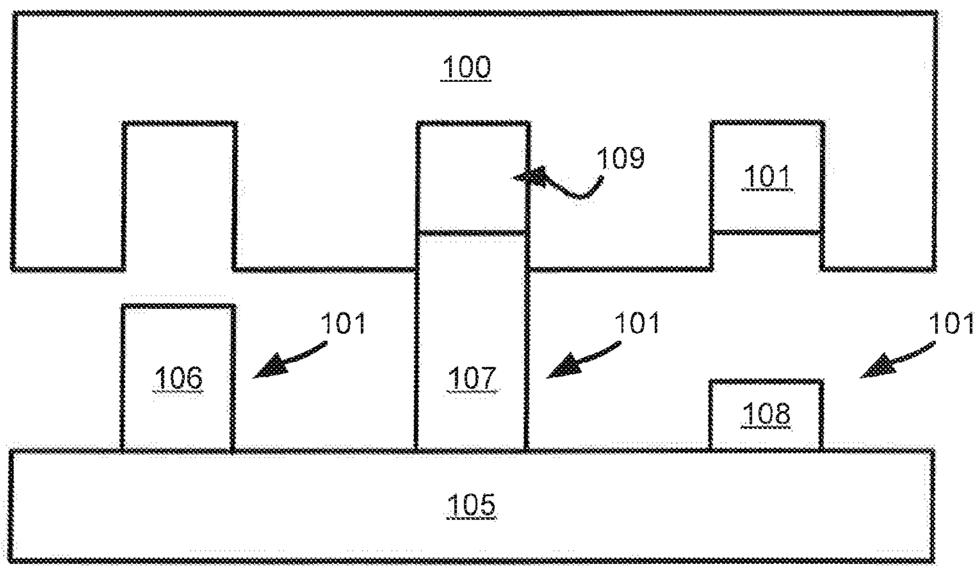



FIG. 2
(Prior Art)

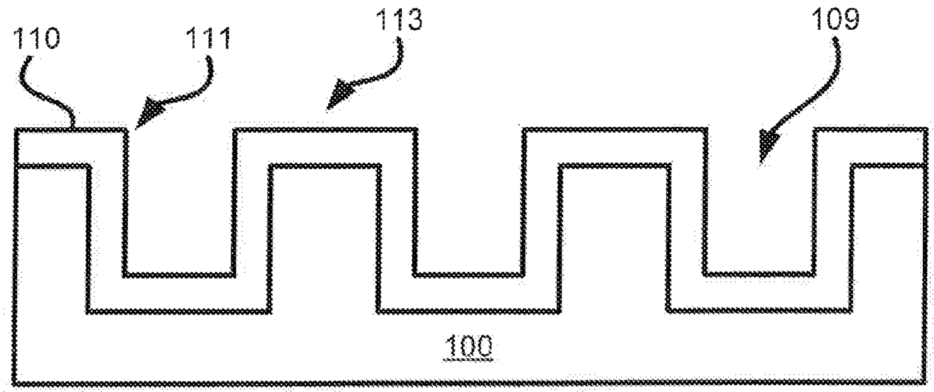



FIG. 3

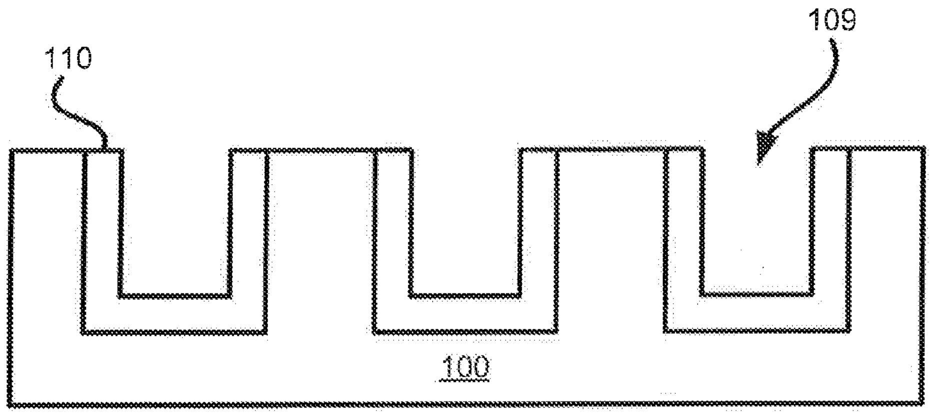



FIG. 4

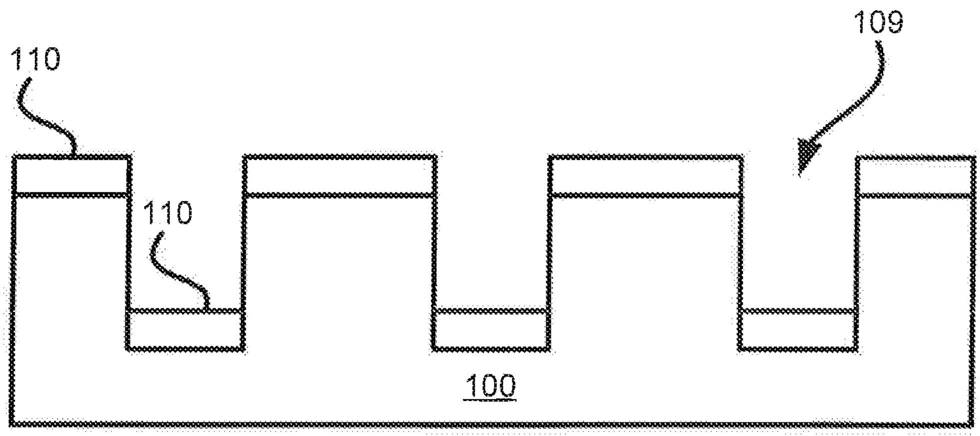



FIG. 5

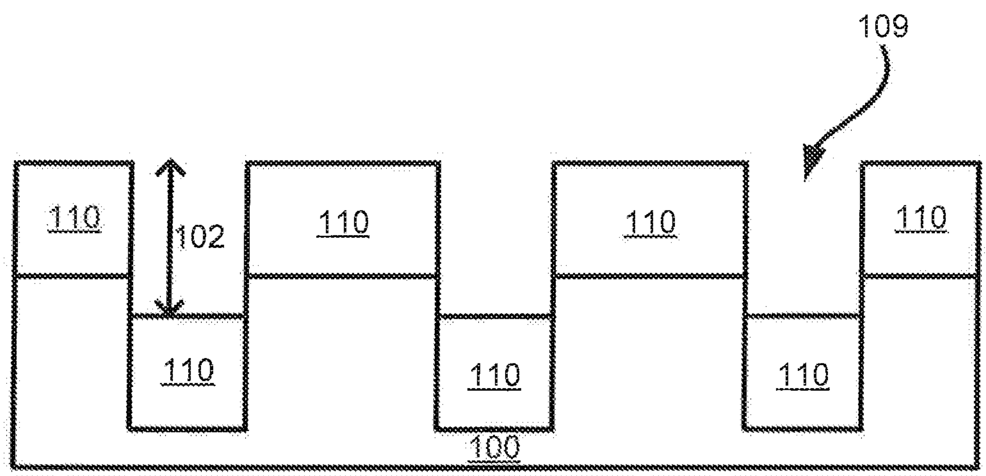



FIG. 6

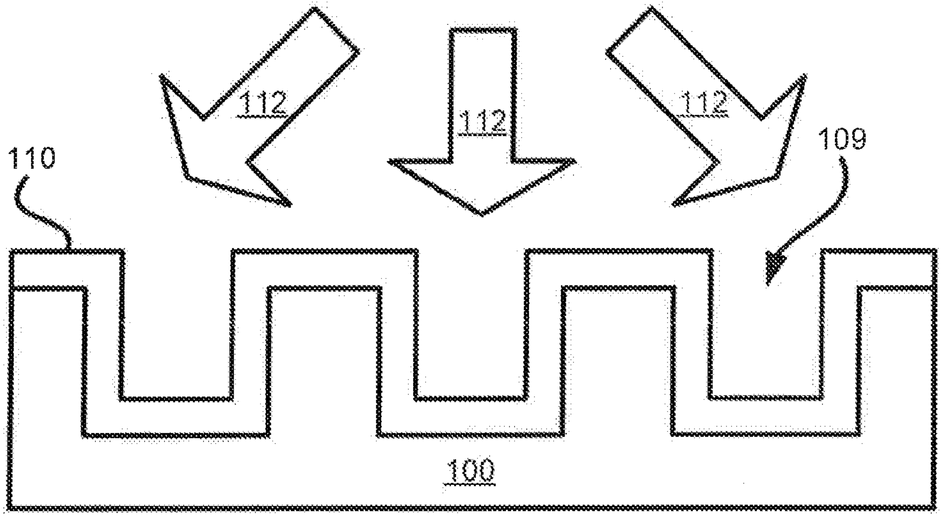



FIG. 7

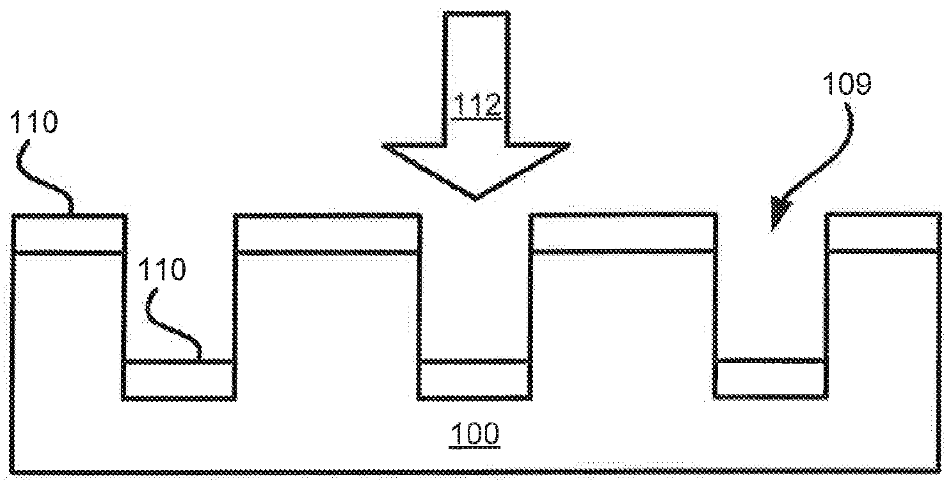



FIG. 8

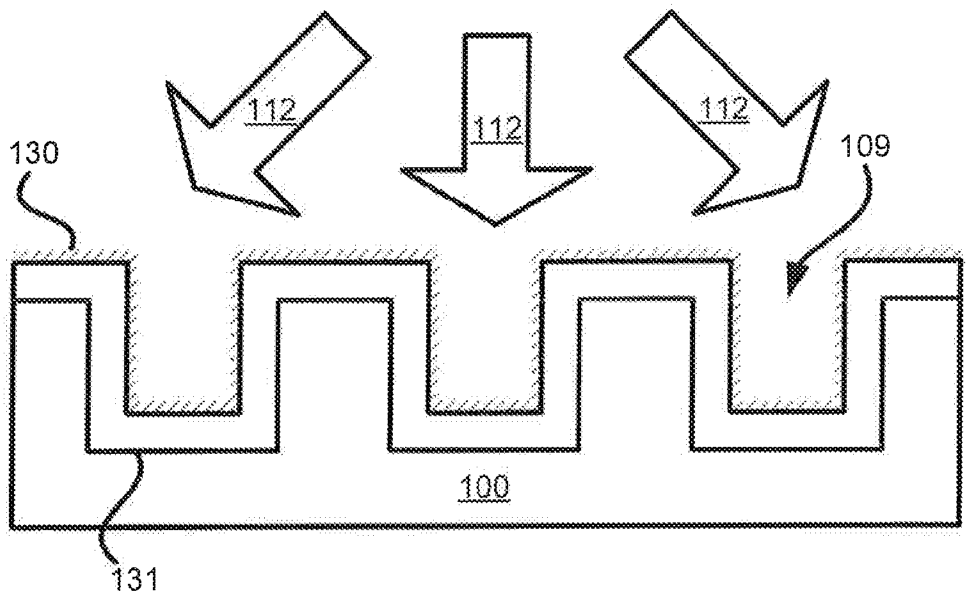



FIG. 9

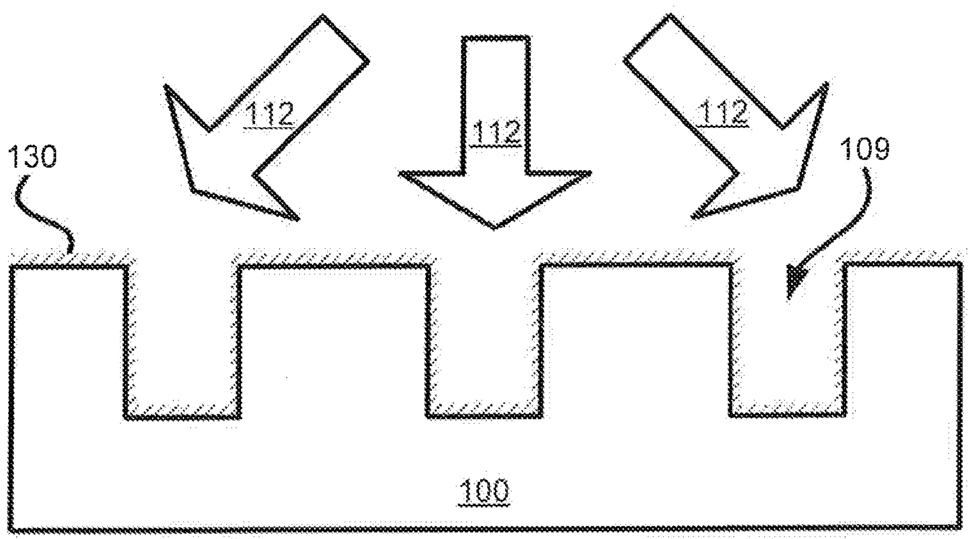



FIG. 10

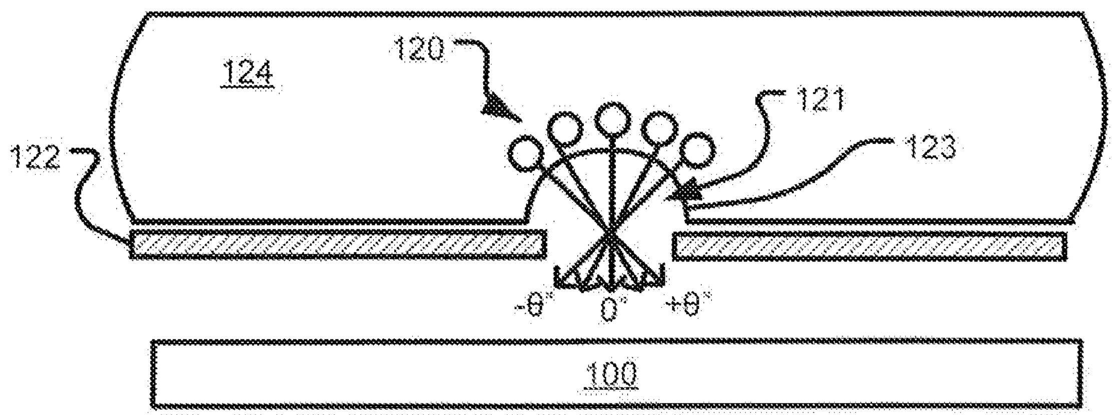



FIG. 11
(Prior Art)

# HYDROPHOBIC PROPERTY ALTERATION USING ION IMPLANTATION

## CROSS-REFERENCE TO RELATED APPLICATIONS

**[0001]** This claims priority to the provisional patent application entitled "Hydrophobic Property Alteration Using Ion Implantation," filed Dec. 3, 2010 and assigned U.S. App. No. 61/419,548, the disclosure of which is hereby incorporated by reference.

## FIELD

**[0002]** This invention relates to implantation to affect properties of materials and, more particularly, to implantation to affect properties of templates used for printing.

## BACKGROUND

**[0003]** Ion implantation is a standard technique for introducing conductivity-altering impurities into a workpiece. A desired impurity material is ionized in an ion source, the ions are accelerated to form an ion beam of prescribed energy, and the ion beam is directed at the surface of the workpiece. The energetic ions in the beam penetrate into the bulk of the workpiece material and are embedded into the lattice of the workpiece material to form an implanted region.

**[0004]** Imprint or nano-imprint technology is a known method to form a pattern on a workpiece. A polymer is dispensed on a workpiece and a template is used to transform the polymer into the desired pattern. This desired pattern may be, for example, lines or stripes across the workpiece. The same template may be used multiple times to form a pattern across a surface of a single workpiece.

**[0005]** FIG. **1** is a cross-sectional view of printing using a template during a first step. The template **100** is positioned above a workpiece **105** with a polymer **101** in between. The polymer may be, for example, a photoresist, though other polymers are possible. In this particular embodiment, the template **100** has multiple indentations **109** with a width **103** and depth **102**. For example, the width **103** may be approximately 30 nm and the depth **102** may be approximately 60 nm. The indentations **109** may vary in exact shape, width, or depth depending on the desired pattern of the polymer **101**. The polymer **101** enters these indentations **109** and is exposed to a wavelength **104**, which may be UV light. In one instance the wavelength **104** is approximately 365 nm. This hardens the polymer **101** into a shape that mirrors the indentations **109** in the template **100**.

**[0006]** FIG. **2** is a cross-sectional view of printing using a template during a second step. The template **100** is separated from the workpiece **105**. However, the polymer **101** may adhere to the template **100**. This polymer **101** is composed of C, O, and H atoms, so polar H atoms may be attracted to the template **100**. However, there may be other mechanisms that cause the polymer **101** to adhere to the template **100** and the embodiments disclosed herein are not limited to any one mechanism.

**[0007]** The pattern **106** of the polymer **101** is desired and approximately matches the width **103** and depth **102** seen in FIG. **1**. However, if the polymer **101** adheres or sticks to the template **100**, then the pattern **107** or pattern **108** illustrated in FIG. **2** may be formed. The pattern **107** is elongated compared to the pattern **106** at least partly because the polymer **101** adhered to the template **100**. The pattern **108** has less fidelity and is the incorrect shape when compared to pattern **106** because part of the polymer **101** broke off and remains in the indentation **109** of the template **100** at least partly because the polymer **101** adhered to the template **100**. If the patterns formed using the template are not accurate or are the wrong dimension, further processing steps may be performed incorrectly. This may lead to more scrapped workpieces and increased production costs. Accordingly, there is a need in the art for an implantation method that affects properties of material and, more particularly, an implantation method that affects properties of templates used for printing.

## SUMMARY

**[0008]** According to a first aspect of the invention, a method of implanting is provided. The method comprises implanting at least one surface of a template with an ion species. This template is configured for printing. A material is printed on a workpiece using the template.

**[0009]** According to a second aspect of the invention, a template apparatus is provided. The template apparatus comprises a template composed of silica having a plurality of surfaces. These surfaces define at least one indentation such that the surfaces exist in multiple planes. Each of the surfaces has an implanted region containing an ion species selected from the group consisting of C, N, H, F, He, Ar, B, As, P, Ge, Ga, Si, Zn, and Al. The implanted region is hydrophobic.

**[0010]** According to a first aspect of the invention, a method of implanting is provided. The method comprises applying a film to at least one surface of a template. This template is configured for printing. An ion species is directed toward the surface of the template. A material is printed on a workpiece using the template.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0011]** For a better understanding of the present disclosure, reference is made to the accompanying drawings, which are incorporated herein by reference and in which:

**[0012]** FIG. **1** is a cross-sectional view of printing using a template during a first step;

**[0013]** FIG. **2** is a cross-sectional view of printing using a template during a second step;

**[0014]** FIG. **3** is a cross-sectional view of a first embodiment of an implanted template;

**[0015]** FIG. **4** is a cross-sectional view of a second embodiment of an implanted template;

**[0016]** FIG. **5** is a cross-sectional view of a third embodiment of an implanted template;

**[0017]** FIG. **6** is a cross-sectional view of a fourth embodiment of an implanted template;

**[0018]** FIG. **7** is a first embodiment of implanting a template;

**[0019]** FIG. **8** is a second embodiment of implanting a template;

**[0020]** FIG. **9** is a third embodiment of implanting a template;

**[0021]** FIG. **10** is a fourth embodiment of implanting a template; and

**[0022]** FIG. **11** is a block diagram of a plasma processing apparatus having an insulating modifier

## DETAILED DESCRIPTION

**[0023]** The embodiments are described herein in connection with an ion implanter. Many different ion implantation systems or plasma processing systems may be used to perform these embodiments. Furthermore, while a template for printing is specifically disclosed, other items and substrates may benefit from the embodiments disclosed herein. The use of the word template is not meant to be limiting. The template may be a stamp or mold for printing or forming patterns on many different materials. Thus, the invention is not limited to the specific embodiments described below.

**[0024]** FIG. **3** is a cross-sectional view of a first embodiment of an implanted template. The template **100** is composed of silica and has multiple indentations **109**. These indentations **109** have surfaces that exist in multiple planes, such as the horizontal or vertical plane as illustrated in FIG. **3**. The silica may be a fused silica or quartz. In an alternate embodiment, the template **100** is composed of alumina, glass, stainless steel, silicon, or a polymer.

**[0025]** The template **100** material is generally hydrophilic. This template **100** has an implanted region **110**. This implanted region **110** follows the contour of the template **100** and all the surfaces of the template **100** and indentations **109**. The implanted region **110** may be implanted with ion species such as, for example, C, N, H, F, He, Ar, B, As, P, Ge, Ga, Si, Zn, Al, other noble gases, or other p-type or n-type dopants at a dose within the approximately 1E15 to 1E17 range. Of course, other ion species or doses also may be used and this list is not exclusive. These ion species may be generated from, for example, $CH_4$, $H_2$, $NF_3$, $BF_3$, $CF_4$, $SF_6$, $N_2$, or He.

**[0026]** The implanted region **110** is generally hydrophobic, while the remainder of the template **100** is generally hydrophilic. The will reduce or prevent adhesion by a polymer used for printing with the template **100**, such as the polymer **101** of FIGS. **1-2**. The ion species that is implanted may in part affect the hydrophobicity. Certain energy levels or doses during implantation may modify the lattice structure of the template **100**, which also may in part affect the hydrophobicity. Other mechanisms due to implant that affect the hydrophobicity may be possible.

**[0027]** The implanted region **110** will remain hydrophobic even if cleaned because the implanted region **110** is part of the template **100** instead of a coating on the surface of the template **100** that may be eroded or washed off. To maintain the hydrophobic state, at least a few monolayers of the template **100** are implanted to form the implanted region **110**. The implanted region **110** may be less than approximately 50 nm in depth. Multiple implant steps on the same template may be needed in one instance to form the implanted region **110**.

**[0028]** Release force between the implanted regions **110** of the template **100** and a polymer is lower than between the material of the template **100** and a polymer. Release force is the force needed to separate the polymer from the template **100**. An improved release force means that the polymer has an increased probability of not sticking to the template **100** when the template **100** is withdrawn from a workpiece after the template is exposed to a wavelength of light. A lower release force increases the probability of accuracy in the pattern formed by the polymer or that the polymer will match the indentations **109** in the template **100**.

**[0029]** The corners **111** of the indentations **109** are not chipped or eroded by the formation of the implanted region **110**. Altering the shape of the indentations **109** may affect the patterns formed later with the polymer. Furthermore, surface roughness of the template may not be affected by the implantation. Defects to the template are managed or prevented using the implantation process. Implantation occurs at vacuum, so there are few particles to cause defects.

**[0030]** The extinction coefficient (k) value is not modified extensively by the formation of the implanted region **110**. This k value refers to the extent the intensity of a beam of light is reduced. By maintaining the k value, then the polymer will set or harden as anticipated during printing. In one example, the k value was altered by less than approximately 15% through formation of the implanted region **110**. The implant species used to form the implanted region **110** affects this k value. Furthermore, this k value is exposure wavelength dependent so depending on the wavelength used to harden the polymer a particular implant species is selected so as to not affect the absorption of the template. This is demonstrated using the following formula:

$$T=(1-r)\exp(-4\pi kt/\text{wavelength})$$

**[0031]** T is transmission, r is reflection, k is the extinction coefficient, t is the thickness of the template **100**, and the wavelength represents the exposure wavelength. The ideal state is when k equals zero and the transmission is related only to the reflection loss. If the reflection loss is zero, then the transmission is proportional to the incident exposure. In one embodiment, the implantation is configured to not affect the transmission through a constant k value, but reflectivity suppression may occur. If transmission at a particular wavelength is affected, it is possible that the polymer may not harden correctly. Thus, the polymer may not form the desired pattern during printing.

**[0032]** Uniformity of the dose and depth implanted region **110** may be controlled. In one instance, uniformity of the dose and depth demonstrated less than approximately 10% variation across the template **100**. If certain areas of the template **100** are implanted in a non-uniform manner or are not implanted at all, this may affect adhesion of the polymer. Furthermore, for certain species an implant that is too deep or at too high a dose may affect adhesion. A non-uniform implant may lead to the polymer adhering to the template in the areas with the non-uniform implant, such as an area with a lower dose or lower implant depth compared with the rest of the implanted region **110**.

**[0033]** The implanted region **110** may densify the material of which the template **100** is composed. This densification is due to the material added to the lattice of the template **100** during implantation. The densification may affect hydrophobic or hydrophilic properties of the template **100**.

**[0034]** The implanted region **110** also may improve the lifetime of the template **100**. The template **100** has a limited lifetime due to, for example, failure of the material properties of the template **100**, cracking or breaking of the template **100**, or the polymer adhering in the indentations **109**. By reducing or preventing adhesion of the polymer to the template **100** or in the indentations **109**, then the lifetime of the template **100** may be improved. This may reduce production costs.

**[0035]** While the embodiment of FIG. **3** is illustrated as having an implanted region **110** that is uniform, in one particular embodiment the walls of the indentations **109** may receive a different dose or implant species than the top surface **113**. The top surface **113** may receive little or no dose. This is because the polymer is shaped using the indentations **109** rather than the top surface **113** and there is little or no polymer disposed against the top surface **113** during printing. The polymer in the indentations **109** may primarily form the desired shape or pattern. FIG. **4** is a cross-sectional view of a second embodiment of an implanted template. In this embodiment, the walls of the indentations **109** have an implanted region **110**, while the top surface **113** receives a low or no dose across the majority of its surface. Various implantation techniques, such as scanning during implant, focusing the ion species during implant of individual indentations **109**, a stencil or shadow mask, or photoresist may be used to enable the embodiment illustrated in FIG. **4**. The mask or photoresist may block implantation to the top surface **113**. In another embodiment, different sides of the indentations **109** may receive a different dose or implant species.

**[0036]** FIG. **5** is a cross-sectional view of a third embodiment of an implanted template. In this embodiment, a plurality of implanted regions **110** are formed. These implanted regions **110** may be formed by implanting the template **100** at an angle perpendicular to the surfaces that have the implanted regions **110**. However, certain surfaces of the indentations **109** of the template **100** that a polymer may contact are not implanted. This embodiment may be sufficient to improve adhesion of a polymer to the template **100**. However, this embodiment also may lead to adhesion of the polymer to the surfaces that are not implanted. Such a result may be desired for certain applications.

**[0037]** FIG. **6** is a cross-sectional view of a fourth embodiment of an implanted template. In this embodiment, a plurality of implanted regions **110** are formed by implanting the template **100** at an angle perpendicular to the surfaces that have the implanted regions **110**. However, the energy of the ions that are implanted to form the implanted regions **110** is higher than that illustrated in FIG. **5**. This leads to a larger implanted depth in the template **100**. Thus, in this particular embodiment, the implanted regions **110** extend almost equal to the depth **102**. In an alternate embodiment, the implanted regions **110** extend beyond the depth **102** and may overlap with the other implanted regions **110**.

**[0038]** FIG. **7** is a first embodiment of implanting a template. In this embodiment, the ion species **112** is implanted using an ion spread or at a plurality of different angles. This may be performed simultaneously or sequentially using multiple implant steps. The ion spread or multiple angles produce an implant region **110** on every surface of the indentations **109** of the template **100**. A plasma doping tool or plasma processing apparatus with an insulating modifier, for example, may be used to produce these angles. A beam-line ion implanter also may be used. For a beam-line ion implanter, the angle between the template **100** and the ion species **112** is changed and multiple implant steps are performed. A platen on which the template **100** is disposed may be translated or rotated or the ion beam containing the ion beams **112** may be directed to form a different implant angle.

**[0039]** FIG. **8** is a second embodiment of implanting a template. In this particular embodiment, the ion species **112** is implanted at a single angle perpendicular to a surface of the template **100**. This results in multiple implanted regions **110** as illustrated in FIGS. **5-6**.

**[0040]** In yet another embodiment, a film containing a species, such as a dopant, is applied to the template **100**. FIG. **9** is a third embodiment of implanting a template. A film **130** is applied to the template **100** (illustrated by the shaded region). This film **130** may contain a dopant and may be deposited on at least one surface of the indentations **109**. In an alternate embodiment, the film **130** is selectively applied to the template **100** such that only certain regions, such as the surfaces of the indentations **109**, are covered.

**[0041]** The ion species **112** drive in or knock in the species from the film **130** into the lattice of the template **100** to form the doped region **131**. The film **130** may be $CF_x$ or an n-type or p-type dopant-containing molecule. The ion species **112** may drive in or knock in the species from the film **130** a few nanometers or to other depths. This ion species **112** may be, for example, Ar, Ne, or Xe. The ion species **112** is illustrated in FIG. **9** as using an ion spread or a plurality of different angles, but in an alternate embodiment the ion species **112** is implanted at a single angle perpendicular to a surface of the template **100** similar to that illustrated in FIG. **8**. The film **130** may be removed in some embodiments after the implantation step or the process illustrated in FIG. **9** may be repeated.

**[0042]** FIG. **10** is a fourth embodiment of implanting a template. In this embodiment, the ion species **112** may be used to harden the film **130** applied to the template **100**. This increases the number of cycles the film **130** may be used before replacement and, by use of hardening, the film **130** is less likely to be removed during cleaning steps. The ion species **112** is illustrated in FIG. **10** as using an ion spread or a plurality of different angles, but in an alternate embodiment the ion species **112** is implanted at a single angle perpendicular to a surface of the template **100** similar to that illustrated in FIG. **8**.

**[0043]** FIG. **11** is a block diagram of a plasma processing apparatus having an insulating modifier. The plasma **124** is generated as is known in the art and is generally a quasi-neutral collection of positively-charged molecular or atomic ions and negatively-charged electrons. In a system containing the plasma **124**, ions **120** from the plasma **124** are attracted toward a template **100**, which is illustrated as flat in this embodiment for simplicity but may contain the indentations illustrated elsewhere. The plasma **124** is bounded by a region proximate the template **100** referred to as a plasma sheath **121**. The plasma sheath **121** is a region that has fewer electrons than the plasma **124**. Hence, the differences between the negative and positive charges cause a sheath potential in the plasma sheath **121**. The light emission from this plasma sheath **121** is less intense than the plasma **124** because fewer electrons are present and, hence, few excitation-relaxation collisions occur. Thus, the plasma sheath **121** is sometimes referred to as "dark space."

**[0044]** The insulating modifier **122** is configured to modify an electric field within the plasma sheath **121** to control a shape of a boundary **123** between the plasma **124** and the plasma sheath **121**. Accordingly, ions **120** that are attracted from the plasma **124** across the plasma sheath **121** may strike the template **100** at a large range of incident angles or trajectories, such as, for example, between +θ° and −θ° centered around 0°. This is one example of implanting using an ion spread or a plurality of different angles. The distance between the insulating modifier **122** and the template **100** or the size of the aperture in the insulating modifier **122** that the ions **120** pass through may affect this range of incident angles. By adjusting these variables, the ions **120** may be focused on a particular point on the template **100**, such as the indentations **109** illustrated in FIG. **4**, or widened to implant the entire template **100** with a wide ion spread. This insulating modifier **122** may be referred to as, for example, a focusing plate or sheath engineering plate. While an insulating modifier **122** is specifically disclosed, semiconductors or conductors may be used instead of insulators.

**[0045]** Ions **120** may be attracted from the plasma **124** across the plasma sheath **121** by different mechanisms. In one instance, the template **100** is biased to attract ions **120** from the plasma **124** across the plasma sheath **121**. In another instance, a plasma source that generates the plasma **124** and walls surrounding the plasma **124** are biased positively and the template **100** may be grounded. The biasing may be pulsed in one particular embodiment. In yet another instance, electric or magnetic fields are used to attract ions **120** from the plasma **124** toward the template **100**. When the template **100** is biased, for example, the ions **120** are attracted across the plasma sheath **121** through the aperture in the insulating modifier **122**.

**[0046]** The embodiment of FIG. **11** may provide benefits to implanting the template **100**. For example, the range of incident angles may be controlled or specific areas of the template **100** may be implanted while other areas are not. Scanning the template **100** when the ions **120** are not implanted may enable these selective or patterned implants in one instance. Use of the insulating modifier **122** may be beneficial, for example, to implant the indentations of a template without implanting other surfaces of the template. Furthermore, if all surfaces of an indentation in a template are treated simultaneously using the large range of incident angles or trajectories, this may reduce processing time to implant a template.

**[0047]** The template described herein may be used for printing in semiconductor applications such as logic, dynamic random access memory (DRAM), flash memory, or analog devices. Of course, other applications are possible. For example, the workpiece being printed also may be bit patterned media such as a computer hard drive. The workpiece being printed also may be a micro mirror or a microelectromechanical systems (MEMS) device, for example. Of course, other applications will be apparent to those skilled in the art. If adhesion is reduced, it may be possible to print or form smaller structures or patterns of the polymer using the template.

**[0048]** The template described herein also may be used for biomedical applications. The indentations in the template may be used to produce a series of channels on a workpiece with walls composed of the polymer. The channels may be used, for example, to allow the flow of blood or other body fluids for testing or diagnostics. "Microfluidics" is one example of such a process.

**[0049]** The template also may be used with workpieces that are organic light emitting diodes (organic LED or OLED). While such a template may have indentations, in other instances the template may not have indentations. Instead, the template may be a flat sheet used to make a uniform polymer layer of a certain thickness. Such a template may still benefit from a reduction in adhesion with the polymer. The hydrophobic surface of the template may allow the polymer to spread more easily and not have non-uniformities caused by sticking to the template. Of course, one skilled in the art will recognize that many different template shapes are possible and may benefit from the embodiments described herein.

**[0050]** The template may be used to print other materials than a polymer. For example, the template may be used to print or press graphite into particular shapes or patterns. In another instance, a master mold is formed using the implanted template and this master mold is used multiple times. Thus, polymers are merely one example of a material that is printed.

**[0051]** The present disclosure is not to be limited in scope by the specific embodiments described herein. Indeed, other various embodiments of and modifications to the present disclosure, in addition to those described herein, will be apparent to those of ordinary skill in the art from the foregoing description and accompanying drawings. Thus, such other embodiments and modifications are intended to fall within the scope of the present disclosure. Furthermore, although the present disclosure has been described herein in the context of a particular implementation in a particular environment for a particular purpose, those of ordinary skill in the art will recognize that its usefulness is not limited thereto and that the present disclosure may be beneficially implemented in any number of environments for any number of purposes. Accordingly, the claims set forth below should be construed in view of the full breadth and spirit of the present disclosure as described herein.

**1**. A method of implanting comprising:

implanting at least one surface of a template with an ion species, said template configured for printing; and

printing a material on a workpiece using said template.

**2**. The method of claim **1**, wherein said at least one surface is hydrophilic prior to said implanting and is hydrophobic after said implanting.

**3**. The method of claim **1**, wherein said ion species is selected from the group consisting of C, N, H, F, He, Ar, B, As, P, Ge, Ga, Si, Zn, and Al.

**4**. The method of claim **1**, wherein said template is composed of silica.

**5**. The method of claim **1**, wherein said template comprises a plurality of surfaces that define an indentation in said template, and wherein said implanting is into all of said plurality of surfaces around said indentation.

**6**. The method of claim **1**, further comprising densifying said surface.

**7**. The method of claim **1**, wherein said implanting comprises using an ion spread of said ion species.

**8**. The method of claim **1**, wherein said implanting comprises simultaneously implanting said ion species at a plurality of angles with respect to said template.

**9**. The method of claim **1**, further comprising modifying a plasma sheath of said ion species to spread said ion species into a plurality of trajectories.

**10**. The method of claim **1**, wherein said material is a polymer and said printing comprises dispensing said polymer on said workpiece, lowering said template onto said polymer, applying a wavelength of light to said template, and removing said template from said polymer.

**11**. The method of claim **1**, wherein said workpiece comprises one of a bit-patterned media, an organic LED, a biomedical chip, a microfluidic channel, a MEMS device, and a semiconductor device.

**12**. A template apparatus comprising:

a template composed of silica having a plurality of surfaces, said plurality of surfaces defining at least one indentation such that said plurality of surfaces exist in multiple planes, wherein each of said plurality of surfaces has an implanted region containing an ion species selected from the group consisting of C, N, H, F, He, Ar, B, As, P, Ge, Ga, Si, Zn, and Al, and wherein said implanted region is hydrophobic.

**13**. The template apparatus of claim **12**, wherein said silica below said implanted region is hydrophilic.

**14**. The template apparatus of claim **12**, wherein said indentation is configured to match a pattern printed on a workpiece using a polymer.

**15**. A method of implanting comprising:

applying a film to at least one surface of a template, said template configured for printing;

directing an ion species toward said at least one surface of said template; and

printing a material on a workpiece using said template.

**16**. The method of claim **15**, wherein said ion species is selected from the group consisting of C, N, H, F, He, Ar, B, As, P, Ge, Ga, Si, Zn, and Al.

**17**. The method of claim **15**, further comprising hardening said film.

**18**. The method of claim **15**, further comprising knocking in a species from said film into a lattice of said template using said ion species.

**19**. The method of claim **15**, wherein said implanting comprises simultaneously implanting said ion species at a plurality of angles with respect to said template.

**20**. The method of claim **15**, wherein said material is a polymer and said printing comprises dispensing said polymer on said workpiece, lowering said template onto said polymer, applying a wavelength of light to said template, and removing said template from said polymer.

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