US 20160326636A1

(19) **United States**

(12) **Patent Application Publication**

Godet et al.

(10) **Pub. No.: US 2016/0326636 A1**

(43) **Pub. Date: Nov. 10, 2016**

(54) **METHODS OF AFFECTING MATERIAL PROPERTIES AND APPLICATIONS THEREFOR**

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(21) Appl. No.: **15/214,676**

(22) Filed: **Jul. 20, 2016**

Related U.S. Application Data

(62) Division of application No. 13/470,731, filed on May 14, 2012, now Pat. No. 9,425,027.

(60) Provisional application No. 61/486,296, filed on May 15, 2011, provisional application No. 61/486,297, filed on May 15, 2011, provisional application No. 61/486,299, filed on May 15, 2011.

Publication Classification

(51) **Int. Cl.**

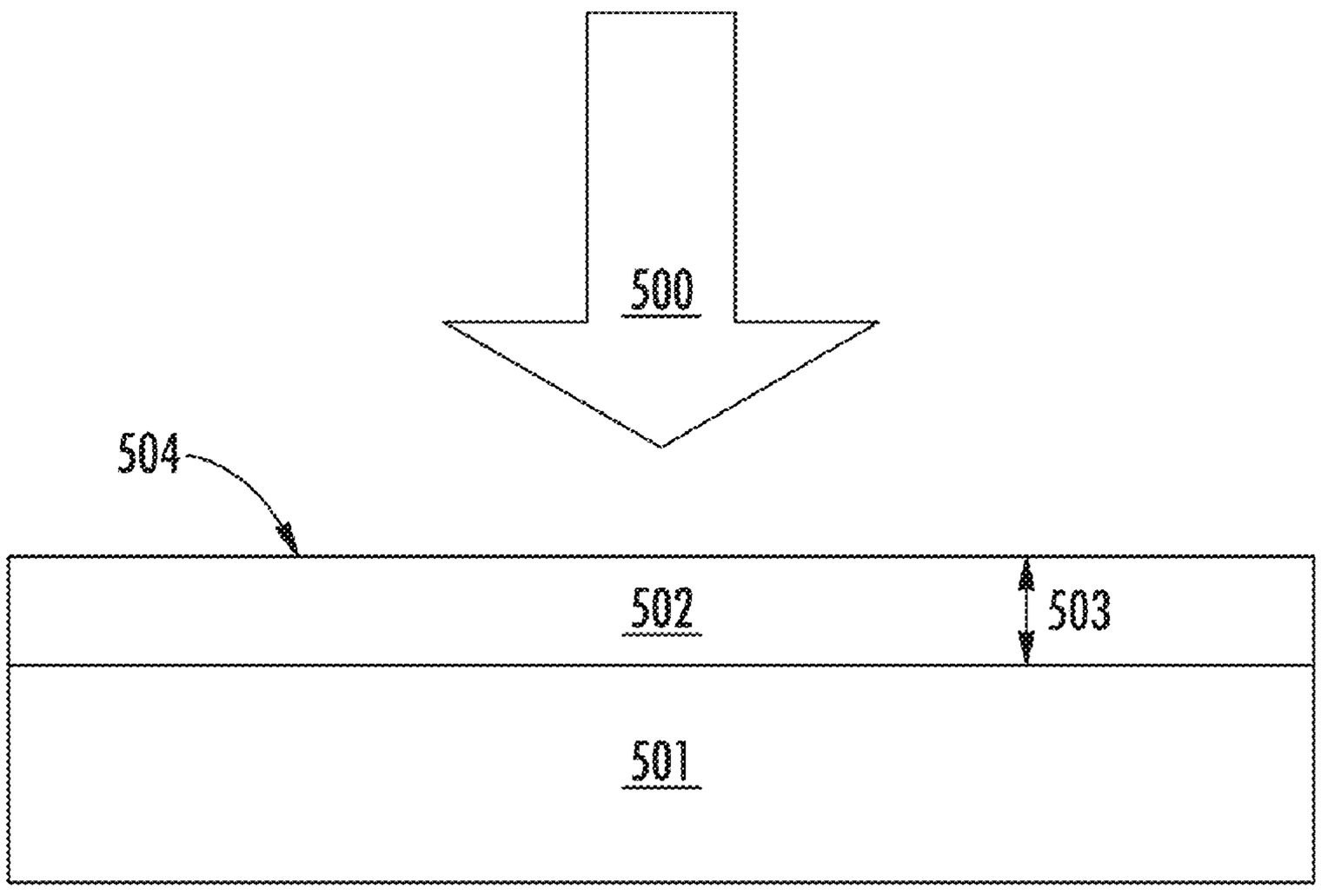
C23C 14/48	(2006.01)
H01J 37/32	(2006.01)

(52) **U.S. Cl.**

CPC ***C23C 14/48*** (2013.01); ***H01J 37/32422*** (2013.01); ***H01J 37/32412*** (2013.01)

(57) **ABSTRACT**

Methods of affecting a material's properties through the implantation of ions, such as by using a plasma processing apparatus with a plasma sheath modifier. In this way, properties such as resistance to chemicals, adhesiveness, hydrophobicity, and hydrophilicity, may be affected. These methods can be applied to a variety of technologies. In some cases, ion implantation is used in the manufacture of printer heads to reduce clogging by increasing the materials hydrophobicity. In other embodiments, MEMS and NEMS devices are produced using ion implantation to change the properties of fluid channels and other structures. In addition, ion implantation can be used to affect a material's resistance to chemicals, such as acids.



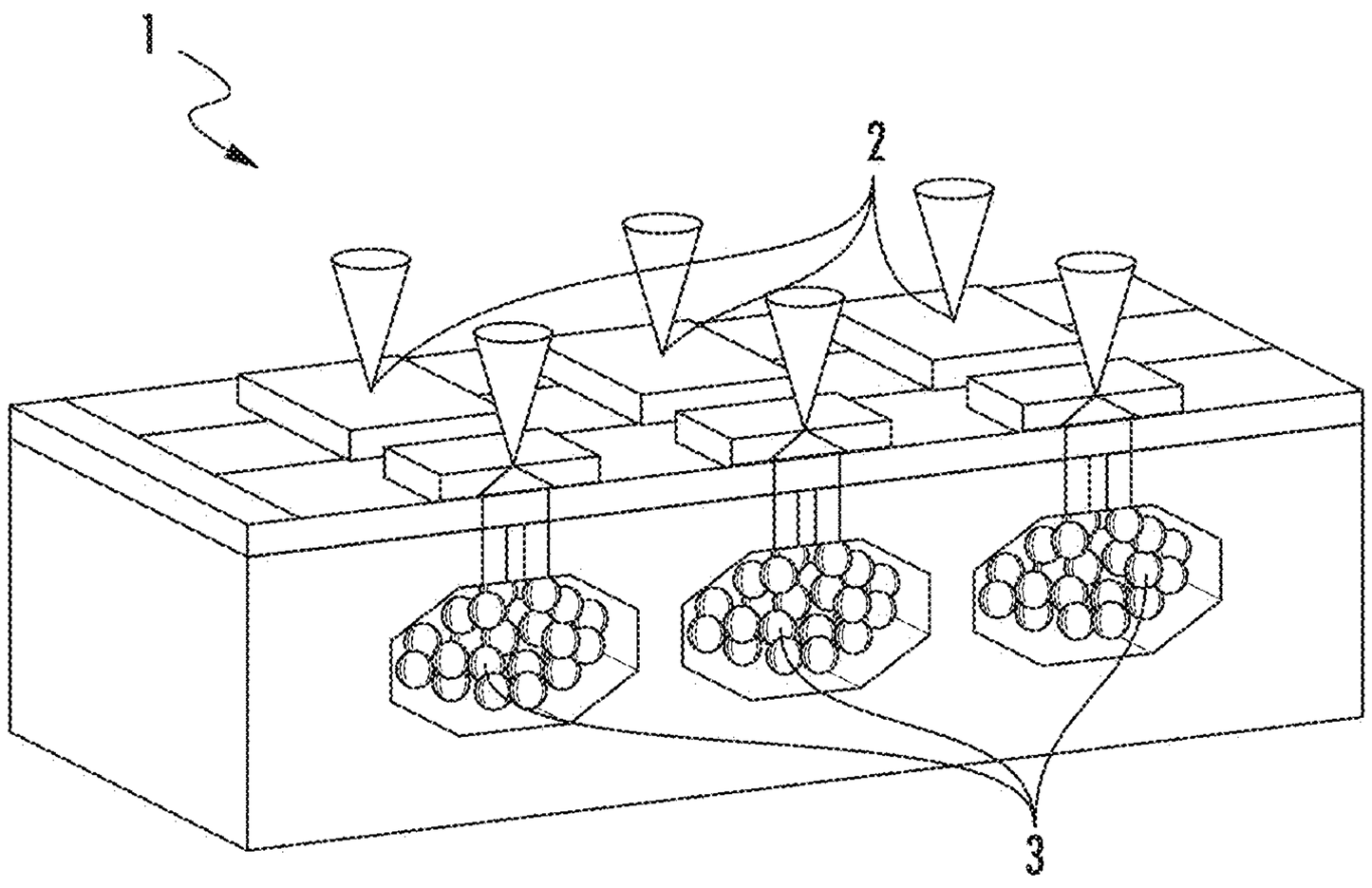


FIG. 1
(PRIOR ART)

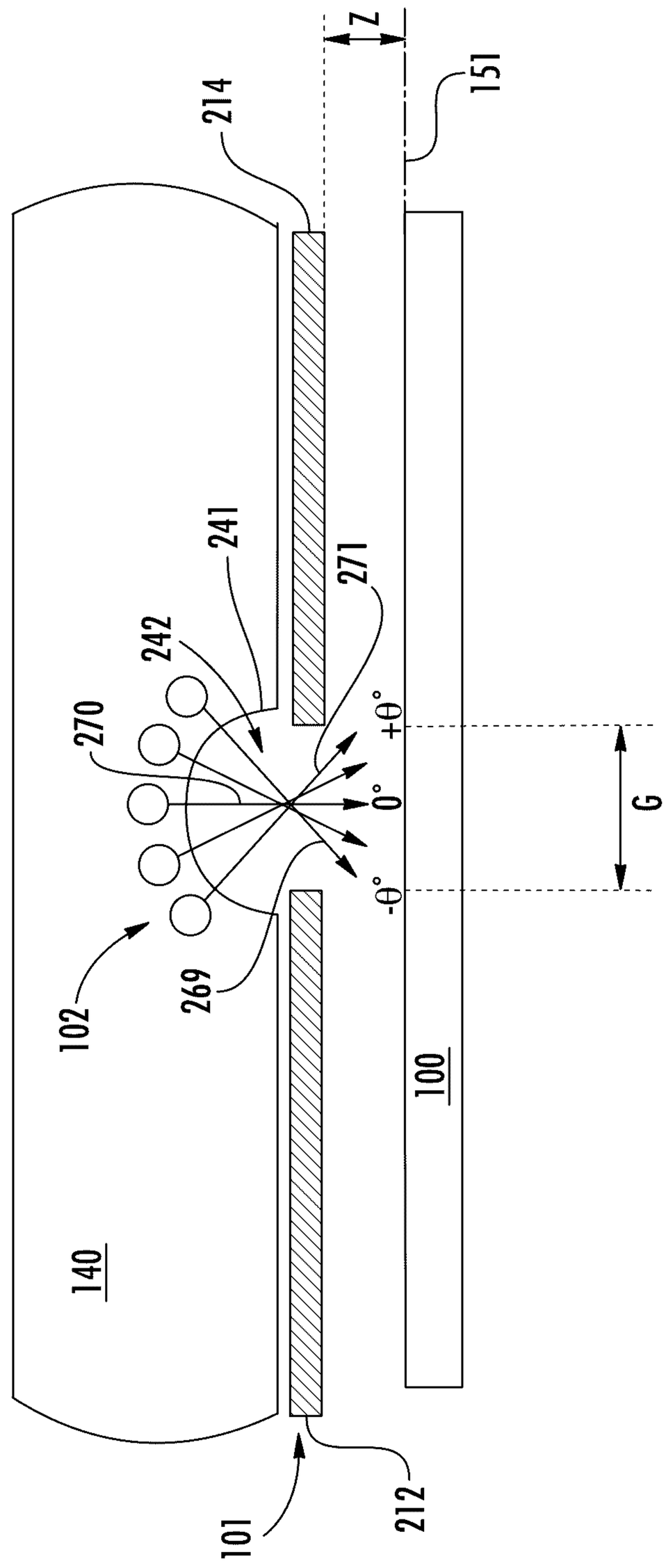


FIG. 2

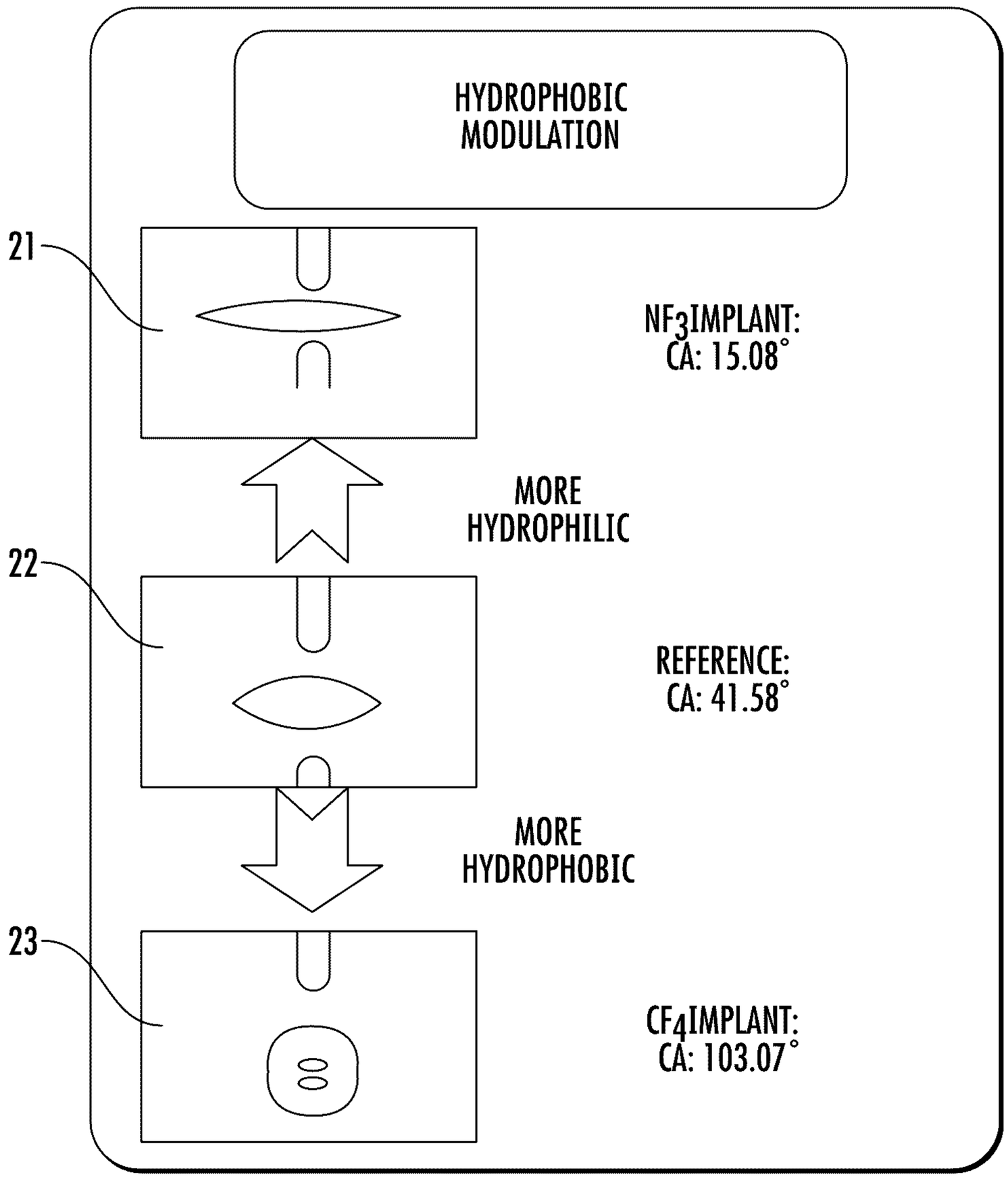

HYDROPHOBIC MODULATION
21
NF3IMPLANT:
CA: 15.08°
MORE HYDROPHILIC
22
REFERENCE:
CA: 41.58°
MORE HYDROPHOBIC
23
CF4IMPLANT:
CA: 103.07°

FIG. 3

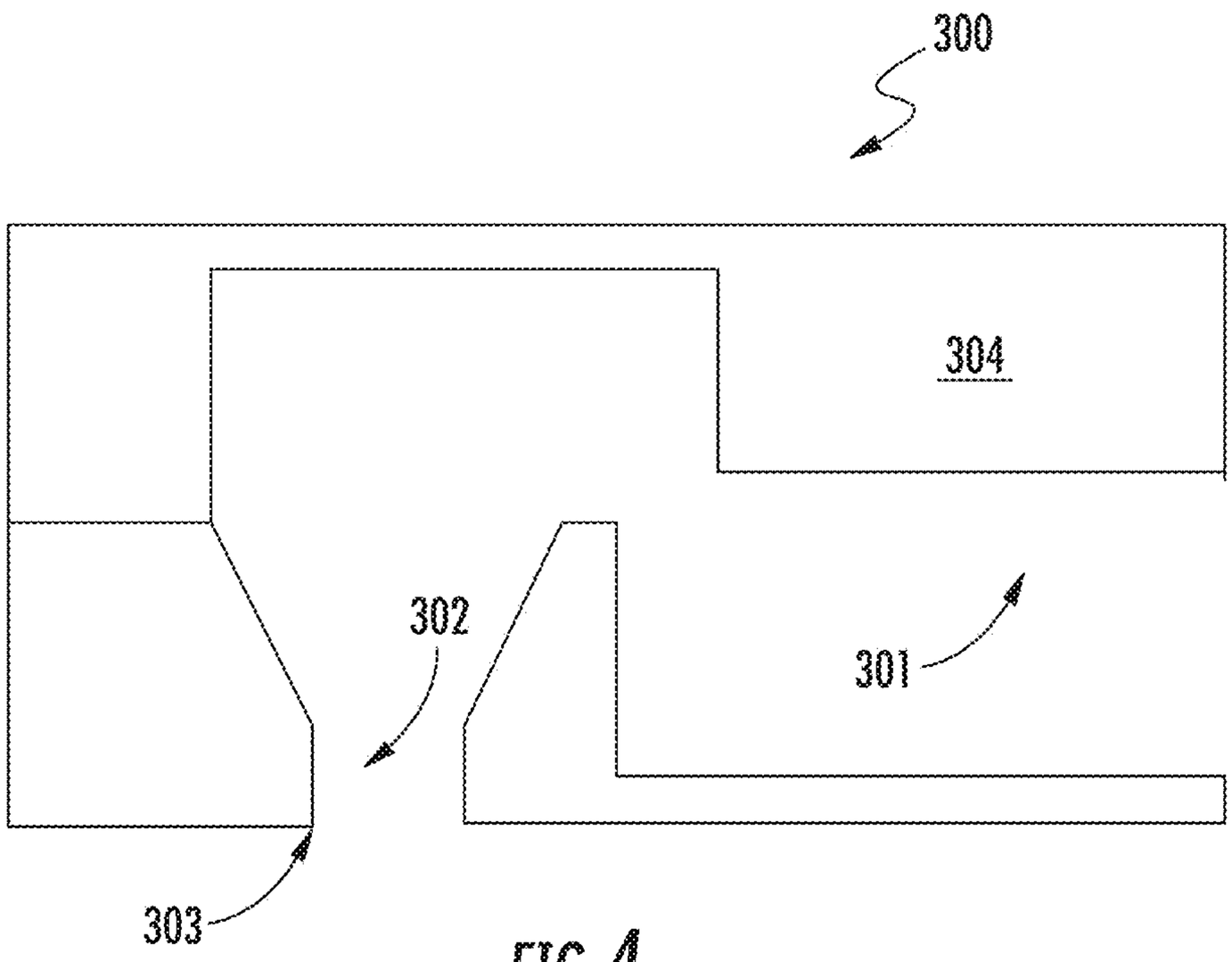


FIG. 4

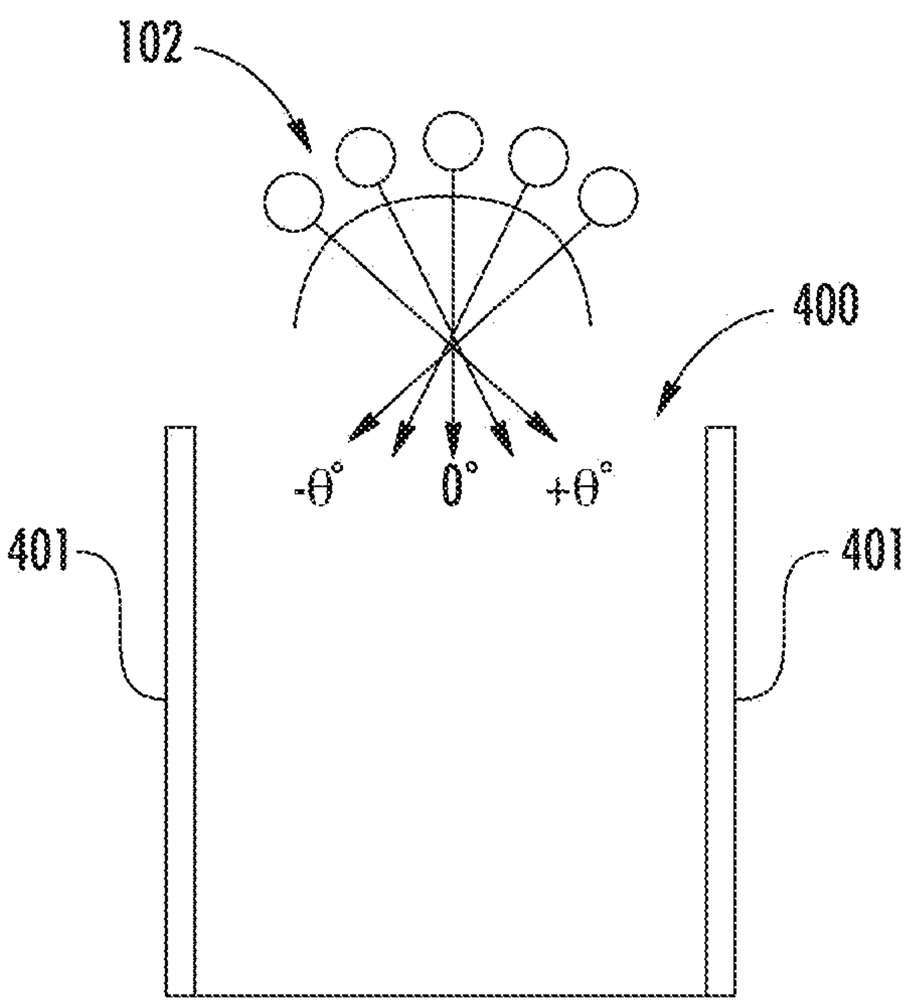


FIG. 5

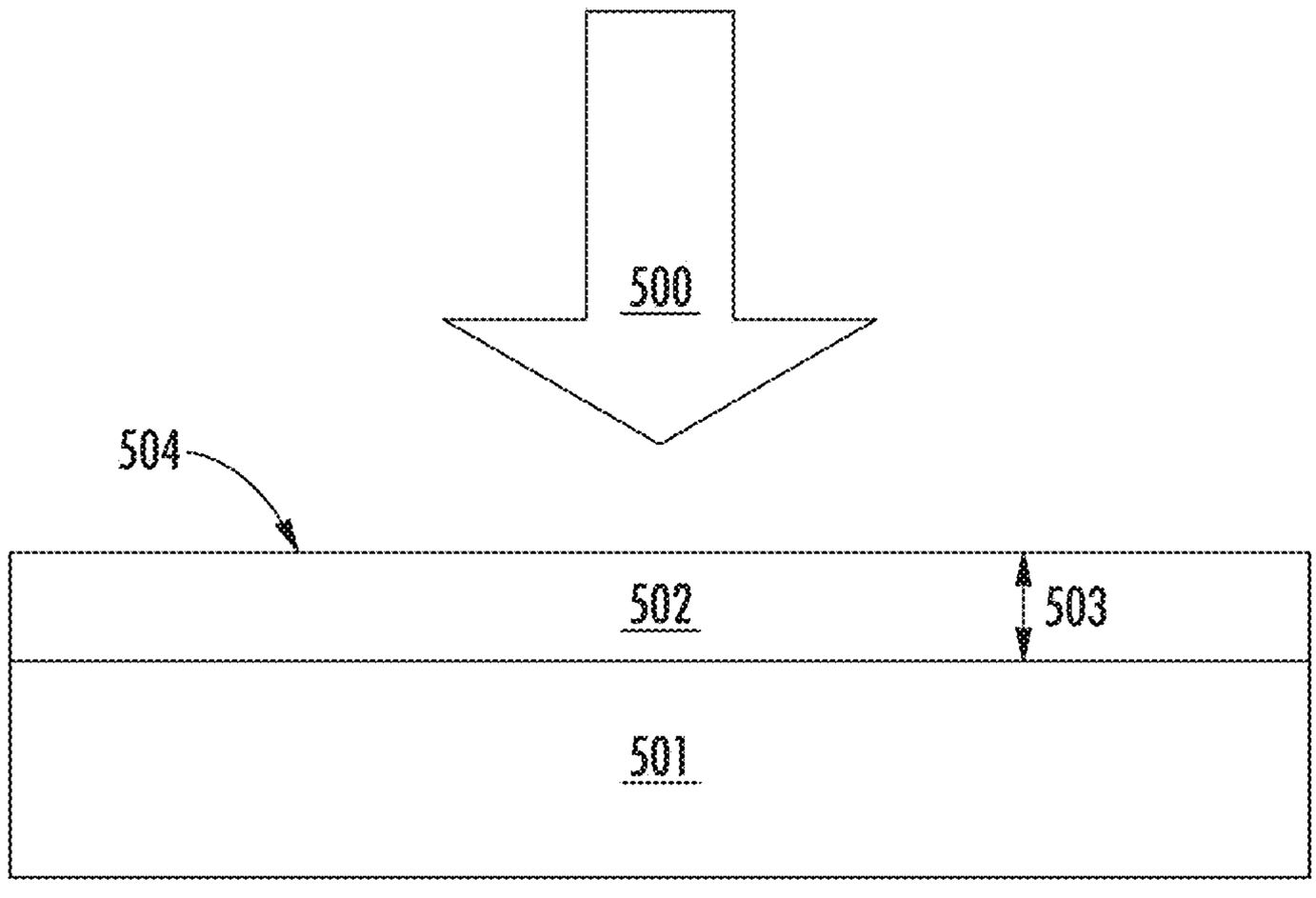


FIG. 6

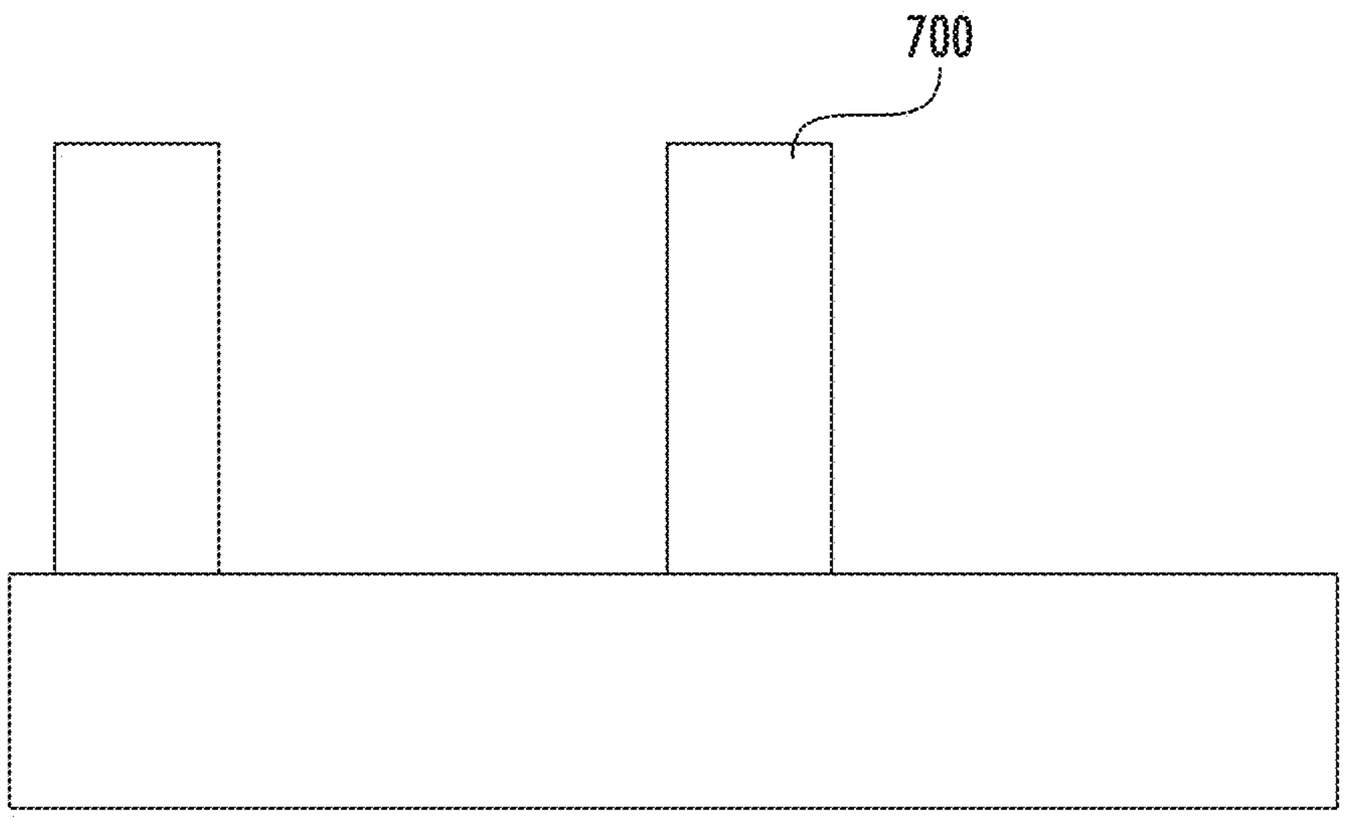


FIG. 7A
PHOTORESIST PATTERNED

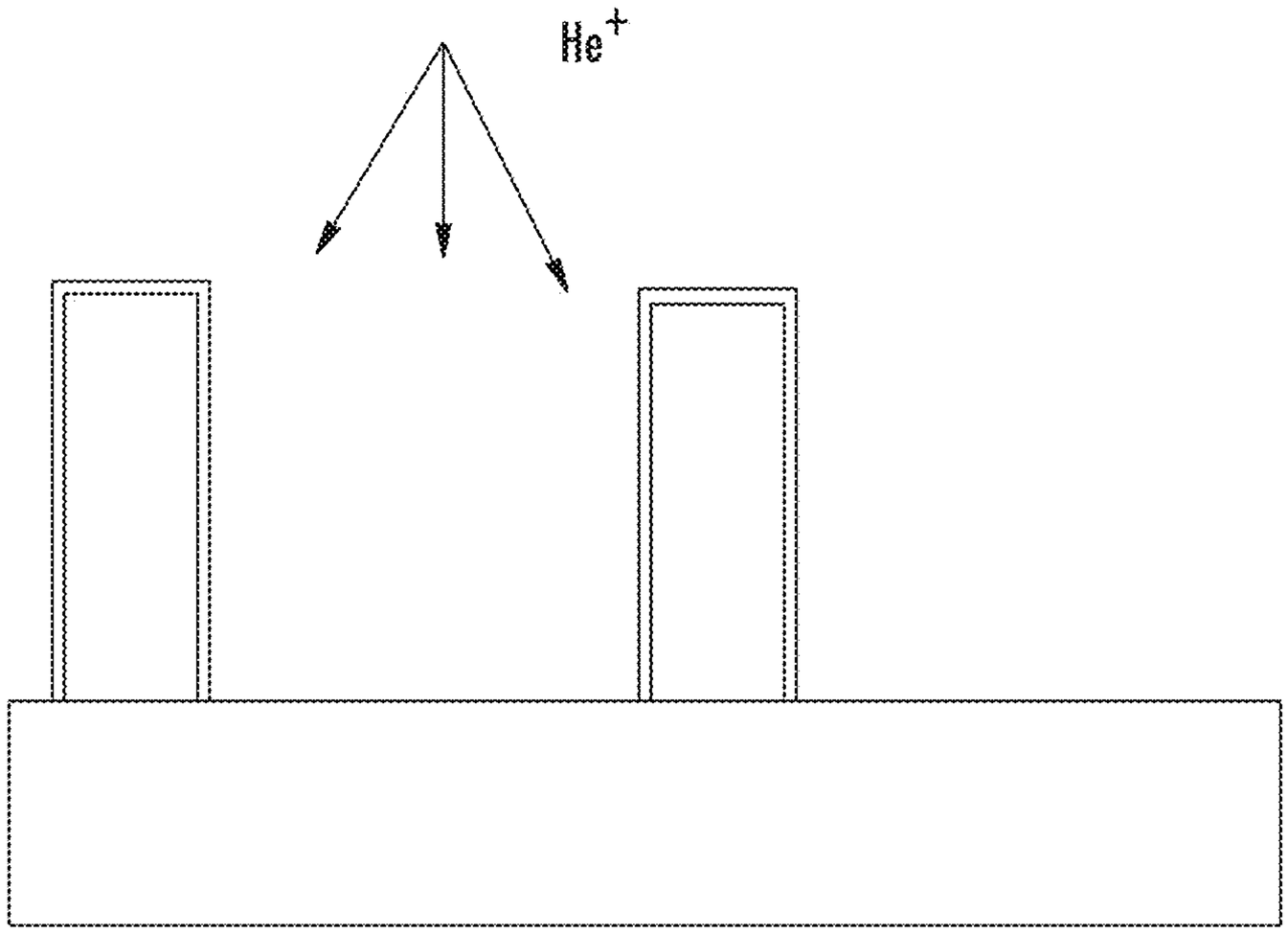


FIG. 7B
PHOTORESIST HARDENED WITH HELIUM IMPLANT

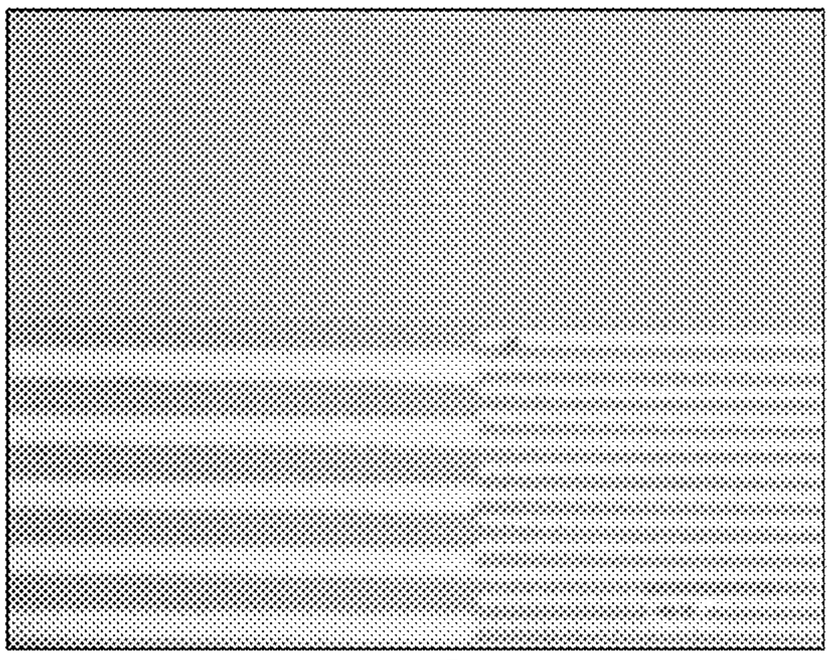


FIG. 8A
REFERENCE SAMPLE

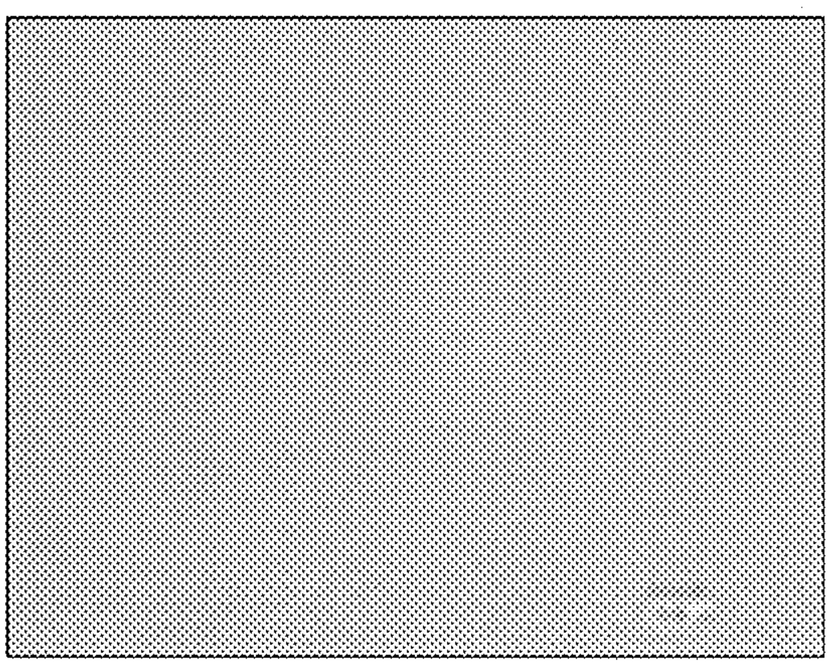


FIG. 8B
NO IMPLANT;
5 SEC ACETONE RINSE

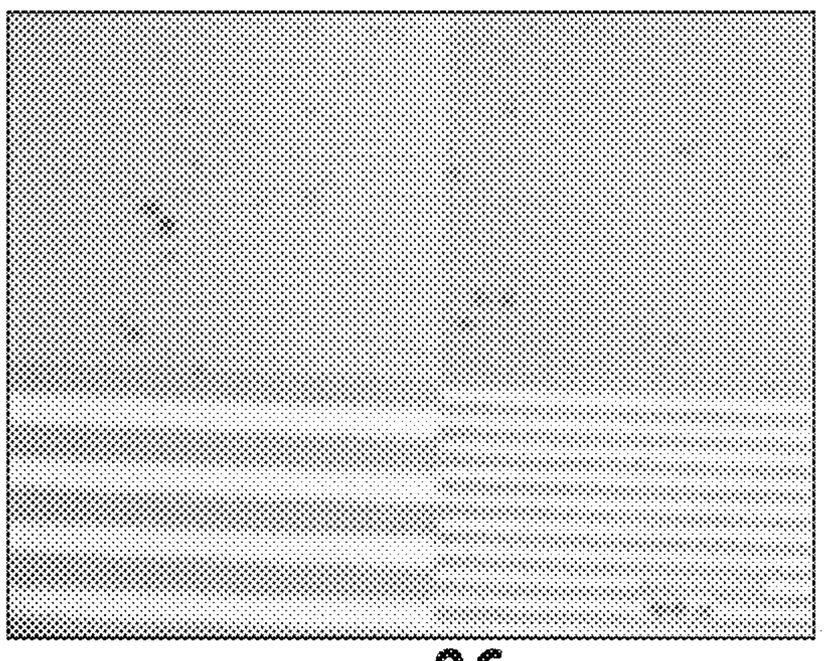


FIG. 8C
He IMPLANT;
5 SEC ACETONE RINSE

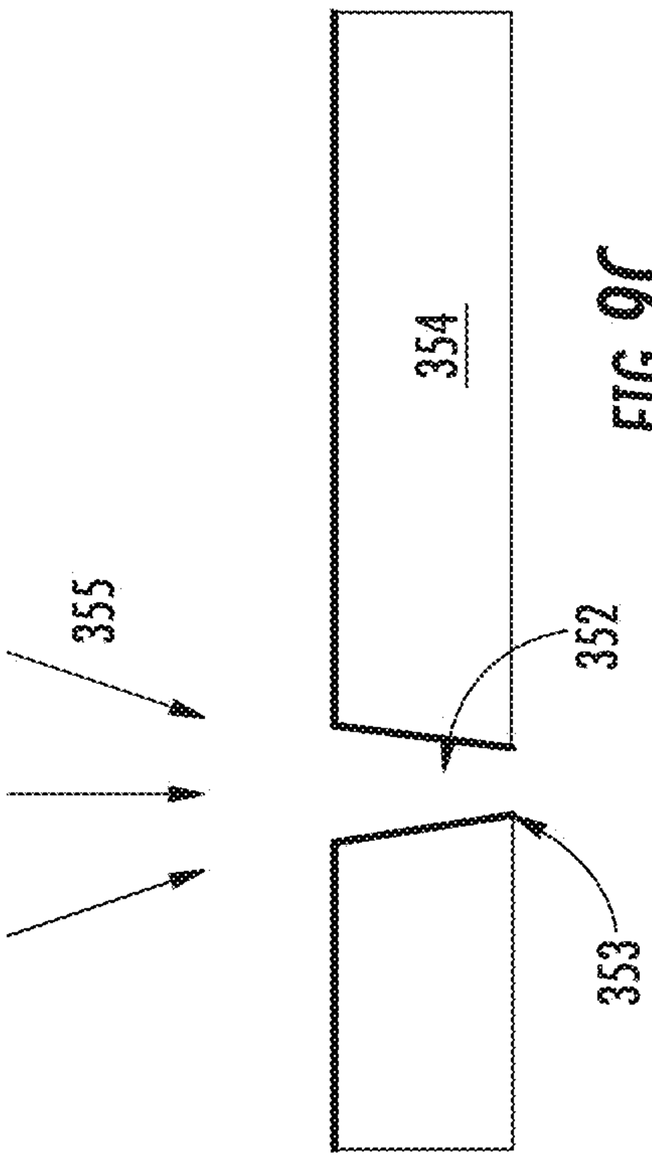


FIG. 9C

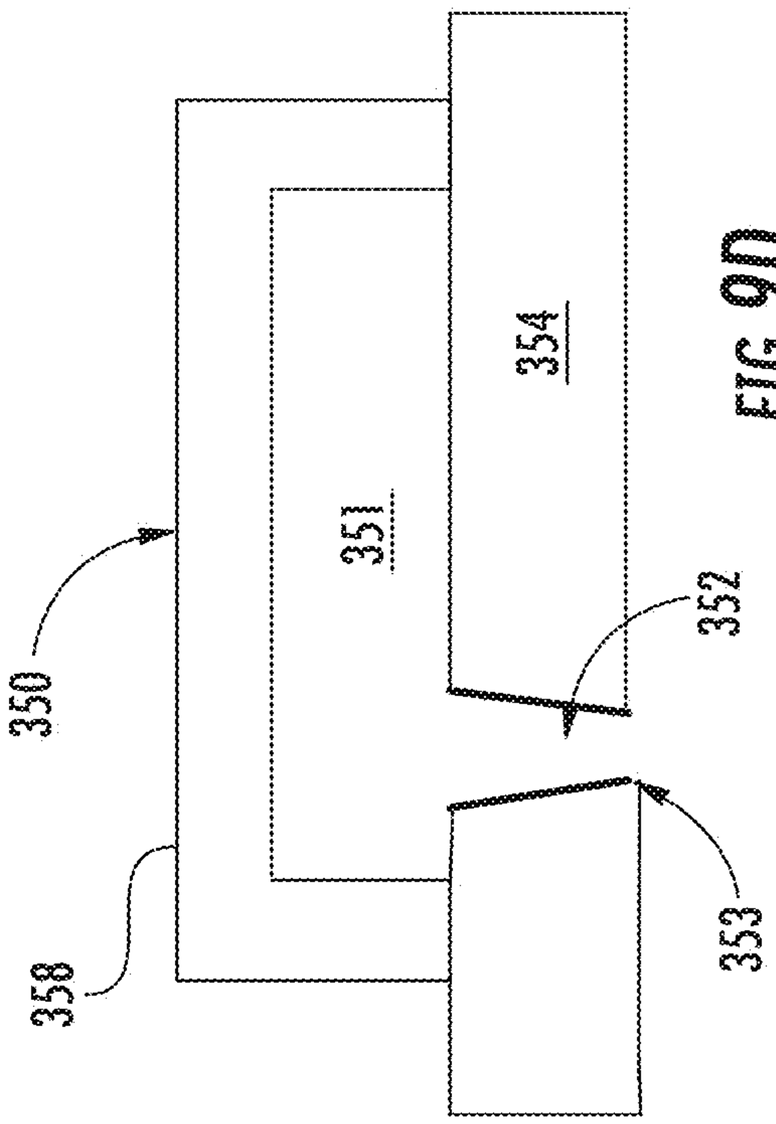


FIG. 9D

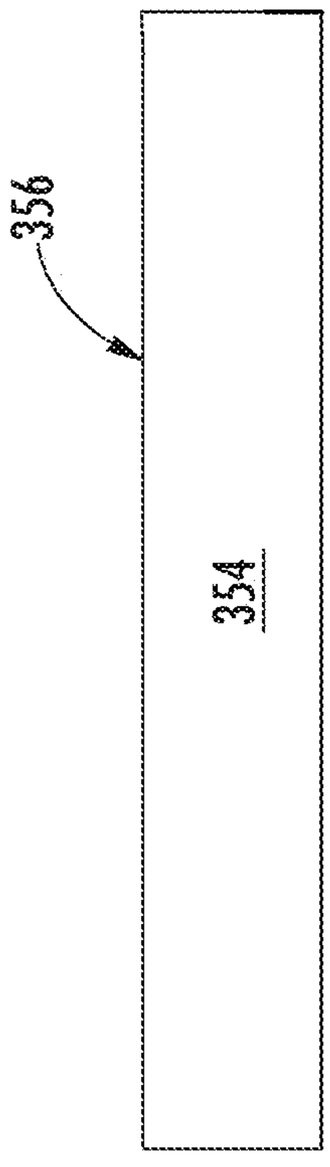


FIG. 9A

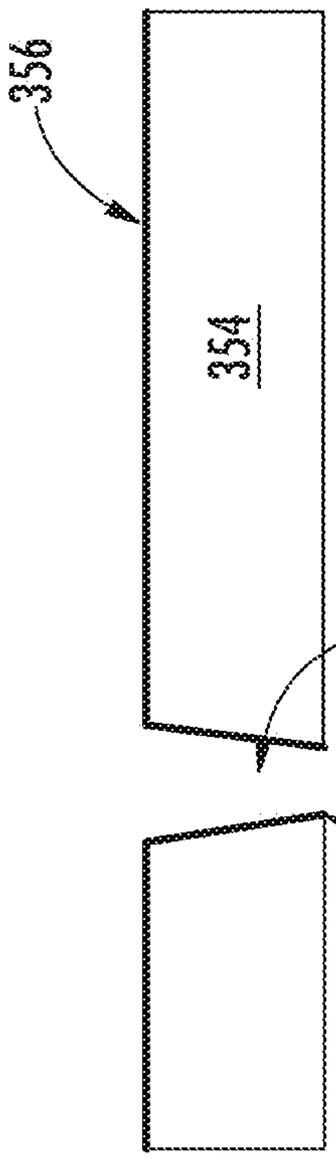


FIG. 9B

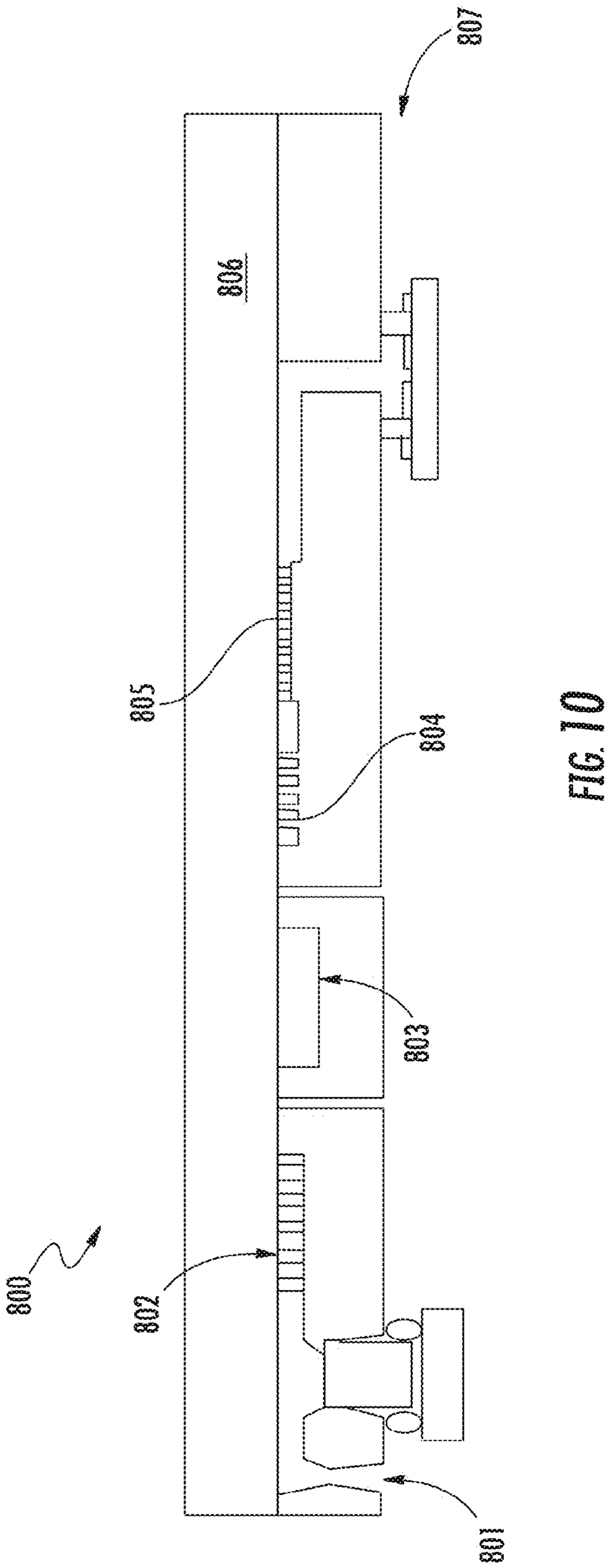


FIG. 10

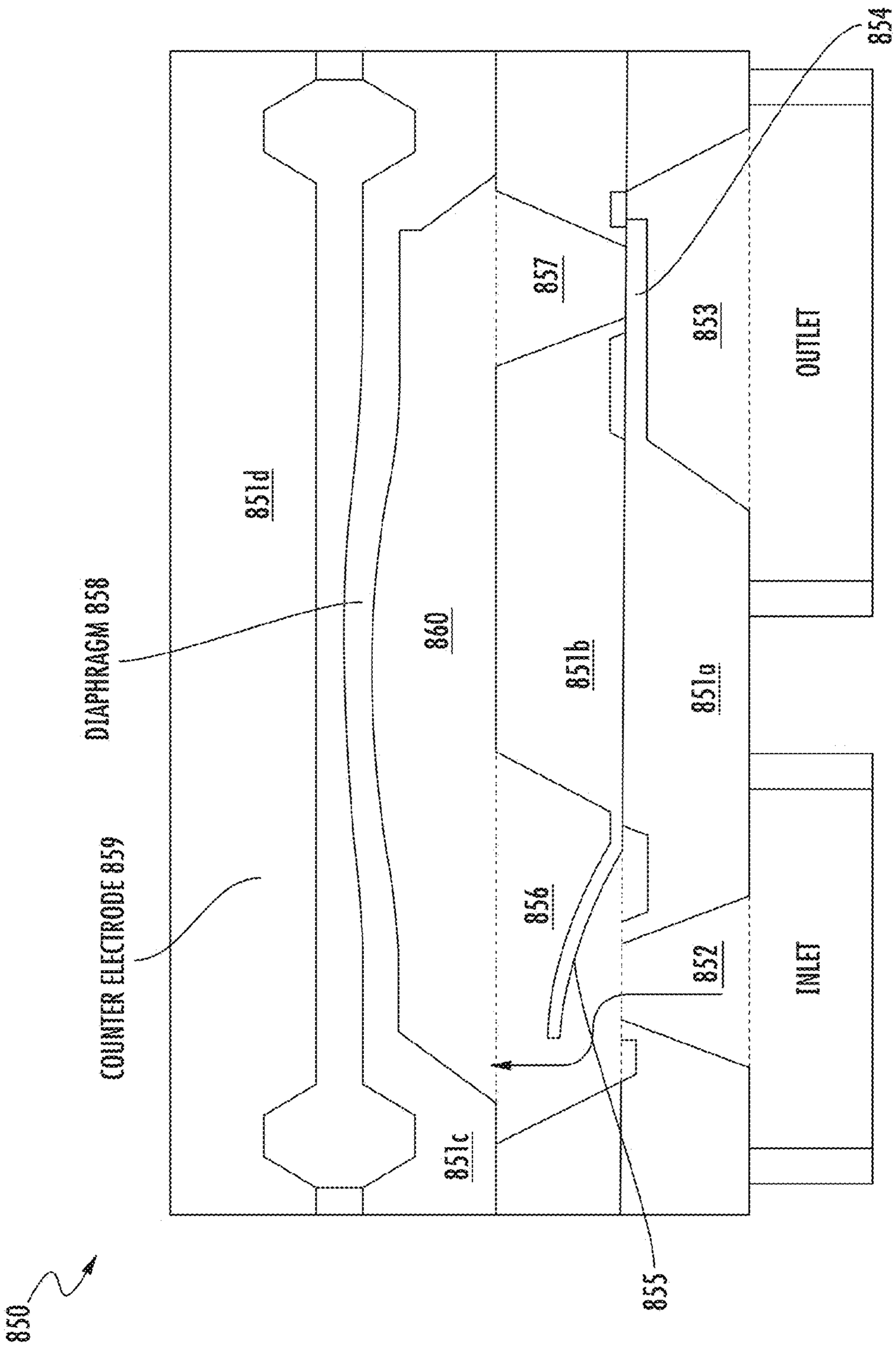

850
COUNTER ELECTRODE 859
DIAPHRAGM 858
851d
860
857
856
851c
851b
851a
853
852
854
855
OUTLET
INLET

FIG. 7I

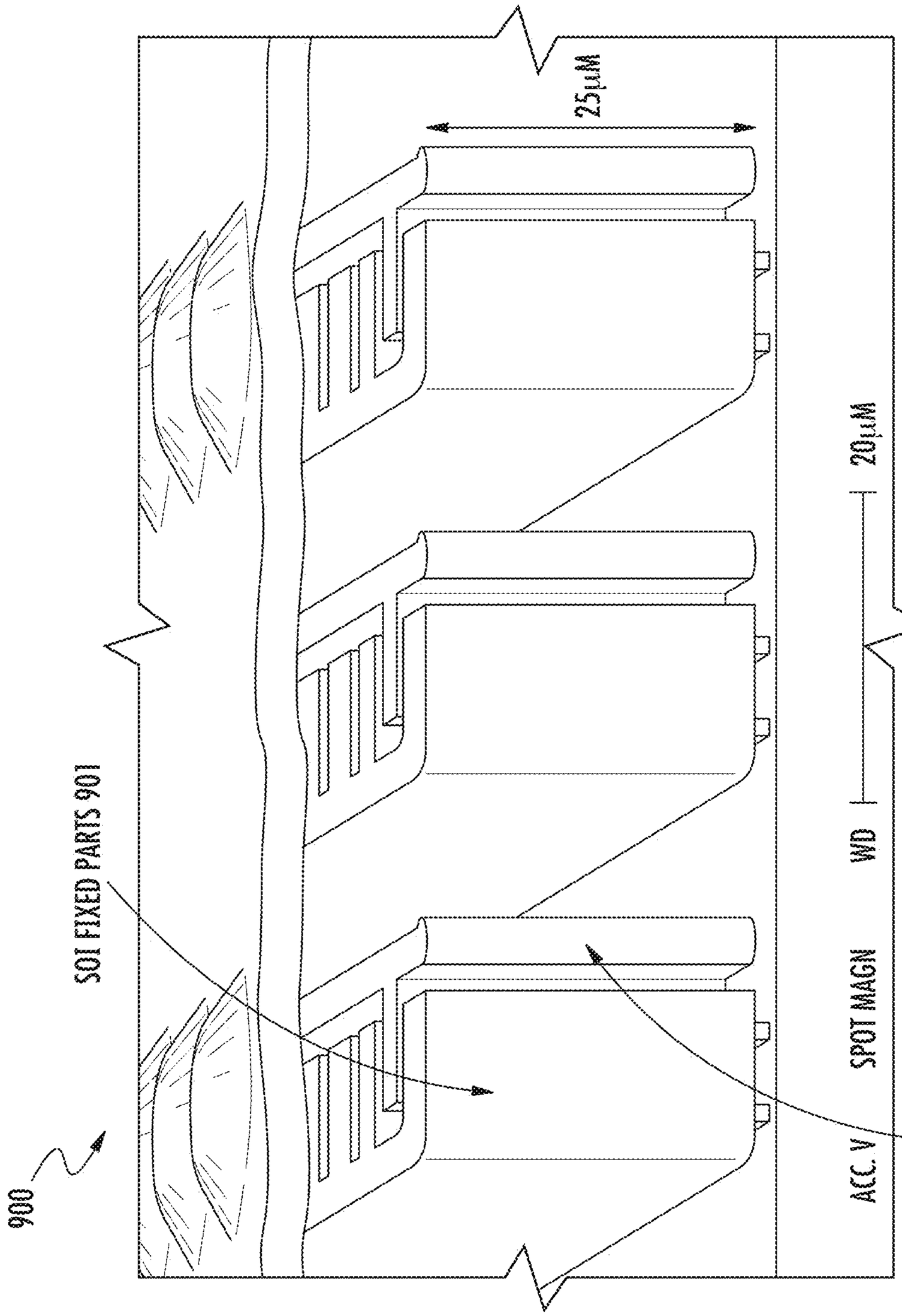

900
SOI FIXED PARTS 901
SOI MOVING PARTS 902
ACC.V
SPOT MAGN
WD
25μM
20μM

FIG. 12

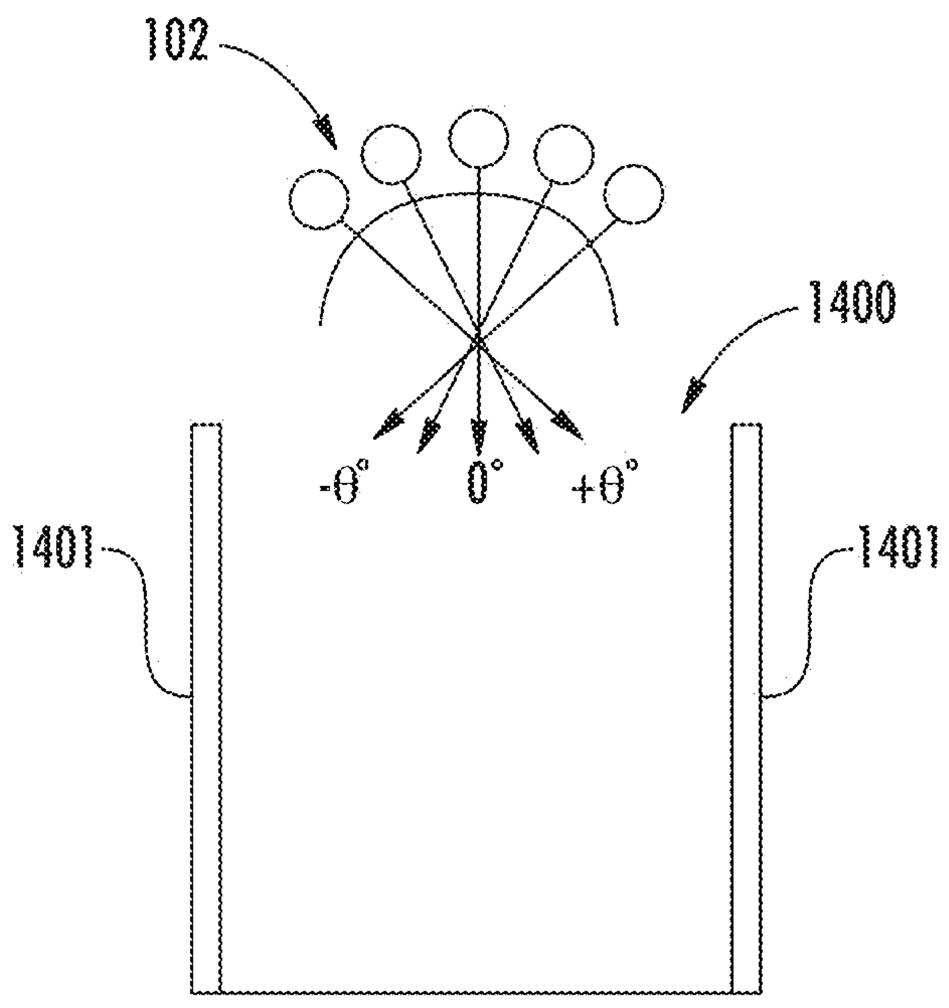


FIG. 13

METHODS OF AFFECTING MATERIAL PROPERTIES AND APPLICATIONS THEREFOR

[0001] This application is a divisional of U.S. patent application Ser. No. 13/470,731 filed May 14, 2012, which claims priority of U.S. Provisional Patent Application Ser. No. 61/486,296, 61/486,297 and 61/486,299, all filed May 15, 2011, the disclosures of which are all incorporated by reference in their entireties.

FIELD

[0002] This invention relates to ion implantation and, more particularly, to ion implantation for precision material modification.

BACKGROUND

[0003] Ion implantation is a standard technique for introducing material into a workpiece. A desired implant 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 affect both the surface and depth of the workpiece material under certain conditions.

[0004] While ion implantation is typically used to alter the electrical properties of a workpiece, it can also be used to affect other material properties, such as resistance to specific chemicals, adhesion, hydrophobicity, hydrophilicity, and others.

[0005] Inkjet printing is a technique that ejects liquid ink onto paper. The inkjet print head (or cartridge) has nozzles that are about the size of a needlepoint through which the ink is ejected. FIG. **1** is a view of an embodiment of an inkjet printer head **1**. In some embodiments, such as that shown in FIG. **1**, the head **1** may include multiple nozzles **2** to accommodate a plurality of colored inks **3**. The printing process may involve a nucleation step using the ink, bubble growth, ejection of an ink drop, and refilling of the inkjet head.

[0006] Printing resolution and lifetime are both limited by the inkjet aperture size. Smaller apertures can provide higher resolution, but the lifetime is reduced due to clogging of the aperture with the ink. Applying inkjet printing to new fields such as, for example, biochips, metal wiring, liquid crystal displays (LCDs), organic light-emitting diodes (OLEDs), or MEMS devices is being investigated. However, suitable printing heads are required for each application before widespread adoption can occur. For example, ejection of high viscosity ink droplets may need to provide high precision, high frequency, no chemical reaction, and no clogging. Thus, it may be beneficial to affect the properties of the material used to create the print head to minimize the interaction between the ink and the print head.

[0007] Another application where affecting material properties may be beneficial is MEMS and NEMS devices. MEMS devices relate to small mechanical devices driven by electricity. NEMS devices relate to devices integrating electrical and mechanical functionality on the nanoscale. Examples of these devices are accelerometers and gyroscopes, though there are countless others. MEMS and NEMS processing is extremely complex. One difficulty is that precise material modification to locally affect material properties has not been effectively demonstrated.

[0008] In addition, many materials would benefit from increased or modified chemical resistance. High energy ion implantation has been used in the past to affect chemical resistance of some materials. High energy implants may be time-consuming and may lead to increased manufacturing costs. These high energy implants also typically used exotic species such as Al, Mg, or Ti, which may be expensive. Furthermore, previous methods only treated a thick layer on the surface of the material and in some instances hardened the surface, which affected flexibility of the material.

[0009] Therefore, in each of these examples, it would be beneficial to have an improved method of precisely affecting material properties. Such an improved method could then be applied to various technologies, including inkjet printing, biochips and MEMS and NEMS devices, such as accelerometers, pressure sensors and gyroscopes.

SUMMARY

[0010] Methods of affecting a material's properties through the implantation of ions, such as by using a plasma processing apparatus with a plasma sheath modifier. In this way, properties such as resistance to chemicals, adhesion, hydrophobicity and hydrophilicity, may be affected. These methods can be applied to a variety of technologies. In some cases, ion implantation is used in the manufacture of printer heads to reduce clogging by increasing the material's hydrophobicity. In other embodiments, MEMS and NEMS devices are produced using ion implantation to change the properties of fluid channels and other structures. In addition, ion implantation can be used to affect a material's resistance to chemicals, such as acids.

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 view of an embodiment of an inkjet printer;

[0013] FIG. **2** is a block diagram of a plasma processing apparatus having a plasma sheath modifier;

[0014] FIG. **3** illustrates hydrophobic modulation;

[0015] FIG. **4** is a cross-sectional side view of an embodiment of a print head;

[0016] FIG. **5** is a cross-sectional side view of sidewall porous material formation;

[0017] FIG. **6** is a cross-sectional side view of a workpiece being implanted;

[0018] FIGS. **7**A-B represents an embodiment of helium implantation into a structure;

[0019] FIGS. **8**A-C show the results of implantation according to FIG. **7**;

[0020] FIGS. **9**A-D show a representative sequence to treat an inkjet print head;

[0021] FIG. **10** represents a typical biochip;

[0022] FIG. **11** represents a micropump;

[0023] FIG. **12** is an exploded view of the internals of an accelerometer; and

[0024] FIG. **13** is a cross-sectional side view of one embodiment of a 3D structure or feature being implanted.

DETAILED DESCRIPTION

[0025] The embodiments are described herein in connection with specific materials and devices, but these embodi-

ments should not be limited merely to the materials and devices listed. For example, some of the embodiments are described herein in connection with MEMS and NEMS, but these embodiments also may be used with other devices. Similarly, some of the embodiments are described herein in connection with printers such as inkjet printers, but these embodiments also may be used with other printing devices. These inkjet printers or other printing devices can be used for paper or other applications known to a person skilled in the art. While a specific type of implanter is disclosed, other ion implantation systems known to those skilled in the art that can focus an ion beam or that can implant particular regions of a workpiece with or without a mask on, above, or a distance from the workpiece also may be used in the embodiments described herein. While the term "hydrophobic" is used, throughout, it may be advantageous to render a surface hydrophilic instead. Thus, the invention is not limited to the specific embodiments described below.

[0026] While a beamline or plasma doping tool may be used to implant ions to affect a material's properties, a plasma processing apparatus having a plasma sheath modifier may be used. This has an advantage that selective implantation of 2D or 3D surfaces may be performed without using photoresist, other hard masks, or proximity masks. This sort of patterned implant reduces processing time and manufacturing costs. Scanning the workpiece or device to be implanted may be combined with biasing such a workpiece or device or changing the plasma parameters to accomplish this selective implantation.

[0027] FIG. **2** is a block diagram of a plasma processing apparatus having a plasma sheath modifier. The plasma **140** is generated as is known in the art. This plasma **140** is generally a quasi-neutral collection of ions and electrons. The ions typically have a positive charge while the electrons have a negative charge. The plasma **140** may have an electric field of, for example, approximately 0 V/cm in the bulk of the plasma **140**. In a system containing the plasma **140**, ions **102** from the plasma **140** are attracted toward a workpiece **100**. These ions **102** may be attracted with sufficient energy to be implanted into the workpiece **100**. The plasma **140** is bounded by a region proximate the workpiece **100** referred to as a plasma sheath **242**. The plasma sheath **242** is a region that has fewer electrons than the plasma **140**. Hence, the differences between the negative and positive charges cause a sheath potential in the plasma sheath **242**. The light emission from this plasma sheath **242** is less intense than the plasma **140** because fewer electrons are present and, hence, few excitation-relaxation collisions occur. Thus, the plasma sheath **242** is sometimes referred to as "dark space."

[0028] The plasma sheath modifier **101** is configured to modify an electric field within the plasma sheath **242** to control a shape of a boundary **241** between the plasma **140** and the plasma sheath **242**. Accordingly, ions **102** that are attracted from the plasma **140** across the plasma sheath **242** may strike the workpiece **100** at a large range of incident angles. This plasma sheath modifier **101** may be referred to as, for example, a focusing plate or sheath engineering plate.

[0029] In the embodiment of FIG. **2**, the plasma sheath modifier **101** includes a pair of panels **212** and **214** defining an aperture there between having a horizontal spacing (G). The panels **212** and **214** may be an insulator, semiconductor, or conductor. In other embodiments, the plasma sheath modifier **101** may include only one panel or more than two panels. The panels **212** and **214** may be a pair of sheets having a thin, flat shape. In other embodiments, the panels **212** and **214** may be other shapes such as tube-shaped, wedge-shaped, and/or have a beveled edge proximate the aperture. The panels **212** and **214** also may be positioned a vertical spacing (Z) above the plane **151** defined by the front surface of the workpiece **100**. In one embodiment, the vertical spacing (Z) may be about 1.0 to 10.0 mm.

[0030] Ions **102** may be attracted from the plasma **140** across the plasma sheath **242** by different mechanisms. In one instance, the workpiece **100** is biased to attract ions **102** from the plasma **140** across the plasma sheath **242**. In another instance, a plasma source that generates the plasma **140** and walls surrounding the plasma **140** are biased positively and the workpiece **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 **102** from the plasma **140** toward the workpiece **100**.

[0031] Advantageously, the plasma sheath modifier **101** modifies the electric field within the plasma sheath **242** to control a shape of the boundary **241** between the plasma **140** and the plasma sheath **242**. The boundary **241** between the plasma **140** and the plasma sheath **242** may have a convex shape relative to the plane **151** in one instance. When the workpiece **100** is biased, for example, the ions **102** are attracted across the plasma sheath **242** through the aperture between the panels **212** and **214** at a large range of incident angles. For instance, ions **102** following trajectory path **271** may strike the workpiece **100** at an angle of $+\theta°$ relative to the plane **151**. Ions **102** following trajectory path **270** may strike the workpiece **100** at about an angle of 0° relative to the same plane **151**. Ions **102** following trajectory path **269** may strike the workpiece **100** an angle of $-\theta°$ relative to the plane **151**. Accordingly, the range of incident angles may be between $+\theta°$ and $-\theta°$ centered about 0°. In addition, some ion trajectories paths such as paths **269** and **271** may cross each other. Depending on a number of factors including, but not limited to, the horizontal spacing (G) between the panels **212** and **214**, the vertical spacing (Z) of the panels **212** and **214** above the plane **151**, the dielectric constant of the panels **212** and **214**, or other process parameters of the plasma **140**, the range of incident angles (θ) may be between +60° and −60° centered about 0°.

[0032] The plasma processing apparatus of FIG. **2** can be used to affect the properties of a material. This technique can then be applied to various technologies, as described in more detail below.

[0033] In one embodiment, use of multi-angle ion implantation can modify the property of a nozzle, channel, and inkjet printer head. These may be fabricated of, for example, silicon, polymers, semiconductors, poly(dimethylsiloxane) (PDMS), SU8 photoresist or conductors. FIG. **3** illustrates hydrophobic modulation can be caused by ion implantation. The hydrophobicity of a surface was modulated after implants of NF_3 and CF_4 using a plasma doping tool. A reference material, shown in the center of FIG. **3**, has an initial contact angle of 41.58°. The accompanying illustration **22** depicts the shape of a droplet on the material. By implanting the material with NF_3, the contact angle was reduced to 15.08°, indicating that the material has become more hydrophilic. As shown in the upper illustration **21**, the droplet is more spread across the surface of the material. Conversely, the bottom illustration **23** shows the effect of a CF_4 implant. In this case, the contact angle increases to

103.07°, indicating a high degree of hydrophobicity. Using a multi-angle ion implant can enable changing the hydrophobic or porosity properties of either a 2D or 3D surface. This will allow the correct inkjet droplet properties for a particular printing application.

[0034] As shown in FIG. **3**, ion implant can change a surface to be hydrophobic or hydrophilic. Thus, the adhesion of the ink droplets to the surface can be changed. The chemical compatibility or chemical resistance of the surface also can be altered by physical changes to the implanted surface caused by ion implantation. Finally, different liquids may become suitable as inks using inkjet printing (polymers, special inks, metals, oils, nanoparticles, or others) by affecting adhesion or chemical compatibility. Besides enabling new printing applications, all this may lead to higher inkjet printer nozzle lifetimes.

[0035] FIG. **4** is a cross-sectional side view of an embodiment of a print head. Other designs known to those skilled in the art are possible. In one instance, the print head **300** is fabricated from a silicon workpiece through processes such as etching. The silicon devices or parts produced are then bonded to a cover **304** using an adhesion layer. This cover **304** may be metal, glass, SiO_2, Si, PDMS, or SU8. In another instance, the print head **300** is made of plastic.

[0036] The print head **300** has multiple surfaces. It has a channel **301** that leads to the nozzle **302**. It also has an exit area **303**, where the nozzle **302** meets the external environment. All or some of the surfaces of the channel **301**, the nozzle **302** and the exit area **303** may be implanted. These surfaces may be implanted with, for example, C, N, H, F, He, Ar, B, As, P, Ge, Ga, Si, Zn, Al, other noble gases, other p-type or n-type dopants, or other atomic or molecular species known to those skilled in the art. The implant depth may be less than 100 nm or, more particularly, between approximately 1 nm and 30 nm, with a surface peak or retrograde profile to modulate the surface energy.

[0037] In one instance, the entirety of the surfaces that contact the ink in the print head **300** is implanted. With a blanket implant, a multi-angle implant can enable implantation of a 3D structure. The nozzle **302** and the sidewalls and bottom of channel **301** may be implanted. The lower surface of the glass cover **304** also may be implanted. This enables liquid to flow without adhering or sticking to the bottom, sides, or top of the channel **301** or nozzle **302**.

[0038] In another instance, only a portion of the surfaces that contact the ink in the print head **300** is implanted. This portion may coincide with areas where clogging is common, where ink transport is desired, or other areas. In one particular embodiment, any corners of the print head **300** are implanted to prevent ink from being retained. The corners also may be implanted with a higher dose than other regions of the print head **300**.

[0039] Implanting the area where adhesion occurs between, for example, silicon and glass parts of the print head **300** may affect bonding between these two parts. Photoresist or selective implants may prevent this from occurring. In another instance, a selective implant is performed to render certain surfaces hydrophobic while a second selective implant is used to improve or enable the bonding step between the various workpieces.

[0040] The implant will reduce or prevent adhesion by the ink to the print head **300**. The ion species that is implanted may in part affect the hydrophobicity, as shown in FIG. **3**. Certain energy levels or doses during implantation may modify the lattice structure of the surfaces of the print head **300** in FIG. **4**, which also may in part affect the hydrophobicity. Other mechanisms due to implant that affect the hydrophobicity may be possible. Since these regions are implanted, they will remain hydrophobic even if cleaned because these implanted regions are an integral part of the surface of the print head **300** instead of a coating on the surface of the print head **300** that may be eroded or washed off. To maintain the hydrophobic state, at least a few monolayers of the surface are implanted. Uniformity of the dose and depth implanted regions may be controlled. If certain areas of the surface are implanted in a non-uniform manner or are not implanted at all, this may affect adhesion of the ink. In one embodiment, CF_4 is implanted at energies between 0.5 and 6.0 kV. In a further embodiment, the voltage is decreased over time to improve adhesion and provide interface mixing between the starting material and the new layer being created. In some embodiments, this material is implanted. In other embodiments, the material may be implanted and deposited.

[0041] In some instances, the inkjet printer head may need to be implanted to affect different regions in opposite ways. For example, referring to FIG. **9**D, the ink is stored in an ink chamber **351**. The path from the ink chamber **351** to the external environment passes through a nozzle **352**, and ultimately through an exit area **353**. Two important aspects of an inkjet print head **350** are the ability for the ink droplets to travel through the ink chamber **351** and nozzle **352** with minimal impedance, and the ability of the ink to not adhere to the exit area **353**, thus causing unwanted stains on paper and a clogged nozzle. These requirements demand that the interior of the nozzle **352** has the highest ink wettability and the outside surface near the exit area **353** has the lowest ink wettability. Current practices often rely on materials selection combined with CVD/PVD processes to deposit a wetting and/or anti-wetting layers on these surfaces. These types of surface treatment often have poor adhesion between surface deposition and the substrate, and can be difficult to apply to the small nozzle features without clogging the orifice. According to one embodiment, ion implantation technology is utilized, which produces high-strength interfaces with long service life time. Ion implantation can be precisely controlled, making it possible to fine tune wettability on different parts of the inkjet print head **350**. In addition, ion implantation can be used to process features in nanometer scales with excellent uniformity and is compatible with the existing microelectronics manufacturing processes. Ion implantation also enable longer lifetime of the inkjet print head **350**.

[0042] In operation, the print heat **350** is formed from a processed workpiece **354** and a cover **358**. The cover **358** may be glass or some other material and is applied to the workpiece **354** after processing. Referring to FIG. **9**A, the workpiece **354** may be of any suitable material, including silicon. The workpiece **354** may be etched to form the nozzle **352**, as shown in FIG. **9**B. The nozzle **352** may be formed so as to be wider at the top surface **356** than at the exit area **353**, which is defined as the area where the nozzle **352** meets the bottom surface. Often the dimension of the nozzle **352** is limited by the tendency of the ink to clog. After etching, it may be desirable to make the nozzle **352** hydrophobic. Thus, as shown in FIG. **9**C, a focused ion implant **355** using the plasma processing apparatus of FIG. **2**, for example, may be used to make this nozzle area **352** hydrophobic. As

described earlier, an implant of CF_4 may be used. In some embodiments, the exit area **353** is made to have a different level of hydrophobicity than the rest of the nozzle **352**. In some embodiments, the hydrophobicity may be varied by controlling the implant angle of the ions. This may also be done by performing another ion implant from the top surface **356**, or may be done via an ion implant from the bottom surface. Furthermore, in some embodiments, the rest of the top surface **356** may be treated to change the hydrophobicity of the top surface **356**. For example, the rest of the top surface **356** may be less hydrophobic than the nozzle **352**. After the implantation is performed, the print head **350** can be assembled by attaching the cover **358** to the workpiece **354**, as shown in FIG. **9**D.

[0043] The implanted region may densify the material of which the surface is composed. This densification is due to the material added to the lattice of the surface during implantation. The densification may affect hydrophobic or hydrophilic properties of the surface. For example in the case of polymer based MEMS/inkjet heads, such as PDMS and SU8, the implantation may break some of the bonds of the polymer and create a graphitic skin layer, which is denser than the original polymer. This can be done using inert gas or active species, such as carbon-based species.

[0044] Another application that would beneficial from affecting material properties is electromechanical devices, such as MEMS and NEMS devices. These devices use polymers of various designs and for various purposes. These polymers include, for example, SU8 photoresist, PDMS, polymethyl methacrylate (PMMA), or others known to those skilled in the art. All or part of the polymers may be frozen (i.e. the shape of the feature will not change after implantation) or hardened using ions. For example, in the case of implantation of resist, a conformal implant can freeze the resist such that it is capable of going through two litho processes for dual patterning lithography. In one instance, only part of a 2D or 3D polymer structure in a MEMS or NEMS device is implanted. For example, in a micro-valve, the fluid channel can be hardened or rendered more resistant to a liquid though implantation. The micro-valve membrane may be implanted with a different species or not implanted at all such that it does not get jammed. Thus, localized implantation and control of localized implantation is important both due to the scale of the devices and the different functions of these devices. This polymer hardening or freezing may involve implantation of inert species such as a noble gas or an active species such as Si, NF_3, C_xH_y, C_xF_y, SiF_4, SiH_4, disilane or CF_4. Of course, other species can be implanted.

[0045] MEMS and NEMS devices also may need sidewall smoothing. Masking steps or other processing steps may cause a large amount of roughness. Smoothing the sidewalls of, for example, a polymer can improve MEMS or NEMS device performance. A noble gas may be implanted to a depth between 1 nm and 100 nm, for example, and cause physical changes to the sidewall surface. Similar to polymer freezing or hardening, localized implantation and control of localized implantation is important both due to the scale of the devices and the different functions of these devices.

[0046] Metal films in the MEMS or NEMS device can be implanted to modulate the stress. These metal films may be extremely small. Patterned or selective implantation of these metal films can be accomplished without implanting neighboring or adjacent areas of the MEMS or NEMS device.

[0047] Localized processing of a MEMS or NEMS device can affect physical properties. For example, as described above for print heads, the hydrophobicity or porosity can be adjusted in all or part of a NEMS or MEMS device using ion implantation on either a 2D or 3D surface. The surfaces may be implanted with, for example, C, N, H, F, He, Ar, B, As, P, Ge, Ga, Si, Zn, Al, other noble gases, other p-type or n-type dopants, or other species known to those skilled in the art. These may be atomic or molecular ions that contain, for example, the ions previously listed or other species known to those skilled in the art.

[0048] In one instance, the entirety of a surface is implanted. In another instance, only a portion of a surface is implanted. For example, in a biochip or microfluidics device, a channel or region where a fluid will flow or collect can be implanted. This will affect whether the fluid adheres to the surface. Thus, to improve performance of a device, it may be desirable to identify regions where fluids pass, or are likely to get clogged. These identified regions can then be ion implanted to affect their hydrophobicity, reducing risk of clogging and improve device performance.

[0049] FIG. **10** shows a representative biochip. The biochip **800** may be used for single nucleotide polymorphism (SNP) detection in DNA. The biochip **800** includes a variety of different functions, which are physically separated in the device **800**. For example, fluids may enter the device **800** via an entrance **801**. This fluid may pass through a meander mixer with obstacles **802**. After sufficient mixing, the fluid enters a thermal chamber **803**. After being heated, the fluid enters a filter section, including a coarse filter **804** and a fast and selective micropillar filter **805**. These sections are each created by processing a suitable workpiece **807**. After the workpiece **807** is processed, it is covered, such as by a glass plate **806**.

[0050] These different functions within the device **800** may have differing requirements. For example, to enhance the mixing ability, it may be beneficial to affect the properties of the material in the meander mixer, but not in other areas. Furthermore, enhanced mixing may occur if the hydrophobicity within different regions of the meander mixer differ. A focused or patterned ion implant to selectively affect the hydrophobicity (or hydrophilicity) of various portions of the material in the meander mixer may enhance mixing. Similarly, the micropillar filter **805** may benefit from increasing hydrophobicity. Since the micropillars are very small features with high aspect ratio, conformally coating each of them, as is currently done, is ineffective. A conformal ion implant, using the apparatus of FIG. **2**, may affect the material properties without increasing the size of the individual micropillars. This ion implant enables a better control of the conformal treatment and the adhesion of the treatment to the micropillar with minimal increase of micropillar size. In addition, it may be advantageous to not affect the properties of other parts of the biochip **800**. For example, the thermal chamber **803** may not be treated at all. Of course, other variations are also possible. This only serves to illustrate the ability to selectively affect a material's properties on a very small scale to improve device performance. In addition, it would be advantageous if these treatments do not affect the bonding of the workpiece **807** to the glass cover **806**. These precise treatments of the regions may be important in this respect.

[0051] FIG. **11** shows another example of a MEMs device **850**. This device is a micropump, and includes a number of

individual workpieces **851***a-d* which all affixed to each other after processing to form the pump **850**. The lower workpiece **851***a* includes an inlet area **852**, an outlet area **853** and an outlet membrane, or flap **854**. The first intermediate workpiece **851***b* includes an inlet membrane or flap **855**, an inlet area **856**, and an outlet area **857**. The second intermediate workpiece **851***c* has a movable diaphragm **858**. The top workpiece **851***d* has a counter electrode **859**. In operation, the diaphragm **858** moves upward, creating a partial vacuum in the chamber **860**. This causes liquid to push the inlet membrane **855** upward, allowing fluid to pass through the inlet areas **852**, **856** and into the chamber **860**. When the diaphragm **858** moves downward, it forces the fluid in the chamber **860** to push the outlet flap **854** downward, allowing the fluid to exit the outlet areas **857**, **853**. For proper operation, it may be beneficial to affect those parts of the device which are movable, such as the material that comprises the inlet membrane **855** and the outlet flap **854**. It may be beneficial to insure that these portions do not adhere to the other portions of the workpieces **851***a-d*. This may involve changing the adhesion properties or hydrophobicity of the membranes **854**, **855**, or the portions of the workpieces that contact these membranes **854**, **855**. It may also be beneficial to treat the diaphragm **858** to insure that it does not adhere to the counter electrode **859**. Alternatively, the counter electrode **859** may be treated. In some embodiments, treatments for the micropump are focused only on a portion of the workpiece so that other portions are not treated at all, or may receive a different treatment.

[0052] As described above, the implant will reduce or prevent adhesion by a fluid. 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 surfaces, which also may in part affect the hydrophobicity. Other mechanisms due to implant that affect the hydrophobicity may be possible. The implanted regions will remain hydrophobic even if cleaned because the implanted regions are part of the surface instead of a coating on the surface that may be eroded or washed off. To maintain the hydrophobic state, at least a few monolayers of the surface may be implanted. Uniformity of the dose and depth implanted regions may be controlled.

[0053] MEMS and NEMS devices can include any micro or nano mechanical device. This includes accelerometers, gyroscopes, sensors, micro-actuators (such as micro-pumps, micro-flaps, micro-valves, optical switches, or mirrors), thermalactuators, micromirrors, micro-resonators, piezoelectric detectors, cantilevers, microbalances, pressure sensors, bio-MEMS, biosensors, chemosensory, microphones, electrostatic motors, microfluidics devices, interferometric modulator displays, pico projectors, RF MEMS antennas, RF filters, RF MEMS phase shifters, or other devices. Other localized blanket or patterned implants, etching, or deposition steps also can be performed on a MEMS or NEMS device. Electrical, optical, or magnetic properties also can be affected by these implants or treatments. Focused multi-angle processing can be performed on a 2D or 3D device. In some instance, localized regions down to approximately 5 μm feature size can be treated.

[0054] While much of this disclosure describes implanting ions into a surface, the disclosure is not limited to this embodiment. For example, the apparatus of FIG. **2** may be used to add coatings or layers to an existing feature or structure. FIG. **5** is a cross-sectional side view of sidewall porous material formation. Certain MEMS and NEMS devices require sidewall porous material formation, but the small dimensions make deposition difficult. For example, silicon, porous silicon, diamond-like carbon, or other materials may be formed on a sidewall. Ions **102** are used to form a layer **401** on the sidewalls of the feature **400**. The layer **401** may be between 5 nm to 100 nm thick, for instance. This can be performed by adjusting the angles of the ions **102**. In some instances, forming a layer on the base of the feature **400** or only on one sidewall of the feature **400** is possible. Different thicknesses of the layer **401** are possible on different surfaces by adjusting the angle spread of the ions **102** or the relative doses within the angle spread of the ions **102**.

[0055] This porous material formation may occur on many types of device. For example in one embodiment, the sidewalls of an accelerometer **900** are treated to add porous material, as shown in FIG. **12**. Capacitance, or sensitivity, of an accelerometer is proportional to surface area. Increased surface area of the accelerometer sidewall can make it more sensitive to movements. Since porous materials have a much larger surface area than planar surfaces, this can significantly increase the sensitivity of the device **900**. In some embodiments, one or both of the SOI fixed parts **901** and the SOI moving parts **902** are treated to add porous material on their sidewalls.

[0056] Porous material deposition can be used to form a protective layer around a device. In one embodiment, devices intended for placement in the body may be coated using the apparatus of FIG. **2** to make them biocompatible. Devices can also be coating to change other properties, such as hydrophobicity.

[0057] In yet other embodiments, it may be beneficial to use ion implantation to affect the material's resistance to various chemicals. In one embodiment, the treatment disclosed herein uses a low energy implant, which is faster and less complex than a high energy implant. These embodiments also only may affect the first 0 to 100 nm of a material, though other depths are possible. By only affecting a small layer of the implanted material, less of the overall material will have its properties changed and the flexibility of the material is not negatively impacted. Thus, the properties at the surface of the material may be affected without affecting the entire workpiece. This may be advantageous, in that it is possible to change the chemical resistance of some materials or devices without affecting their flexibility.

[0058] FIG. **6** is a cross-sectional side view of workpiece being implanted. The workpiece **501** may be composed of, for example, polymer, glass, plastic, insulators, metals, or other materials. While the workpiece **501** may have a 2D or planar surface **504** as illustrated in FIG. **6**, this implant also can apply to 3D structures. With such a 3D structure, a multi-angle implant can treat all surfaces of the 3D structure. Also, while the entire surface **504** is illustrated as being treated with the ions **500**, a selective or patterned implant may be performed. A selective implant will scan the surface **504** with respect to the ions **500** and adjust the bias to the surface **504** (or workpiece **501** containing the surface **504**) or plasma conditions such that only a portion of the surface **504** is implanted.

[0059] The ions **500** form an implant region **502** that penetrates the surface **504** of the workpiece **501**. The depth of the implant region **502** (i.e. dimension **503**) may be between approximately 0 to 100 nm, for example. The implant profile can be Gaussian or a surface peak to accom-

modate different chemical resistance properties. The ions **500** may be, for example, a noble gas or other inert species, though other species are possible. In one instance, the ions **500** are Ar, Ne, Kr, Xe or He and these ions break some of the bonds on the surface **504** and in the implant region **502** that make this surface **504** sensitive to certain chemicals. Thus, the workpiece **501** has its surface properties altered. Cross-linking of the surface **504** also may be affected by the low energy implantation. For example, lactone or ester groups of a polymer can be destroyed using such a low energy plasma treatment. In yet another embodiment, an active species is used for the implant, such as N_2, H_2, NF_3 C_xH_y, C_xF_y, SiF_4, SiH_4, disilane or CF_4. This active species can be implanted to cause a chemical change in the surface **504**. This may be used instead of or to supplement the physical changes caused by the implant.

[0060] FIG. **13** is a cross-sectional side view of one embodiment of a 3D feature **1400** being implanted. The incidence angles of the ions **102** are used such that implant regions **1401** are formed only on the sidewalls of the 3D structure **1400**. Of course, only the base of the 3D structure **1400** may be implanted in an alternate embodiment. In yet another embodiment, the sidewalls and base of the 3D structure **1400** are implanted to different depths or with different doses. This can be accomplished, for example, by adjusting the angle spread of the ions **102** or relative doses of ions **102** within the angle spread. Other 3D structures are possible and selective implant can be performed on only some surfaces while other surfaces are not treated. In some cases, only one side of the feature needs to be implanted. An example of this may be MEMS sensors.

[0061] In one particular embodiment, a sealing layer is placed on a surface using a helium (He) implant. This implant with He reduces sputtering and damage to the areas below the implant region. In one instance, this can be used with polymers. This sealing layer may be between 1 nm and 30 nm in one instance and may break some bonds of the surface to change the local composition.

[0062] Experiments have shown that implanting He into a polymer layer can affect chemical resistance. In the experiment, the polymer was not resistant to acetone prior to the implant but was resistant to acetone after the implant. FIGS. **7**A-B represents an embodiment of He implantation into a structure. In FIG. **7**A, the polymer, in this case photoresist, is patterned. In this embodiment, the photoresist patterning comprises a series of vertical walls **700**. In FIG. **7**B, the photoresist is then implanted with helium to harden the polymer. FIG. **8**A shows the patterned photoresist. Vertical walls of various thicknesses are created on the workpiece. FIG. **8**B shows a workpiece, which did not undergo the process of FIG. **7**B, after a 5 second acetone rinse. Without treatment, the polymer was removed from the sample in acetone. FIG. **8**C shows a workpiece, which underwent the process of FIG. **7**B. With a He implant, the polymer remained intact after an acetone treatment. Thus, the pattern shown in FIG. **8**C is the same as that of the unrinsed reference sample, shown in FIG. **8**A. This He implant can be combined with CF_4 to make the resulting polymer hydrophobic as well.

[0063] The ability to affect chemical resistance has other important applications as well. For example, for industrial printing technology, such as solar metal contact printing, printed electronics, flexible electronics and other application, there is a need for solvent based ink. Because of this, the material used in the printer heads needs to be also compatible with these aggressive liquids. Traditional polymer based cavity and channel may not be compatible. Thus, by introducing an ion implantation, as described above, the hydrophobicity requirement may be maintained while increasing the resistance to chemicals, such as these inks.

[0064] In some embodiments, ultraviolet (UV) light can be used to improve the chemical resistance. Plasma often generates light at various frequencies. Therefore, the light and UV emitted from the plasma additionally can affect chemical resistance by breaking some of the bonds in the polymer. The frequency of the light may be tunable by using different extraction plate materials. In some embodiments, the extraction plate acts as a light filter, when different materials will have different transparencies. Thus, selection of an appropriate material for the extraction plate may change the frequencies which the polymer is exposed to. Therefore, if the materials that surround the plasma or are disposed between the plasma and the implanted workpiece can be selected to transmit certain types of UV light, this energy can supplement the implanted ions.

[0065] One advantage of some of the embodiments described herein is that feature dimensions of the structure or surface may the same after the implant. Unlike other treatments, one or more layers are not added to the surface. Instead, the surface itself is affected. A second advantage is that the ions can smooth a surface using certain implant parameters. This may or may not affect the dimensions of the surface. The scale of the smoothing can vary with the implant parameters.

[0066] Print heads, microfluidics, MEMS devices, NEMS devices or biomedical applications may need chemical resistance when designed to transport liquid from one region to another. This liquid may be an industrial chemical, water, a bodily fluid, or other material. These devices may be 3D structures with high aspect ratios. A third advantage is that the embodiments described herein can enable the dimensions to remain small (or totally unaffected) while providing total or patterned chemical resistance.

[0067] Although reference is made to MEMS devices, NEMS devices and inkjet printer heads, other devices also can benefit. For example, organic light-emitting diodes (OLEDs) can be treated between each organic layer. During production of OLEDS, a first organic layer is deposited by spin coating and then baked. A second organic layer is then deposited. The solvent from the second organic layer may attack the first organic layer. Therefore, implantation of the first organic layer to render it more chemical resistant can improve OLEDs. Other devices that transport or carry liquids or have interfaces between organic layers can also benefit.

[0068] In addition, other materials, such as gloves, boots, fabric, protective clothing, or protective equipment, can be rendered more resistant to chemicals such as, for example, acid. Inkjet printer cartridges, heads, or nozzles can be rendered more resistant to certain inks or chemicals. Other devices or materials also can be implanted to affect chemical resistance.

[0069] 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.

What is claimed is:

1. A method of affecting a workpiece's chemical resistance, comprising:

performing a low energy implant of a species into part of a surface of a workpiece, wherein the species comprises a noble gas.

2. The method of claim **1**, wherein the surface comprises a 3D feature.

3. The method of claim **2**, where the part of the surface comprises a sidewall of the 3D feature.

4. The method of claim **1**, wherein the workpiece comprises a material selected from the group consisting of polymer, glass, plastic, insulators and metal.

5. The method of claim **1**, wherein a depth of the low energy implant is between 1 and 100 nm.

6. The method of claim **1**, wherein bonds on the surface of the workpiece are broken by the low energy implant of the species.

7. The method of claim **1**, wherein the low energy implant of the species creates an implant region in the workpiece, and bonds in the implant region are broken by the low energy implant of the species.

8. The method of claim **1**, wherein the low energy implant has a Gaussian implant profile.

9. The method of claim **1**, wherein the low energy implant has a surface peak implant profile.

10. The method of claim **1**, wherein the workpiece comprises a polymer; and lactone or ester groups of the polymer are destroyed by the low energy implant of the species.

11. The method of claim **1**, wherein the species comprises helium and a sealing layer is created on the surface of the workpiece by the low energy implant.

12. The method of claim **11**, wherein the workpiece comprises a polymer.

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