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(54) Titre : PROCEDE DE NETTOYAGE D'UN ARTICLE
(54) Title: METHOD FOR CLEANING AN ARTICLE

(57) Abrégé/Abstract:
A method for cleaning an article includes the steps of contacting the article with a solvent fluid that includes carbon dioxide, whereby contaminants on the article dissolve in the solvent fluid and displacing the solvent fluid with a displacing fluid, that is other than carbon dioxide. In one aspect, the displacing fluid is at a temperature and pressure sufficient to prevent forming a second phase in the solvent fluid being displaced and at least a portion of the carbon dioxide is recycled to the article. In another aspect, the pressure of the solvent fluid is reduced prior to its displacement with the displacing gas.

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(54) **Title:** METHOD FOR CLEANING AN ARTICLE

(57) **Abstract:** A method for cleaning an article includes the steps of contacting the article with a solvent fluid that includes carbon dioxide, whereby contaminants on the article dissolve in the solvent fluid and displacing the solvent fluid with a displacing fluid, that is other than carbon dioxide. In one aspect, the displacing fluid is at a temperature and pressure sufficient to prevent forming a second phase in the solvent fluid being displaced and at least a portion of the carbon dioxide is recycled to the article. In another aspect, the pressure of the solvent fluid is reduced prior to its displacement with the displacing gas.

METHOD FOR CLEANING AN ARTICLE

RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Application No. 60/346,507, filed January 7, 2002. The entire teachings of the above application is incorporated herein by reference.

BACKGROUND OF THE INVENTION

The manufacture of contaminant-sensitive articles often requires the use of one or more solvents to remove impurities from the article. Traditionally, those solvents have been used in liquid phase. Recently, the use of supercritical carbon dioxide as a replacement for liquid solvents has been growing in popularity. Employing supercritical carbon dioxide often results in reduced water consumption, reduced waste streams, reduced emissions, and/or enhanced solubility characteristics. In the area of semiconductor manufacturing, supercritical carbon dioxide has been utilized for many applications, such as photo-resist developing, photo-resist stripping, wafer cleaning, and wafer drying.

Generally, supercritical fluids are fluids which are above their critical pressure and temperature, and have both gas- and liquid-like properties. Solvent properties of a supercritical fluid, such as supercritical carbon dioxide, depend on the fluid density, which in turn dependents on the pressure/temperature conditions of the fluid. For many organic impurities, the solvating properties of carbon dioxide decrease as the pressure of the fluid is reduced from supercritical to a lower pressure, for instance to atmospheric pressure, as occurs during depressurizing a chamber employed in a cleaning operation. For high purity cleaning operations, such as found in wafer manufacture or processing or during fabrication or processing of optics and other workpieces or substrates, impurities that precipitate out of the carbon dioxide solvent, as the pressure is reduced, can impact the surface being cleaned, thereby contaminating it and thus reducing the effectiveness of the cleaning process.

Therefore, a need exists for a method for cleaning an article, such as a wafer or another workpiece that reduces or minimizes the above-referenced problems.

SUMMARY OF THE INVENTION

The invention is generally related to a method for cleaning an article by contacting an article with a solvent fluid that includes carbon dioxide, thereby removing impurities from the article, and displacing the solvent fluid with a displacing fluid. The displacing fluid is other than carbon dioxide. In one embodiment, the article is a wafer and displacing is conducted at a temperature and pressure sufficient to prevent forming a second phase in the solvent fluid. In another embodiment, displacing is conducted at a temperature and pressure sufficient to prevent forming a second phase in the solvent fluid being displaced and carbon dioxide is recycled to the fluid.

In yet another embodiment, the invention is directed to a method for reducing deposition of non-volatile residues during a workpiece cleaning operation. The method includes the steps of contacting the workpiece with a solvent fluid at a first pressure, the solvent fluid including carbon dioxide, whereby contaminants on the workpiece are removed by the solvent fluid; reducing the pressure of the solvent fluid, whereby non-volatile residues become insoluble in the solvent fluid; and displacing the solvent fluid at the reduced pressure with a displacing gas that is other than carbon dioxide, whereby the time that the workpiece is exposed to insoluble non-volatile residues is reduced, thereby reducing deposition of insoluble non-volatile residues on the workpiece.

In a further embodiment, the invention is directed to a method for supplying cleaning fluids to a vessel. The method includes the steps of supplying a solvent fluid stream at a first pressure to a vessel housing a article, wherein the solvent fluid includes carbon dioxide and is capable of dissolving contaminants on an article in the vessel; supplying a displacing fluid stream to the vessel, wherein the displacing fluid stream has a pressure sufficient to displace the solvent fluid from the vessel and the displacing fluid is other than carbon dioxide; and exhausting the solvent fluid from the vessel.

The invention has numerous advantages. For example, practicing the method of the invention results in preparing ultra-clean surfaces, as required in semiconductor manufacturing and other industries. The method of the invention is economical and can be easily integrated into existing manufacturing facilities. For instance, in one aspect, the method of the invention employs nitrogen displacing gas, as nitrogen lines generally are available at the facility. In one embodiment, low pressure (e.g., 80-100 psig), available nitrogen can be employed. In another embodiment, spent carbon dioxide is recycled thereby reducing carbon dioxide consumption and associated costs. In a further embodiment recycling can be conducted without requiring compression of the spent fluid. Furthermore, the invention takes into account non-volatile residue impurities that can be present in even high purity grades of carbon dioxide and addresses problems caused by their precipitation upon chamber depressurization.

BRIEF DESCRIPTION OF THE DRAWINGS

Figs 1A-1C illustrate the stages in the formation of a second phase as pressure is reduced in a chamber housing an article that is contacted with carbon dioxide solvent.

Figs.2A-2D illustrate method steps in an example of one embodiments of the the invention.

Figs 3A-3E illustrate method steps in an example of another embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of preferred embodiments of the invention, as illustrated in the accompanying drawings in which like reference characters refer to the same parts throughout the different views. The drawings are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the invention.

The invention generally is related to producing clean surfaces, such as, required, for example, during semiconductor manufacturing or processing. The invention is related to removing, preventing or minimizing deposition of contaminants on wafers, such as wafers that include one or more electromechanical devices, one or more integrated circuits or combinations thereof, as known in the art. Other workpieces that can be processed using the invention include parts used in semiconductor manufacture, e.g., sputtering targets and others, optical parts, for example, optical lenses, filters, frequency doubling devices, lasing crystals, light splitting elements, optical cavities, fiber optics, mirrors, and others. Articles such as television, vedeo-recording and photograhic camera components, components used in scientific and medical instruments, in satellite communication, in the aerospace industry and other workpieces also can be processed as described herein.

The article can be fabricated from of any material, including inorganic matter, such as silicon, silicon dioxide, graphite, or metal; organic matter, such as polymers; or a material made from a combination of inorganic and organic materials. This method for cleaning can be applied to a single article, or it can be used to clean two or more articles at a time.

The invention relates to a method for removing contaminants or impurities from an article or from the environment surrounding the article, such as found in a chamber housing the article during its manufacture or processing. The method can itself be a step in a larger manufacturing operation, such as a process for depositing or growing a film, a photolithographic process, an etching process, an ion implantation process, a chemical mechanical planarization process, a diffusion process, a photo-resist development process, a process for developing photosensitive materials, a process for cleaning optical parts, a process for cleaning components useful in aerospace applications, a photo-resist stripping process, a wafer cleaning process, a wafer drying process, a degreasing process, or an extraction process.

Contaminants include organic and/or inorganic materials not desired on the final product. They can be solid, liquid or in gaseous form. Examples include polymers, greases, and other organic materials; silicon; carbon; and/or metals and other impurities. They can be present on the surface of the article or diffused throughout at least a portion of a material comprising of the article.

Impurities can be generated from the article itself, and can include portions of a wafer that are removed during wafer processing or debris produced during an etching process. Impurities also can be delivered to the article with a process fluid. Chemical compounds, such as employed in fabricating or processing an article, also can be left on the surface of the article or can be present in the process chamber once the operation is completed.

The invention is particularly suitable in removing non-volatile residues (NVRs). During operations that employ carbon dioxide at high pressures and in particular at or near critical or supercritical conditions, many NVRs are soluble in the carbon dioxide. As the pressure is reduced, the density and solvent properties of carbon dioxide change and NVRs precipitate generating a second phase, generally in the form of aerosol droplets and/or solid particulates. Once in the second phase, NVRs can impact a surface of the article, thereby contaminating it

Examples of non volatile residues include, but are not limited to heavy organics, such as, for example, hydrocarbons, (e.g., C_{10+}), heavy halocarbons and others.

Sources of NVRs include compressor oils, paints, elastomeric materials that have some solubility in the solvent and are commonly found in gasket and valve seat materials, sealants used in the solvent feed lines and others. NVRs can be generated during a process operation on a workpiece, for instance during wafer cleaning.

NVRs also can be brought into contact with the surface of an article by a fluid employed in the manufacture, processing or in cleaning the article.

In the semiconductor industry, for example, carbon dioxide is used during photo-resist developing; photo-resist stripping; wafer cleaning; and wafer drying. Bulk liquid carbon dioxide is believed to contain NVRs in concentrations of up to 10 parts per million (ppm) by weight. Some higher purity grades, available in cylinders, can contain approximately 0.15 ppm NVRs by weight.

Even the higher purity grades can carry an unacceptable amount of NVRs for sensitive processes which require that the finished article contain less than a specific number of particles of a given size. Some manufacturing processes, for instance, require that gases have less than 100 particles above some critical size (typically on the order of 100 nanometers) per standard cubic meter. It is estimated that vaporization of one liter of the higher purity grades of liquid carbon dioxide (~10 ppb) can result in millions of NVR particles. In order to reach such cleanliness levels, the purity of the carbon dioxide would need to be increased at least a thousand fold over the highest purity carbon dioxide currently available.

The formation of the second phase NVRs during a cleaning process that employs high pressure carbon dioxide is illustrated with respect to Figs. 1A, 1B and 1C. Shown in Fig. 1A is chamber 10 that houses wafer 12. Chamber 10 is a vessel or container such as encountered, for instance, at a tool or process station in a semiconductor fabrication facility. Chamber 10 is designed to receive and hold high pressure fluids such as supercritical carbon dioxide (i.e., carbon dioxide above its critical temperature and pressure, specifically, above 31°C and 1070 pounds per square inch absolute (psia)). Chamber 10 is provided with port(s) for introducing process fluids and other chemicals and with evacuation port(s), as known in the art. Means for introducing and for evacuating chamber 10 can be employed, as known in the art. Examples include compressors, pumps, vent valves and others.

As shown in Fig. 1A, chamber 10 is filled with carbon dioxide at a pressure of 2000 pounds per square inch gauge (psig). At this pressure, contaminants on the wafer are dissolved in the carbon dioxide solvent and the concentration of second phase (insoluble) NVRs is minimal. As chamber 10 is decompressed to a lower pressure, e.g., 200 psig, as shown in Fig. 2B, and then to ambient pressure, as shown in Fig. 1C, the solvating properties of carbon dioxide towards the NVRs diminish and a second phase is formed. The second phase NVRs in chamber 10 can impact the wafer, thereby contaminating it.

In one embodiment, the method of the invention includes contacting an article, e.g., a wafer with a solvent fluid that includes carbon dioxide, whereby contaminants on the article dissolve in the solvent fluid. Higher purity grades of carbon dioxide are preferred. In other embodiments, the method of the invention can be employed with bulk carbon dioxide.

Generally, the solvent fluid includes at least 50 percent (%) by weight carbon dioxide. Preferably, the solvent fluid includes at least 75%, more preferably at least 90% and most preferably, at least 98% carbon dioxide by weight.

The solvent fluid can be 100% carbon dioxide. In other embodiments the solvent fluid includes at least one addtional component such as, for instance, a co-solvent, surfactant or a chelating agent. Examples of components that can be employed in addition to carbon dioxide, alone or in combination, include ammonia, halogenated hydrocarbons, hydrofluoric acid, sulfur dioxide and others. Other examples of cosolvents, surfactants, and/or chelating agents include silane; hydrocarbons, such as methane, ethane, propane, butane, pentane, hexane, ethylene, and propylene; halogenated hydrocarbons such as tetrafluoromethane, chlorodifluoromethane, sulfur hexafluoride, and perfluoropropane; inorganics such as ammonia, helium, krypton, argon, and nitrous oxide; alcohols, such as ethanol, methanol, or isopropyl alcohol; propylene carbonate; atmospheric gasses, such as nitrogen, hydrogen, ozone, or oxygen; water; amines, such as hydroxylamine and alkanolamines; acetone; pyrrolidones such as N-methylpyrrolidone, N-ethylpyrrolidone, N-hydroxyethylpyrrolidone and N-cyclohexylpyrrolidone; amides including dimethylacetamide or dimethylformamide; phenols and derivatives thereof; glycol ethers; 2-pyrrolidone; dialkyl sulfone; organic and inorganic acids and their derivatives, such as hydrofluoric acid, hydrochloric acid, acetic acid, sulfuric acid, gallic acid, or a gallic acid ester; tetraalkylammonium hydroxides; ammonium bifluoride; ammonium-tetramethylammonium bifluoride; alkali metal hydroxides; tartarates; phosphates; ethylenediaminetetraacetic acid (EDTA); ammonia with sodium sulfides and iron sulfate; and mixtures thereof.

Generally, the solvent fluid includes carbon dioxide at conditions under which contaminants such as NVRs are soluble in the solvent fluid. For instance the solvent fluid includes carbon dioxide having a pressure that is at least 800 psig. Preferably, the solvent fluid includes carbon dioxide that is at or near its critical state or at supercritical conditions.

The carbon dioxide solvent may be directed to the container in either a vapor, liquid, or supercritical phase. Once inside the container, the carbon dioxide solvent contacts the article in order to remove the impurities. The removal of the impurities can be accomplished through a physical or chemical mechanism, for example the carbon dioxide solvent may dissolve the impurities; the impurities may diffuse into the carbon dioxide solvent from the material making up the article; or the impurities may react with the carbon dioxide solvent in a way that results in their removal from the article. The removal can also be a mechanical mechanism, for example the or the pressure and/or temperature of the carbon dioxide solvent can be manipulated so that its specific volume increases and/or decreases, resulting in stresses that break the impurities from the article. The removal of the impurities can also be accomplished through a combination of chemical and mechanical mechanisms.

Optionally, the carbon dioxide solvent can also be agitated in order to enhance both a chemical and mechanical mechanism. For example, agitation can increase the speed of chemical removal mechanisms (such as dissolution, diffusion, and reaction) by increasing concentration gradients across the surface of the article, thereby driving the chemical mechanism towards completion. Similarly, agitation can increase the rate of removal for mechanical removal mechanisms because the agitation creates shear forces in the fluid which can assist in pulling the impurities away from the surface of the article.

The temperature and/or pressure of the carbon dioxide solvent can be manipulated to also facilitate the removal of the impurities. These manipulations of process conditions can result in the carbon dioxide solvent undergoing one or more phase shifts between the vapor, liquid, and/or supercritical phases depending on whether the chosen manipulations cross the carbon dioxide solvent's critical temperature and/or pressure and it's condensation pressure and/or temperature. These manipulations are preferably done to enhance the removal of the impurities. If there are several different types of impurities on or in the article, the carbon dioxide solvent can be cycled through various process conditions to enhance the removal of each type of impurity. While the carbon dioxide solvent is undergoing these manipulations, NVRs or removed impurities may dissolve into and/or precipitate out of the solvent fluid.

Optionally, at least a portion of solvent fluid including contaminants can be replaced with fresh solvent fluid or pure carbon dioxide in an intermediate rinsing step, whereby spent solvent fluid is pushed through and additional contaminants can be removed from the surface being cleaned.

The method includes displacing the solvent fluid with a displacing fluid, that is other than carbon dioxide, at a temperature and pressure sufficient to prevent forming a second phase in the solvent fluid being displaced, whereby the contaminants are separated from the wafer, thereby cleaning the wafer.

For example, the solvent fluid is displaced at its pressure in the chamber, without partial or total chamber decompression. If decompression of the chamber is employed, it is to a pressure at which solubility of NVRs in the solvent fluid is maintained.

The displacing fluid can be a gas, a liquid or a supercritical fluid. Suitable displacing fluids include inert gases such as nitrogen, helium, argon or krypton, other gases, such as oxygen, and any combinations thereof. Nitrogen is preferred. In one embodiment of the invention, the displacing fluid is a high purity gas. In another embodiment, the displacing fluid is an ultrahigh purity gas, for instance having purity levels of sub parts per billion in all contaminants or as known in the industry. High purity and ultra-high purity gases, such as nitrogen and others can be obtained commercially.

The method of the invention can be conducted continuously or in batch-wise manner.

An illustration of stages of this embodiment of the invention is shown in Figs 2A - 2D.

Fig 2A shows chamber 14, housing wafer 12. Chamber 14 can be a chamber such as described above. In other embodiments chamber 14 can be designed so that fresh fluid fed to the container mixes to a significant degree with the carbon dioxide solvent already present (for instance, in the fashion of a continuously-stirred tank reactor), or so that the flow path that enhances the displacement of used solvent, impurities, and NVRs (e.g., in a plug-flow fashion). Preferably, the chamber geometry is such that the exposure of the article to impurities and NVRs is minimized during the displacement of the carbon dioxide solvent, impurities, and NVRs. Ports and means for feeding and evacuating fluids from chamber 14 can be provided as known in the art.

As shown in Fig 2A, chamber 14 is filled with carbon dioxide at about 2000 psig that includes dissolved contaminants.

An inert gas at a pressure higher than that of the carbon dioxide in the chamber, e.g., higher than 2000 psig is directed to chamber 14, as shown in Fig 2B. Carbon dioxide together with dissolved contaminants is displaced from chamber 14, as shown in Fig. 2C. Chamber 14, including displacing gas is then depressurized to atmospheric pressure, as shown in Fig. 2D.

The final number of impurities left on the article after evacuation can be improved by using a higher purity displacing fluid and/or carbon dioxide solvent, or by increasing the volume of the displacing fluid used in order to more thoroughly displace the carbon dioxide solvent, impurities, and NVRs.

Once solvent fluid, NVRs and other impurities are displaced from the container, the flow of displacing fluid can be stopped and the container can be evacuated.

Carbon dioxide displaced from the chamber can be exhausted as a waste stream or can be directed to another operation or tool in the facility.

In a preferred embodiment, the fluid displaced from chamber 14 is purified, for example by directing fluid exhausted from the chamber to one or more purification units. As the pressure of fluid exhausted from chamber 14 is high, (e.g., 2000psig), the spent fluid generally can be directed to a purification unit without further compression. Examples of purification techniques that can be employed include distillation, adsorption, absorption, chemical reactions, phase separation and other methods.

The solvent fluid displaced can be purified with respect to NVRs, co-solvents, surfactants and chelating agents. In a further embodiment, the resulting stream can be further purified to separate carbon dioxide from the displacing fluid, e.g., nitrogen. A suitable method for separating carbon dioxide from nitrogen includes distillation.

In a preferred embodiment, carbon dioxide is recycled as described in U.S. Patent Application No 10/274,302, *Recycle for Supercritical Carbon Dioxide*, filed on October 17, 2002, the teachings of which are incorporated herein by reference in their entirety.

Displacing fluid also can be recycled. If helium is used as a displacing fluid, recycling is particularly attractive due to its cost and its significantly light weight to effect an easier removal process.

In another embodiment, the invention is related to a method for reducing deposition of non-volatile residues during a workpiece cleaning operation. The method includes contacting the workpiece with a solvent fluid, essentially as described above. The method includes reducing the pressure of the solvent fluid, whereby contaminants, e.g., NVRs, become insoluble in the solvent fluid. The method further includes displacing the solvent fluid, at the reduced pressure, with a displacing fluid, such as described above, whereby the time during which the workpiece is exposed to insoluble contaminants, e.g., NVRs, is reduced, thereby reducing deposition of insoluble contaminants, e.g., NVRs on the workpiece.

In one embodiment, the pressure of the solvent fluid is reduced to less than about 1000 psig. In another embodiment, the pressure is reduced to less than 200 psig. In further embodiment, the pressure of the solvent fluid is reduced to a value that is lower than the pressure of a nitrogen gas source or line available at the facility, e.g., to less than about 80-100 psig.

Preferably, the wafer is exposed to insoluble NVRs for less than about 30 seconds. More preferably, the wafer is exposed to insoluble NVRs for less than 3 seconds.

Optionally, at least a portion of the solvent fluid, together with dissolved contaminants, can be displaced using fresh solvent fluid or pure carbon dioxide in an intermediate rinsing step. The rinsing step can be conducted before or after chamber depressurization. Carbon dioxide and, optionally, displacing gas recycling can be employed, essentially as described above. Recycling can include a compression step prior to directing fluid that is to be recycled to a purifier.

As discussed above, the method can be conducted continuously or in batch-wise fashion.

An example of the stages of this embodiment of the invention is shown in Figs 3A - 3E. Shown in Fig 3A is chamber 14 housing wafer 12, essentially as described above. Carbon dioxide at a pressure of about 2000 psig is present in chamber 14. Chamber 14 is depressurized to 200 psig, as shown in Fig. 3B. Upon the pressure reduction, NVRs precipitate out of solution, forming a second phase. An inert gas, e.g., nitrogen at a pressure sufficient to push through solvent fluid at 200 psig is directed into chamber 14, as shown in Fig. 3C, thereby displacing carbon dioxide and second phase impurities from chamber 14, as shwon in Fig. 3D. Displacing the carbon dioxide and second phase impurities from the chamber reduces the time that the wafer is exposed to insoluble NVRs, thereby reducing deposition of insoluble NVRs on the wafer. As shown in Fig. 3E, chamber 14 is then depressurized to ambient atmosphere.

In one embodiment, the invention is related to a method for producing an ultraclean article. As used herein, the term "ultra-clean" refers to a substrate contaminated by less than about 2,000 particles per square meter of surface areas, the impurities having an effective diameter greater than about 0.1 micron and being measured by a light scattering technique. Light scattering methods for measuring particles having an effective diameter greater than about 0.1 micron on a solid surface are known in the art. For example, a suitable method is described in Diaz, R.E., *et al.*, "On-Wafer Measurement of Particles in Contamination-Free Manufacturing for Semiconductors and other Precision Products," in *Contamination-Free Manufacturing for Semiconductors and other Precision Products*, edited by R.P. Donovan (Marcell Dekker), p. 79 (2001).

The method includes contacting the article, in a chamber, with carbon dioxide solvent, whereby impurities on the article dissolve in the carbon dioxide solvent and directing a displacing gas into the chamber to reduce the time that the article is exposed to non-volatile residues present in the carbon dioxide, thereby reducing the number of impurities on the article to less than about 2000 particles per square meter of surface area, wherein each of the impurities has an effective diameter greater than 0.1 microns as measured by a light scattering technique.

In a further embodiment, the invention is directed to a method for supplying cleaning fluids to a vessel. The method includes the steps of supplying a solvent fluid stream at a first pressure to a vessel housing a article, wherein the solvent fluid includes carbon dioxide and is capable of dissolving contaminants on an article in the vessel; supplying a displacing fluid stream to the vessel, wherein the displacing fluid stream has a pressure sufficient to displace the solvent fluid from the vessel and the displacing fluid is other than carbon dioxide; and exhausting the solvent fluid from the vessel.

Exhaust fluid from the vessel can be purified, essentially as described above, and carbon dioxide can be recycled to the vessel. Purified carbon dioxide can be compressed prior to being returned to the vessel, by means known in the art.

In one embodiment the displacing fluid stream is at a pressure that is at least as high as the first pressure. In one example, the displacing fluid is no more than about 100 psi greater than the pressure of the solvent fluid that it displaces. In another embodiment, the first pressure is at least 1000 psig. The fluid exhausted from the vessel can be at a pressure higher than the operating pressure of the purification unit.

In yet another embodiment, solvent fluid is exhausted from the vessel at a pressure that is lower than the first pressure and the displacing fluid is at a pressure sufficient to push through the solvent fluid.

EQUIVALENTS

While this invention has been particularly shown and described with references to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the scope of the invention encompassed by the appended claims.

CLAIMS

What is claimed is:

1. A method for cleaning a wafer of contaminants, comprising the steps of:
   a) contacting the wafer with a solvent fluid that includes carbon dioxide, whereby contaminants on the wafer are removed by the solvent fluid; and
   b) displacing the solvent fluid with a displacing fluid, that is other than carbon dioxide, at a temperature and pressure sufficient to prevent forming a second phase in the solvent fluid being displaced, whereby the contaminants are separated from the wafer, thereby cleaning the wafer.

2. A method for cleaning an article of contaminants, comprising the steps of:
   a) contacting the article with a solvent fluid that includes carbon dioxide, whereby contaminants on the article dissolve in the solvent fluid;
   b) displacing the solvent fluid with a displacing fluid, that is other than carbon dioxide, at a temperature and pressure sufficient to prevent forming a second phase in the solvent fluid being displaced, whereby the contaminants are separated from the article, thereby cleaning the article; and
   c) recycling at least a portion of the carbon dioxide to the article.

3. The method of Claim 2, wherein the solvent fluid further includes at least one additional component selected from the group consisting of a cosolvent, a surfactant, and a chelating agent.

4. The method of Claim 3, wherein the additional component is selected from the group consisting of ammonia, halogenated hydrocarbons, hydrofluoric acid, hydrochloric acid, sulfur dioxide, and any combination thereof.

5. The method of Claim 2, wherein the displacing fluid is a gas, a liquid, or a supercritical fluid.

6. The method of Claim 5, wherein the displacing fluid is an ultrahigh purity gas.

7. The method of Claim 5, wherein the displacing fluid is selected from the group consisting of nitrogen, argon, krypton, helium, oxygen and any combination thereof.

8. The method of Claim 7, wherein the displacing fluid is nitrogen.

9. The method of Claim 2, wherein the article is selected from the group consisting of: a wafer, an optical component, an aerospace component and a part used in semiconductor manufacture.

10. The method of Claim 2, wherein the article is a wafer that includes at least one integrated circuit or at least one microelectromechanical device.

11. The method of Claim 2 wherein the article is in a chamber.

12. The method of Claim 11, wherein the carbon dioxide is at or above critical conditions.

13. The method of Claim 11, wherein the solvent fluid is directed into the chamber and includes carbon dioxide at a pressure that is at least 800 pounds per square inch gauge.

14. The method of claim 11, wherein the recycling of the at least a portion of the carbon dioxide being displaced includes a purification operation that is selected from the group consisting of distillation, adsorption, absorption and any combination thereof.

15. The method of Claim 14, wherein the at least a portion of the carbon dioxide being displaced is not compressed prior to the purification operation.

16. A method for reducing deposition of non-volatile residues during a workpiece cleaning operation, comprising the steps of:

a) contacting the workpiece with a solvent fluid at a first pressure, the solvent fluid including carbon dioxide, whereby contaminants on the workpiece are removed by the solvent fluid;

b) reducing the pressure of the solvent fluid, whereby non-volatile residues become insoluble in the solvent fluid; and

c) displacing the solvent fluid at the reduced pressure with a displacing gas that is other than carbon dioxide, whereby the time that the workpiece is exposed to insoluble non-volatile residues is reduced, thereby reducing deposition of insoluble non-volatile residues on the workpiece.

17. The method of Claim 16, wherein the solvent fluid further includes at least one additional component selected from the group consisting of a cosolvent, a surfactant, and a chelating agent.

18. The method of Claim 17, wherein the additional component is selected from the group consisting of ammonia, halogenated hydrocarbons, hydrofluoric acid, hydrochloric acid, sulfur dioxide, and any combination thereof.

19. The method of Claim 16, wherein the displacing fluid is a gas, a liquid or a supercritical fluid.

20. The method of Claim 19, wherein the displacing fluid is an ultrahigh purity gas.

21. The method of Claim 19, wherein the displacing fluid is selected from the group consisting of nitrogen, argon, krypton, helium, oxygen and any combination thereof.

22. The method of Claim 21, wherein the displacing fluid is nitrogen.

23. The method of Claim 16 wherein the article is selected from the group consisting of a wafer, an optical component, an aerospace component and a part used in semiconductor manufacture.

24. The method of Claim 16, wherein the article is a wafer that includes at least one integrated circuit or at least one microelectromechanical system.

25. The method of Claim 16, wherein the article is in a chamber.

26. The method of Claim 25, wherein the pressure of the solvent fluid is reduced to less than about 1000 pounds per square inch gauge.

27. The method of Claim 26, wherein the pressure of the solvent fluid is less than about 200 psig.

28. The method of Claim 25, wherein at least a portion of the carbon dioxide being displaced from the chamber is recycled to the chamber.

29. The method of Claim 28, wherein recycling includes a purification operation selected from the group consisting of distillation, adsorption, absorption and any combination thereof.

30. The method of Claim 29, further includes compressing the purified carbon dioxide prior to its being recycled to the chamber.

31. The method of Claim 16, wherein the time that the article is exposed to precipitated nonvolatile residues is less than 30 seconds.

32. The method of Claim 31, wherein the time that the article is exposed to precipitated nonvolatile residues is less than 3 seconds.

33. A method for producing an ultraclean article, comprising the steps of:

a) contacting a article, in a chamber, with carbon dioxide solvent, whereby impurities on the article dissolve in the carbon dioxide solvent; and

c) directing ultra-high purity displacing gas into the chamber to reduce the time that the article is exposed to non-volatile residues present in the carbon dioxide solvent, thereby reducing the number of impurities on the article to less than about 2000 particles per square meter of surface area, wherein each of the impurities has an effective diameter greater than 0.1 microns as measured by light scattering technique.

34. A method for supplying cleaning fluids to a vessel, comprising the steps of:

a) supplying a solvent fluid stream at a first pressure to a vessel housing a article, wherein the solvent fluid includes carbon dioxide and is capable of dissolving contaminants on an article in the vessel;

b) supplying a displacing fluid stream to the vessel, wherein the displacing fluid stream has a pressure sufficient to displace the solvent fluid from the vessel and the displacing fluid is other than carbon dioxide; and

c) exhausting the solvent fluid from the vessel.

35. The method of Claim 34, wherein the displacing fluid stream is at a pressure that is at least as high as the first pressure.

36. The method of Claim 35, wherein the first pressure is greater than about 1000 pounds per square inch gauge.

37. The method of Claim 34, wherein the solvent fluid exhausted from the vessel is directed to a purification unit.

38. The method of Claim 37, wherein the solvent fluid is exhausted from the vessel at a pressure that is greater than the operating pressure of the purification unit.

39. The method of Claim 38, wherein carbon dioxide obtained from the purification unit is compressed and recycled to the vessel.

40. The method of Claim 37, wherein the displacing fluid is selected from the group consisting of nitrogen, argon, helium, krypton, oxygen and any combination thereof.

41. The method of Claim 40, wherein the displacing fluid is nitrogen

42. The method of Claim 34, wherein the pressure of the displacing fluid stream is no more than about 100 pounds per square inch greater than the pressure of the solvent fluid that it displaces.

43. The method of Claim 34, wherein the solvent fluid is exhausted from the vessel at a second pressure, that is lower than the first pressure, and the displacing fluid stream is directed to the vessel at a pressure that is at least as high as the second pressure.

44. The method of Claim 43, wherein the solvent fluid exhausted from the vessel is directed to a purification unit.

45. The method of Claim 44, wherein the solvent fluid is exhausted from the vessel at a pressure that is greater than the operating pressure of the purification unit.

46. The method of Claim 44, wherein carbon dioxide obtained from the purification unit is compressed and recycled to the vessel.

47. The method of Claim 43, wherein the displacing fluid is selected from the group consisting of nitrogen, argon, helium, krypton, oxygen and any combination thereof

48. The method of Claim 46, where the displacing fluid is nitrogen

49. The method of Claim 43, wherein the pressure of the displacing fluid stream is no more than 100 pounds per square inch greater than the pressure of the solvent fluid it displaces from the vessel.

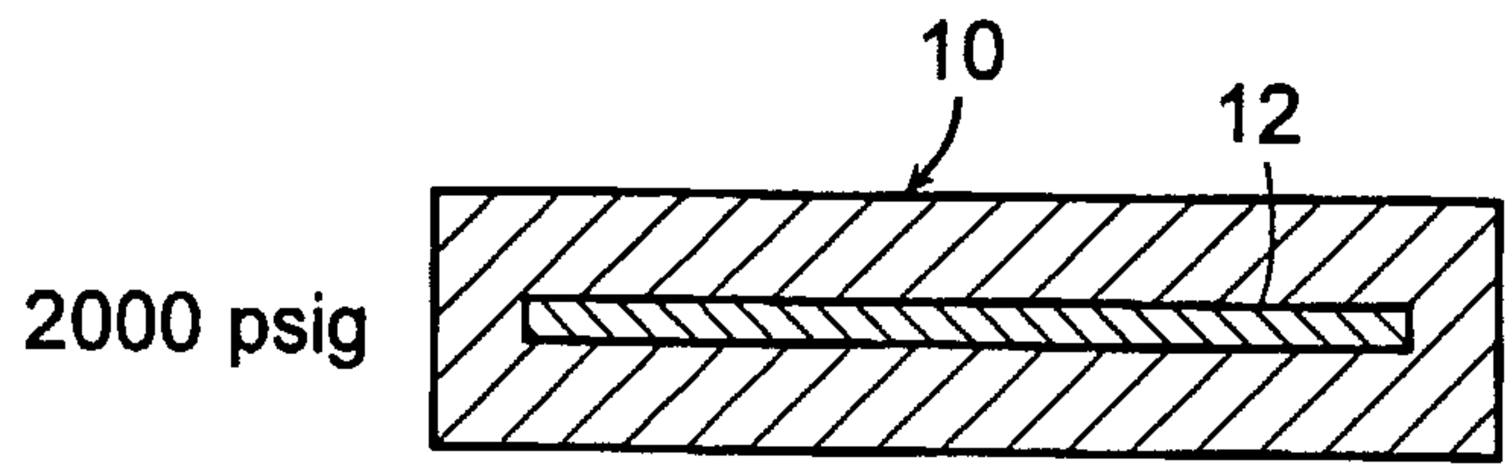

FIG. 1A

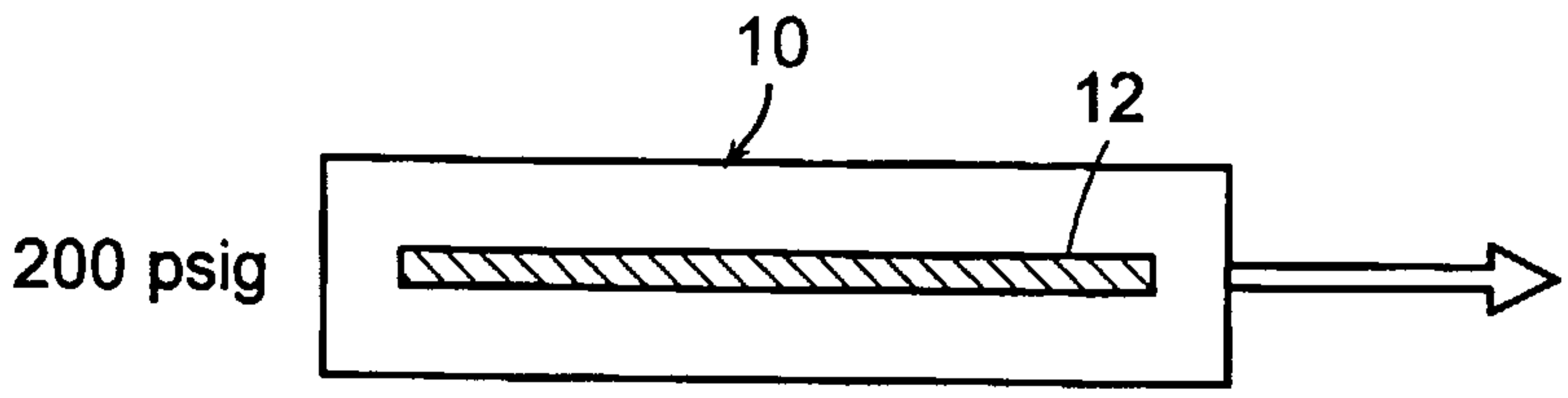

FIG. 1B

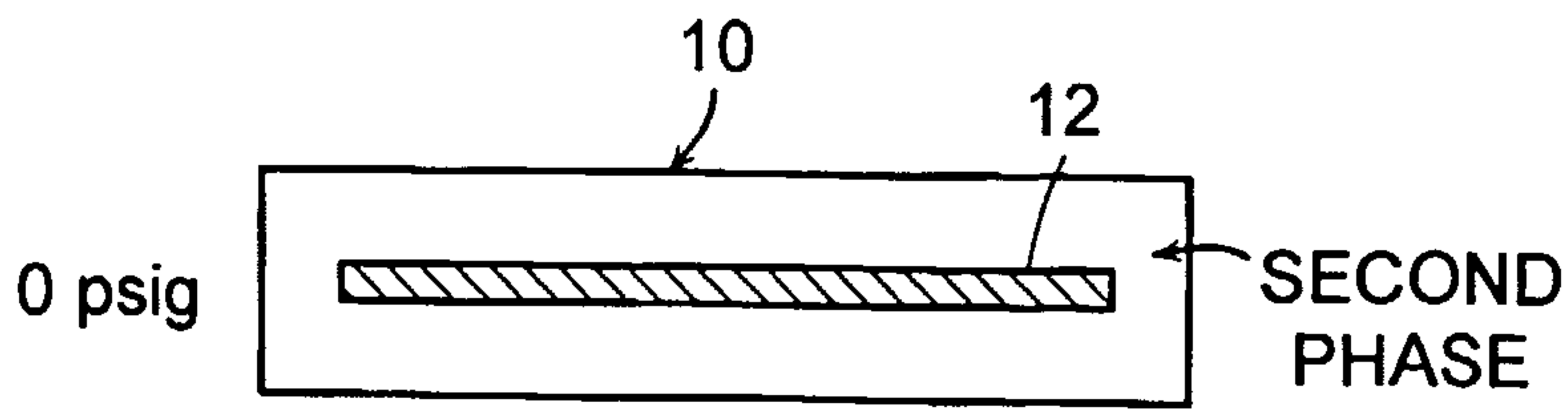

FIG. 1C

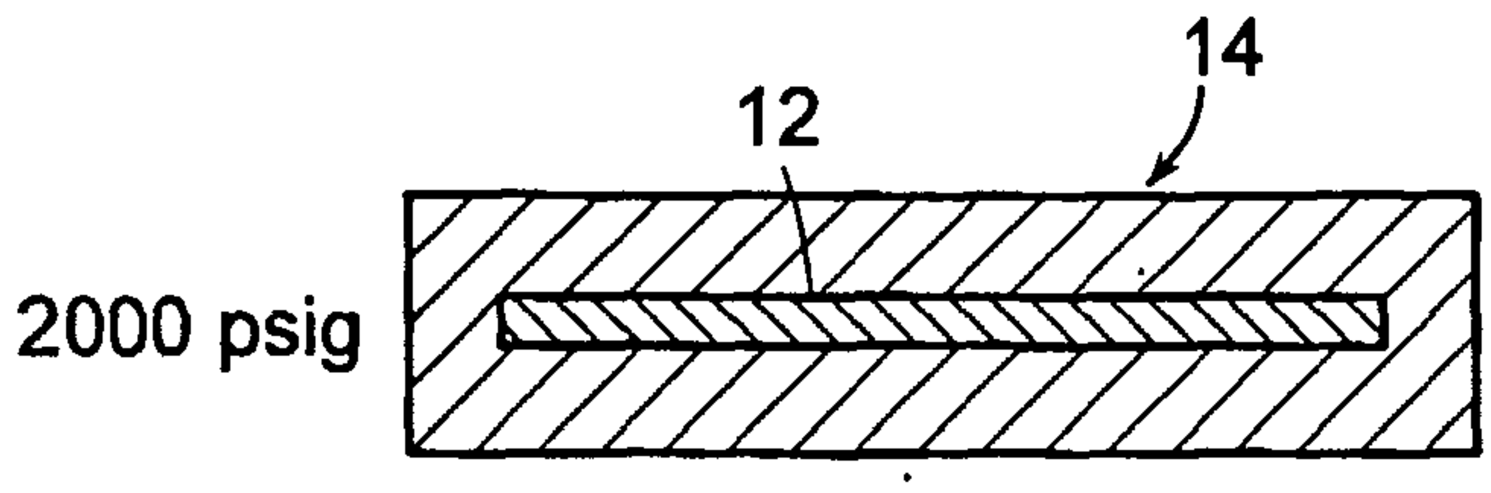

FIG. 2A

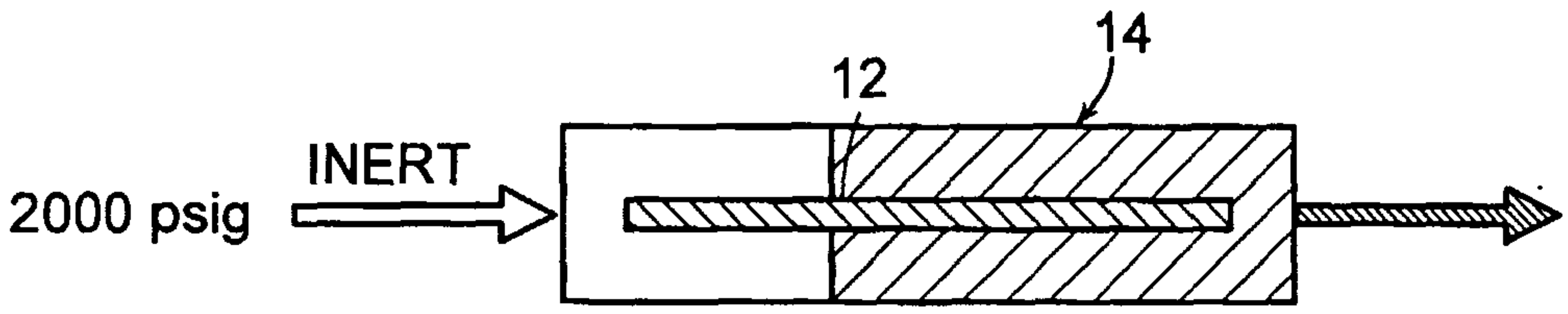

FIG. 2B

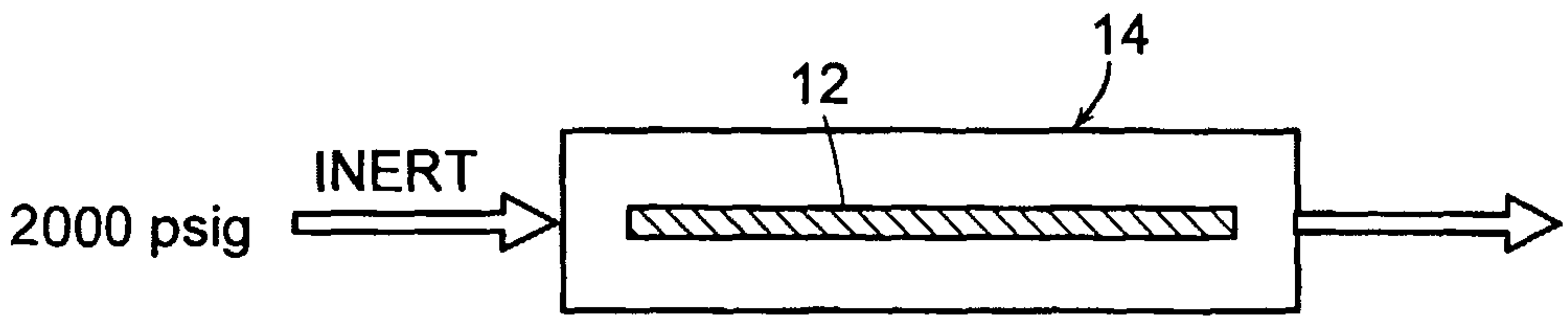

FIG. 2C

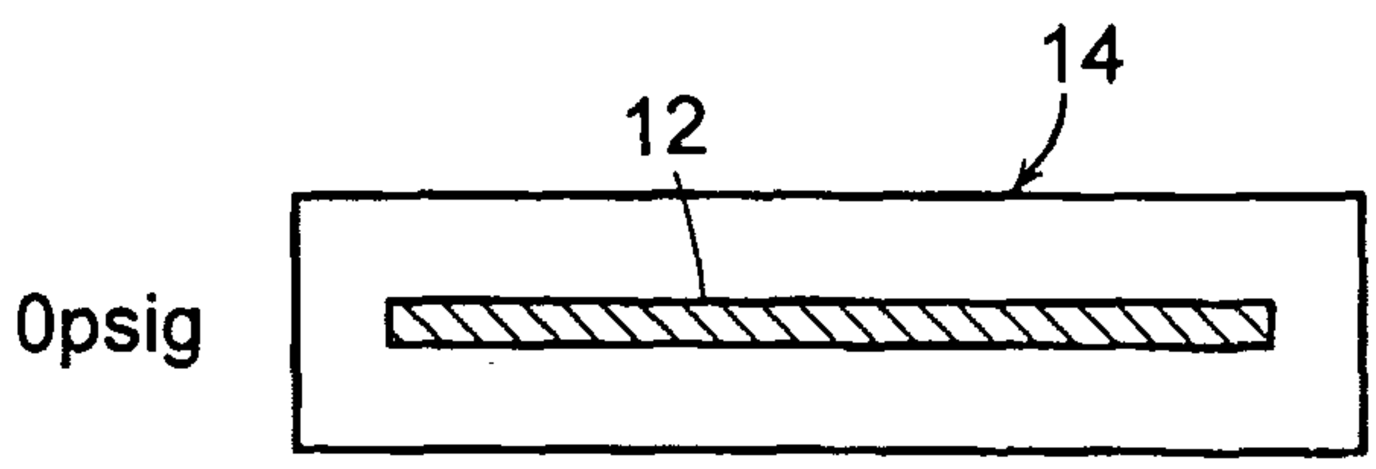

FIG. 2D

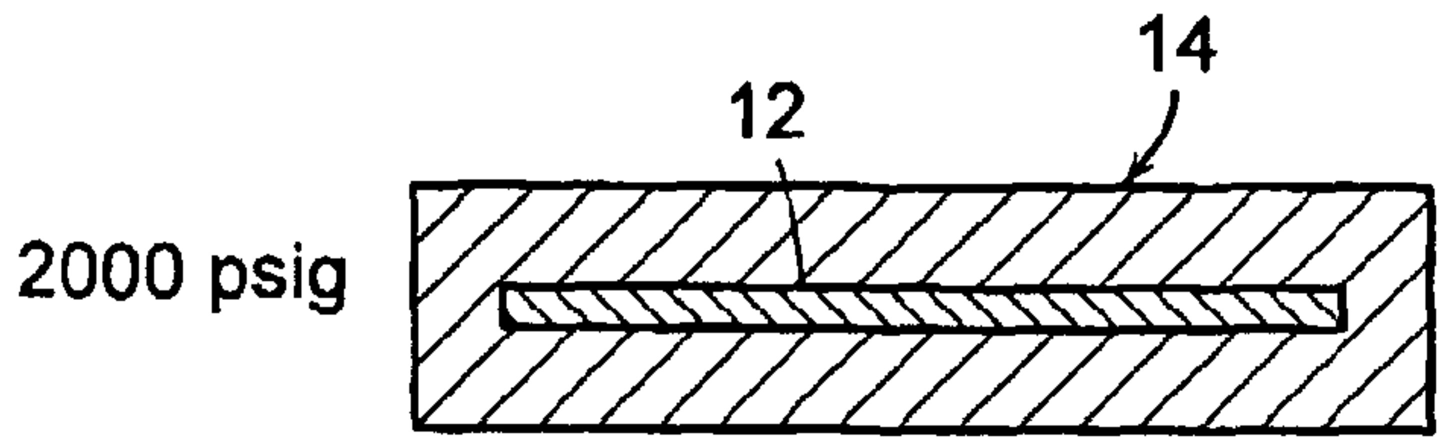

FIG. 3A

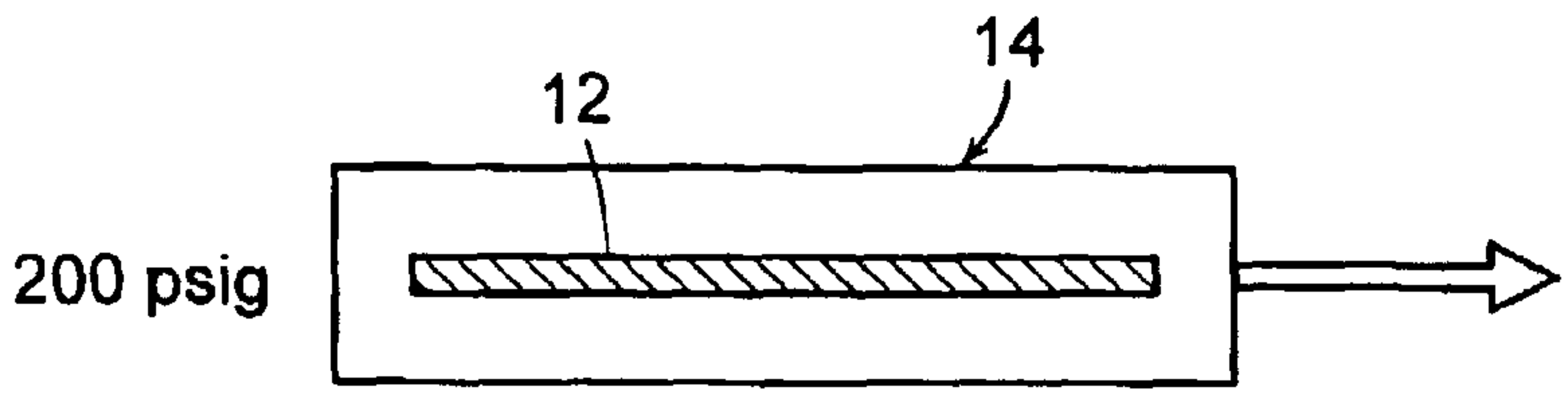

FIG. 3B

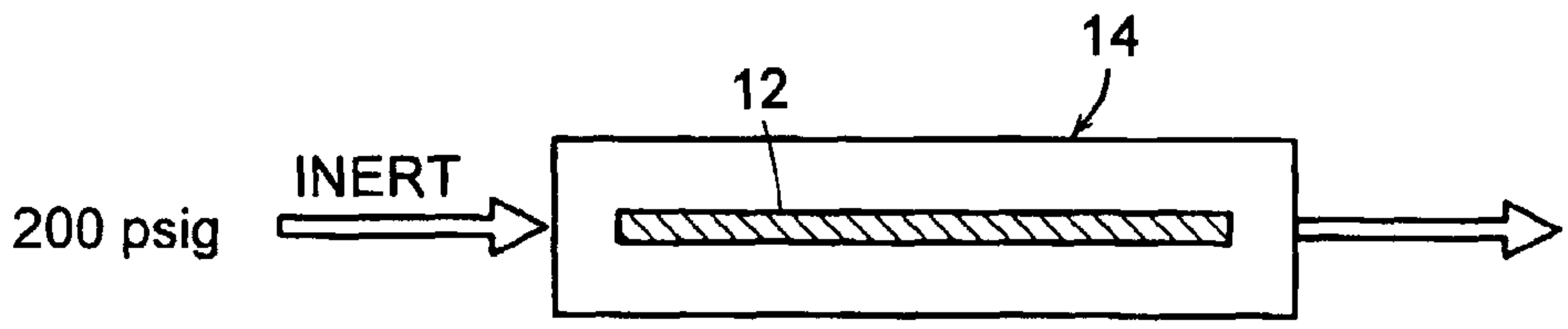

FIG. 3C

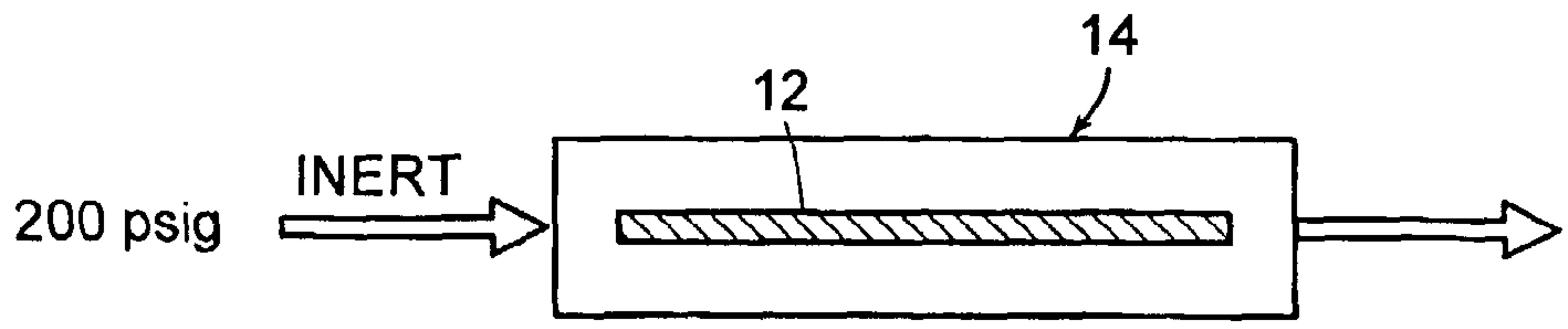

FIG. 3D

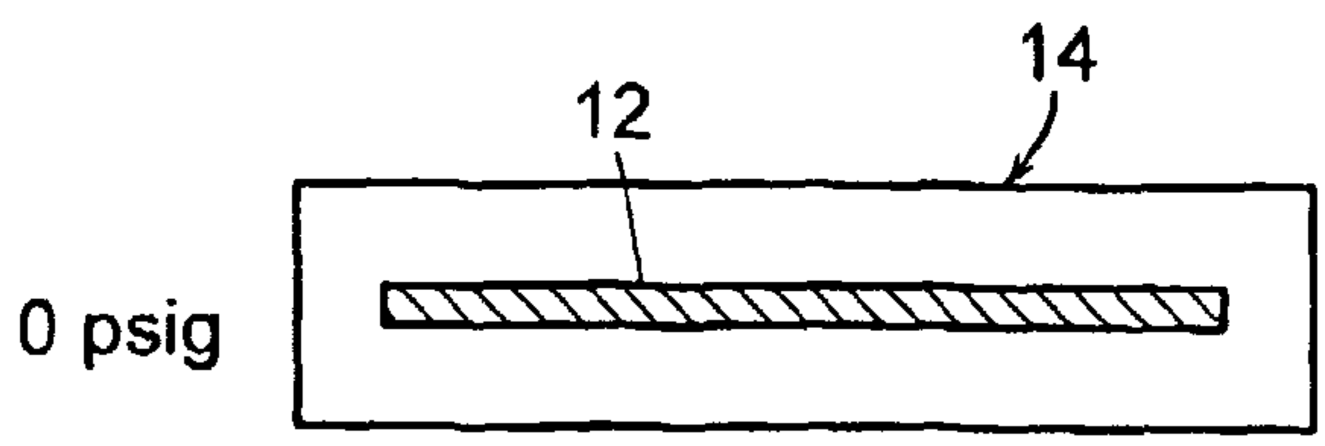

FIG. 3E