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(54) SUBSTRATE CLEANING METHOD, CLEANING SOLUTION, CLEANING APPARATUS AND SEMICONDUCTOR DEVICE

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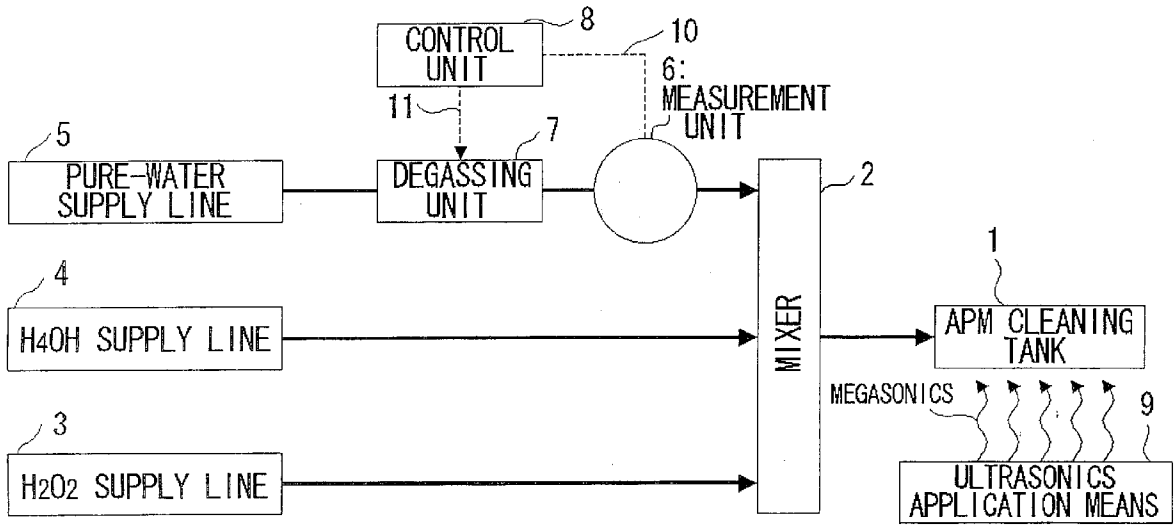
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(57) **ABSTRACT**

Disclosed is a substrate cleaning method for removing particles from a substrate includes a first step of adjusting the concentration of dissolved nitrogen in pure water, so as to be less than or equal to the concentration of dissolved nitrogen in equilibrium with the atmosphere (about 16 ppm), in a supply line that supplies the pure water, and a second step of cleaning a substrate by supplying a cleaning tank with a cleaning solution produced by mixing at least hydrogen peroxide with the pure water adjusted at the first step, and applying an ultrasonic wave to the cleaning solution in which the substrate is immersed.



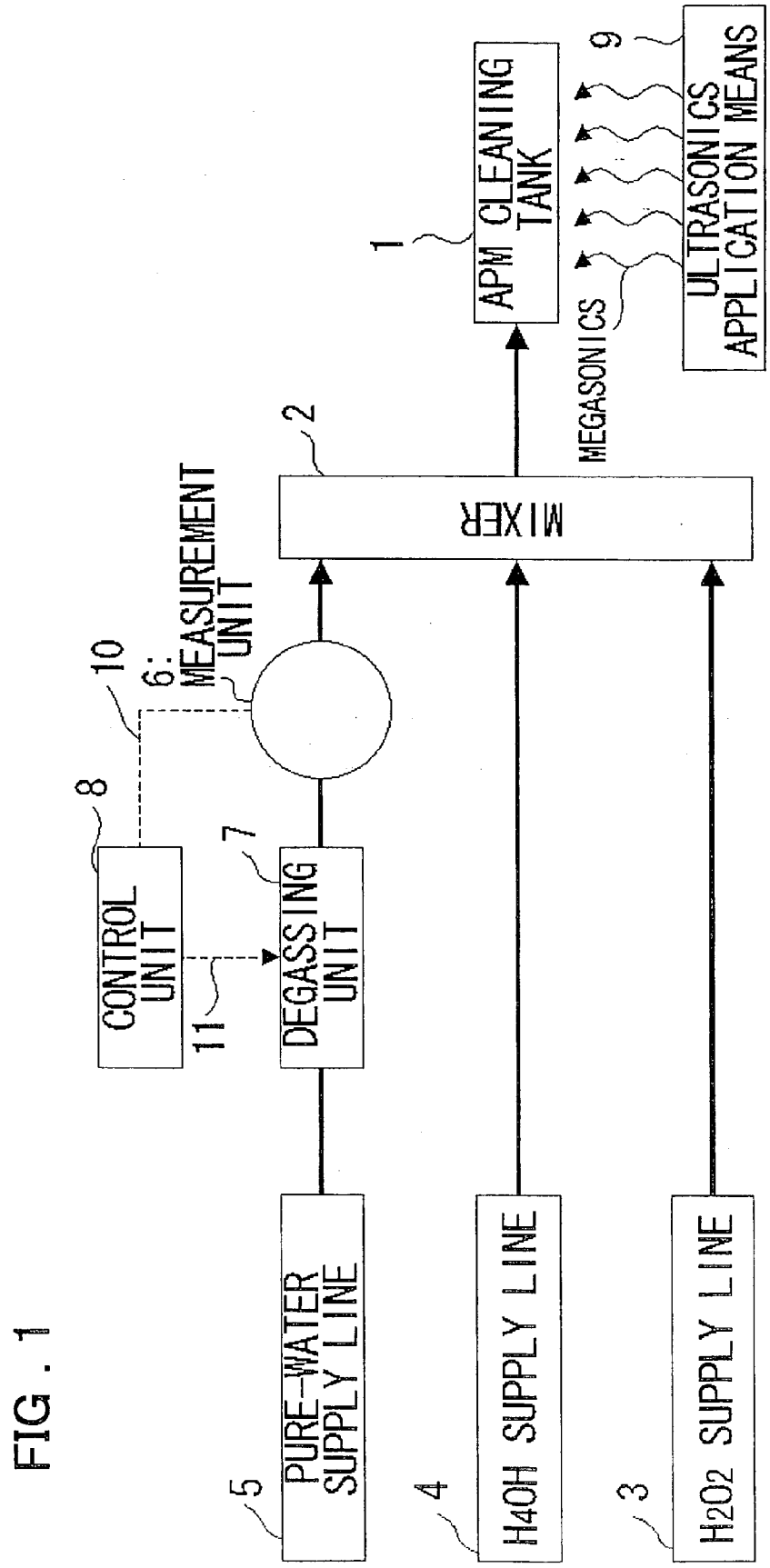

APM CLEANING TANK
1
ULTRASONICS APPLICATION MEANS
9
MEGASONICS
MIXER
2
6: MEASUREMENT UNIT
10
CONTROL UNIT
8
11
DEGASSING UNIT
7
PURE-WATER SUPPLY LINE
5
H4OH SUPPLY LINE
4
H2O2 SUPPLY LINE
3

FIG. 1

FIG . 2

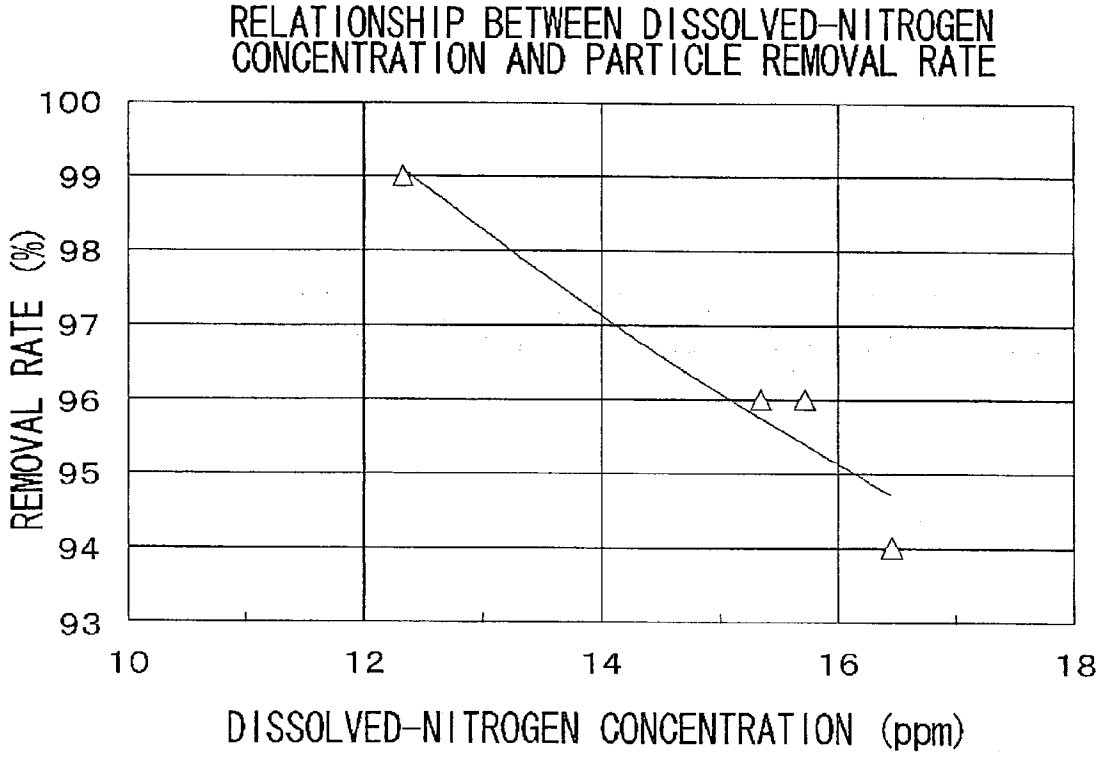
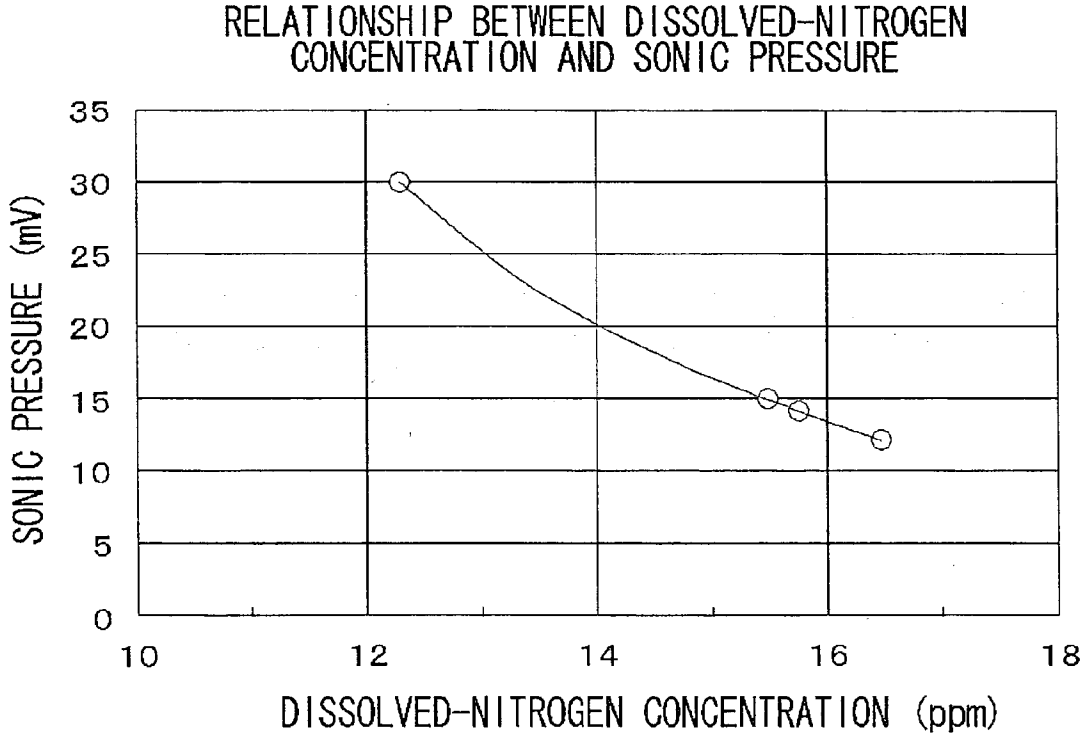

RELATIONSHIP BETWEEN DISSOLVED-NITROGEN CONCENTRATION AND PARTICLE REMOVAL RATE
REMOVAL RATE (%)
100
99
98
97
96
95
94
93
10
12
14
16
18
DISSOLVED-NITROGEN CONCENTRATION (ppm)

FIG . 3


RELATIONSHIP BETWEEN DISSOLVED-NITROGEN CONCENTRATION AND SONIC PRESSURE
SONIC PRESSURE (mV)
35
30
25
20
15
10
5
0
10
12
14
16
18
DISSOLVED-NITROGEN CONCENTRATION (ppm)

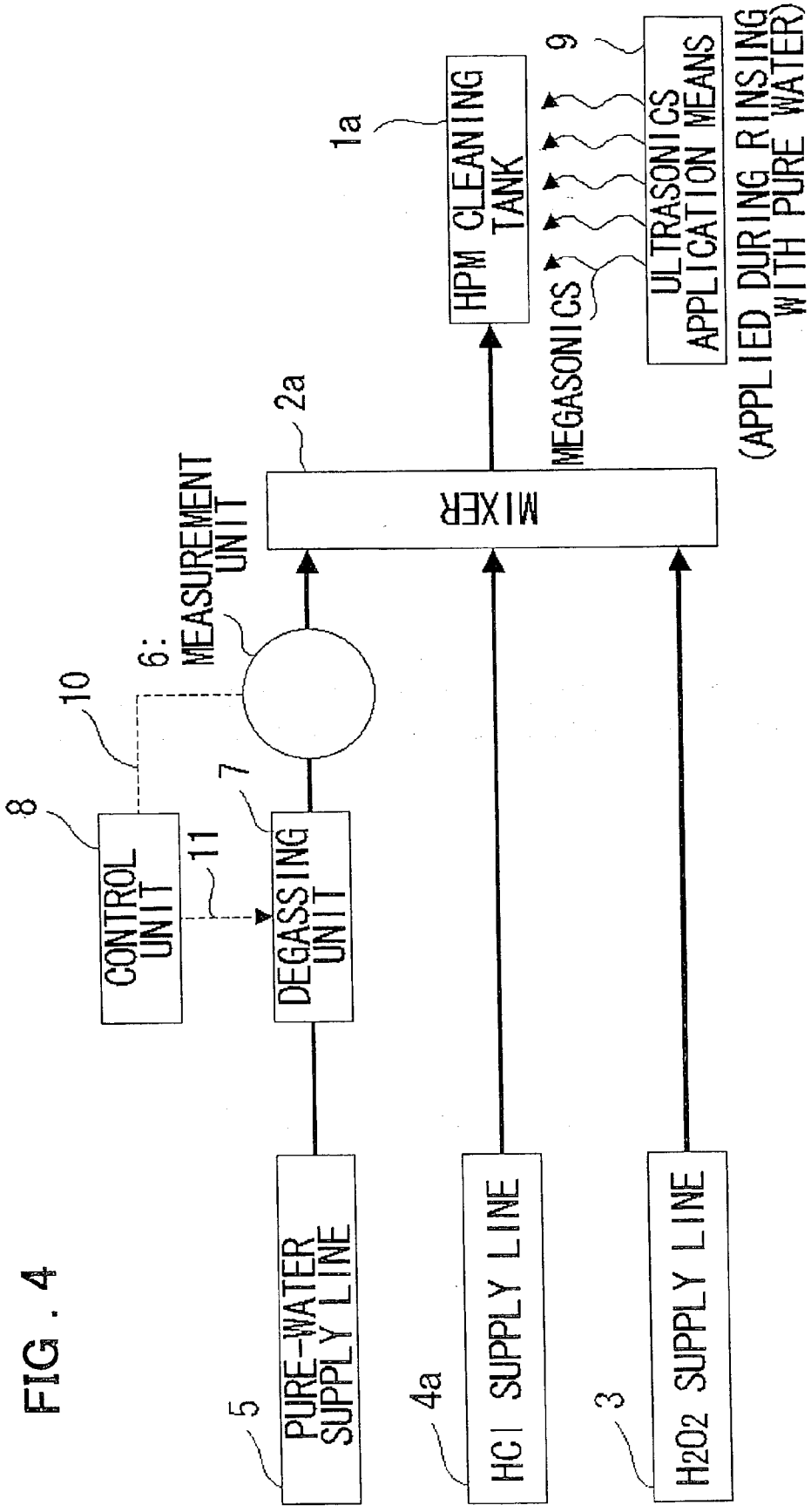
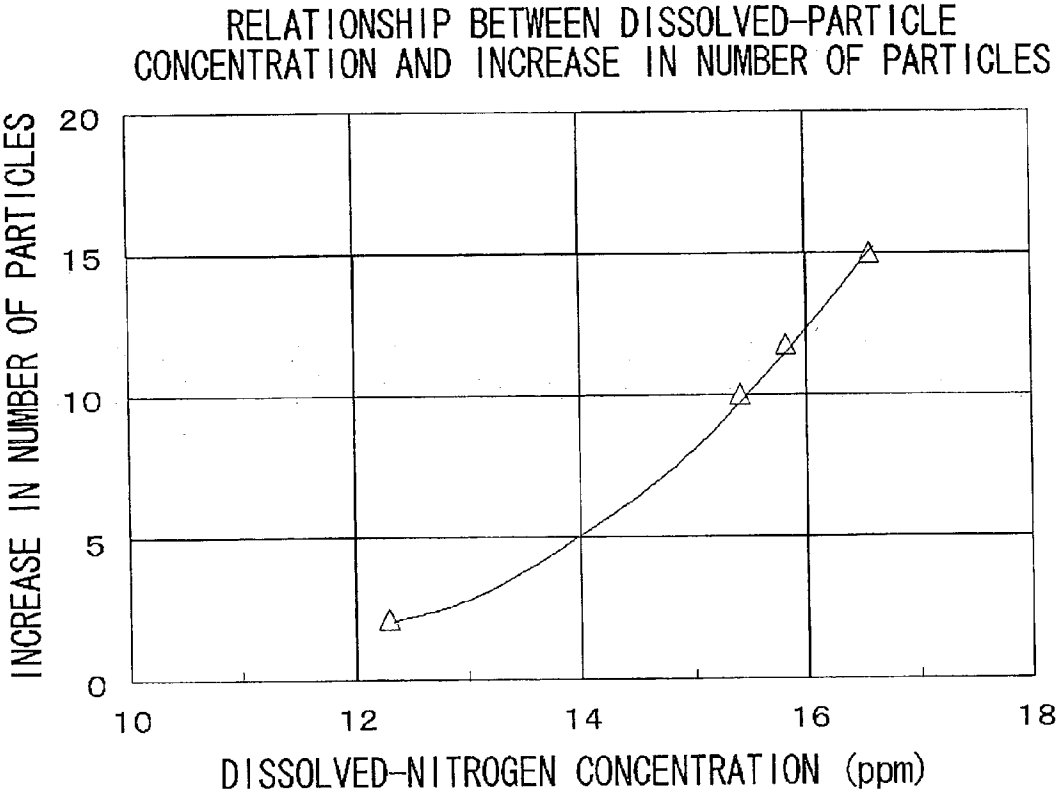

PURE-WATER SUPPLY LINE
5
HCl SUPPLY LINE
4a
H2O2 SUPPLY LINE
3
DEGASSING UNIT
7
CONTROL UNIT
8
11
10
6: MEASUREMENT UNIT
MIXER
2a
HPM CLEANING TANK
1a
MEGASONICS
ULTRASONICS APPLICATION MEANS
9
(APPLIED DURING RINSING WITH PURE WATER)

FIG. 4

FIG . 5


RELATIONSHIP BETWEEN DISSOLVED-PARTICLE CONCENTRATION AND INCREASE IN NUMBER OF PARTICLES
INCREASE IN NUMBER OF PARTICLES
20
15
10
5
0
10
12
14
16
18
DISSOLVED-NITROGEN CONCENTRATION (ppm)

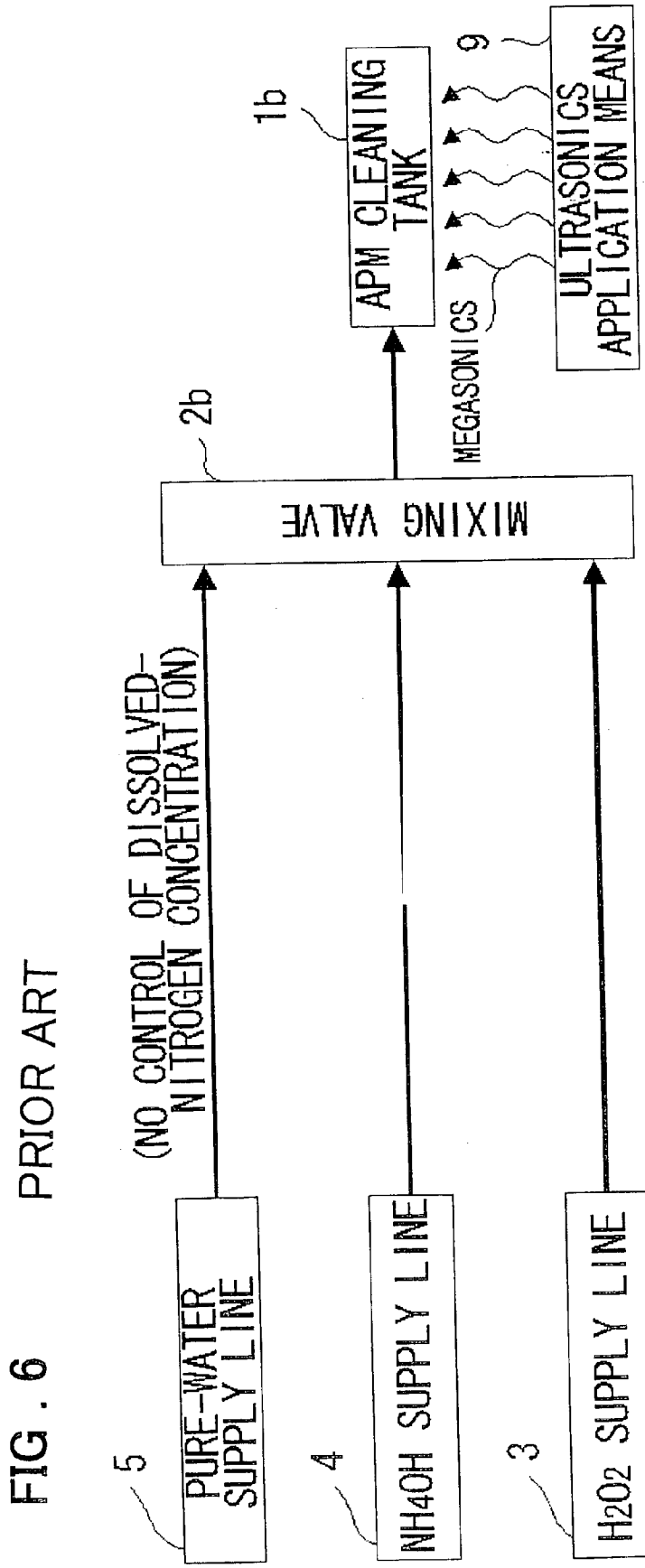


FIG. 6 PRIOR ART

SUBSTRATE CLEANING METHOD, CLEANING SOLUTION, CLEANING APPARATUS AND SEMICONDUCTOR DEVICE

FIELD OF THE INVENTION

[0001] This invention relates to a cleaning method, cleaning solution and cleaning apparatus for cleaning a substrate by application of ultrasonics, and to a semiconductor device that has been cleaned by the cleaning method. More particularly, the invention relates to a substrate cleaning method, cleaning solution and cleaning apparatus exhibiting a high particle removing capability with regard to particles adhering to a substrate, and to a semiconductor device cleaned by this cleaning method.

BACKGROUND OF THE INVENTION

[0002] According to a conventional cleaning technology, particles and the like adhering to a substrate such as a semiconductor substrate, liquid-crystal glass substrate or magnetic disk are removed by immersing the substrate in a cleaning solution accommodated in a cleaning tank and applying ultrasonic waves to the substrate.

[0003] The conventional method (ultrasonic cleaning method) of cleaning a semiconductor substrate will be described with reference to the drawings.

[0004] As shown in **FIG. 6**, NH_4OH (ammonium hydroxide), H_2O_2 (hydrogen peroxide) and pure water (ultra-pure water) are supplied separately to a mixing valve **2***b* from plant lines **4**, **3**, and **5** that furnish these fluids respectively. The NH_4OH, H_2O_2 and pure water supplied to the mixing valve **2***b* are mixed and a mixed solution is fed into a cleaning tank **1***b* as an APM solution. APM, which is commonly called SC-1 chemistry, is a mixture of pure-water, hydrogen peroxide and ammonium hydroxide. A semiconductor substrate(not shown) is immersed in the APM solution contained in the APM cleaning tank **1***b* and ultrasonics application means **9** applies megasonics (ultrasonic waves using high frequencies on the order of several hundred kilohertz) to the APM solution. The semiconductor substrate is subjected to the chemical action by the APM solution and a thin film is formed on the substrate surface. As a result, particles (particle-like impurities) are lifted from the surface slightly as compared with the conditions prior to formation of the thin film. This phenomenon is referred to as "lift-up". The particles (particle-like impurities) that have been lifted up are physically peeled (stripped) off together with the thin film formed on the substrate surface by etching effect of the NH_4OH and the molecular motion of the APM solution (the action of the medium) ascribable to the applied megasonics. The particles are discharged from the tank **11** together with the waste solution. The particles that were adhering to the substrate surface are thus removed.

[0005] The common practice is to use ultra-pure water as the aforesaid pure water. Ultra-pure water is obtained by degassing to eliminate dissolved gases such as dissolved oxygen, dissolved nitrogen and dissolved carbon dioxide gas. The reason for this is that using ultra-pure water suppresses the bubbling of the dissolved gases (bubbling cavitation) induced by application of the megasonics, as a result of which more of the megasonic energy (or power) can be imparted by the molecular motion (or vibration) of the APM solution. Other advantages of using ultra-pure water are that the growth of a native oxide film can be suppressed, the occurrence of bacteria in piping can be prevented and so can deterioration of the ion exchange resin in the pure-water equipment.

[0006] However, it has recently been found that cavitation in ultrasonic cleaning is efficacious in the removal of particles. The reason for this is as follows: When megasonics is applied to ultra-pure water, the transmittance of the megasonics is enhanced. When an interface resides in the traveling direction of the megasonic waves, therefore, the megasonic waves are reflected at the interface and standing waves are produced by the traveling waves and reflected waves. Owing to the existence of the standing waves, portions of high and low sonic pressure are formed in the cleaning solution, particles floating in the cleaning solution collect in the portions of low sonic pressure and then re-attach themselves to the substrate. A problem which arises is uneven cleaning. However, when gas forms as bubbles in the cleaning solution, the reflected waves are absorbed into the gas bubbles in the vicinity of the interface in the traveling direction of the megasonic energy. This has the effect of preventing the generation of standing waves and can prevent the occurrence of uneven cleaning.

[0007] For this reason, ultrasonic cleaning is now being carried out using pure water in which has been dissolved an inert gas such as nitrogen that has no influence upon the growth of a native oxide film, the occurrence of bacteria and deterioration of the ion exchange resin while cavitation is produced. Examples of the prior art indicative of this tendency will now be described.

[0008] For example, a technique described in the specification of Japanese Patent Kokai Publication JP-A-10-335294 raises the concentration of dissolved nitrogen gas to super-saturation while avoiding the dissolving of oxygen and carbon dioxide in pure water, thereby producing a great deal of cavitation to reconcile both the suppression of growth of a naturally oxidized film and raise the particle removal efficiency.

[0009] Further, a technique described in the specification of Japanese Patent Kokai Publication JP-A-10-109072 controls the dissolved gas concentration (e.g., regulates nitrogen, argon and helium, etc., to a predetermined concentration of 5 to 10 ppm), whereby the ultrasonic waves become traveling waves only and no standing waves are produced. This eliminates uneven cleaning, prevents reverse contamination and improves particle removability.

SUMMARY OF THE DISCLOSURE

[0010] In the cleaning of substrates, use is made of a solution, such as APM solution, in which hydrogen peroxide has been dissolved in pure water. Owing to continued miniaturization in design rule of a semiconductor in recent years, the width of patterns formed on substrates and the spacing between the patterns have become increasingly smaller. As a result, particles of much smaller size must now to be removed in substrate cleaning and the number of particles that remain on a substrate after its cleaning is required to be a value more close to zero. However, even if the concentration of dissolved nitrogen gas in pure water used in an APM solution or the like is controlled by the conventional method, it is difficult to achieve the cleaning

ability sought for the substrate cleaning fluid by employing the solutions of the aforementioned type.

[0011] Accordingly, it is an object of the present invention to provide a substrate cleaning method, cleaning solution and cleaning apparatus capable of removing particles from a substrate with a high degree of performance, as well as a semiconductor device cleaned by the cleaning method.

[0012] Through repeated experimentation and analysis of result of the experimentation, the Inventor has found that H_2O_2, which is vital in the cleaning process, fails to function in such solutions as APM solution (a solution that is a mixture of NH_4OH, H_2O_2 and pure water) and HPM solution (a solution that is a mixture of HCl, H_2O_2 and pure water) used in ultrasonic cleaning. In other words, the Inventor has clarified that cavitation by bubbling of H_2O_2 is inadequate. The cause of inadequate cavitation of H_2O_2 is as follows: Dissolved nitrogen in the pure water constituting the major part of APM solution is fed into the cleaning tank directly without being reduced. As a consequence, more than half the megasonic energy impressed upon the cleaning solution is consumed in the bubbling (cavitation) of the dissolved nitrogen, which plays no direct role in cleaning. The result is inactivity of the cleaning-solution molecules, a failure to increase the number of volatile bubbles produced by the H_2O_2 molecules and a failure to achieve an efficacious particle removal effect.

[0013] An inert gas such as nitrogen is dissolved beforehand in pure water that is supplied. This is to prevent oxygen from dissolving in the pure water in the process of delivering the pure water to the cleaning tank.

[0014] Though there is only weak bonding force (hydrogen bonds) between H_2O_2 and water, even a weaker bonding force than that between H_2O_2 and water acts between nitrogen and water. Dissolved nitrogen, therefore, is caused to form bubbles preferentially by ultrasonic waves (megasonics). Though dissolved H_2O_2 forms bubbles less easily than dissolved nitrogen, this does not mean that it does not form bubbles at all. The dissolved H_2O_2 is bubbled but the bubbles implode immediately thereafter and the H_2O_2 goes into solution. The H_2O_2 produces shock waves ascribable to the implosion of the bubbles that were induced, and the shock waves contribute greatly to cleaning. In other words, the shock waves contribute to the stripping off of particles in a state in which the thin film is thinner than that when only the motion (vibration) of the solution molecules is utilized.

[0015] Bubble formation (cavitation) of H_2O_2 can be achieved to some extent if power (sonic pressure) is applied appropriately. However, application of power may result in damage to the substrate (e.g., destruction of the patterns).

[0016] The foregoing and other objects are attained a method of cleaning a substrate in accordance with one aspect of the present invention, the method comprising a first step of adjusting concentration of dissolved nitrogen in pure water, so as to be less than or equal to concentration of dissolved nitrogen in equilibrium with the atmosphere (about 16 ppm), in a pure-water supply line that supplies the pure water; and a second step of cleaning a substrate by supplying a cleaning tank with a cleaning solution produced by mixing at least hydrogen peroxide with the pure water adjusted at the first step, and applying an ultrasonic wave to the cleaning solution in which the substrate has been immersed. This method makes the hydrogen peroxide, which is vital for the cleaning process, function by adjusting the concentration of dissolved nitrogen so as to be less than the concentration of dissolved nitrogen in a state of equilibrium with the atmosphere. Here the term "equilibrium dissolved-nitrogen concentration" refers to the concentration of dissolved nitrogen in pure water in a state of equilibrium with the atmosphere.

[0017] According to another aspect of the present invention, the foregoing object is attained by providing a method of cleaning a substrate comprising a first step of adjusting concentration of dissolved nitrogen in pure water, so as to be less than or equal to concentration of dissolved nitrogen in equilibrium with the atmosphere (about 16 ppm), in a pure-water supply line that supplies the pure water; and a second step of cleaning a substrate by supplying a cleaning tank with a cleaning solution produced by mixing hydrogen peroxide and ammonia with the pure water adjusted at the first step, and applying an ultrasonic wave to the cleaning solution in which the substrate has been immersed. This method makes the hydrogen peroxide function even in a case where APM solution (a solution that is a mixture of NH_4OH, H_2O_2 and pure water) is used. It should be noted that since ammonia exhibits strong hydrogen bonding with respect to water, almost no bubbling of ammonia due to the application of an ultrasonic wave (megasonics) occurs.

[0018] In the substrate cleaning method set forth above, the cleaning of the substrate at the second step preferably includes inducing bubbling, by application of ultrasonic waves, of at least the hydrogen peroxide dissolved in the cleaning solution and causing the bubbles of the hydrogen peroxide to implode. The reason for this is that more efficient cleaning can be performed owing to the shock waves produced by the implosion of the bubbles of hydrogen peroxide.

[0019] In the substrate cleaning method set forth above, it is preferred that the concentration of dissolved nitrogen in pure water be such that the generation of standing waves can be prevented by inducing bubbling of nitrogen and hydrogen peroxide (i.e., such that reflected waves are impeded in the vicinity of the boundary surface). A concentration of 10 to 16 ppm is preferable. The reason for this is that not only the bubbles of nitrogen but also the bubbles of hydrogen peroxide contribute to the prevention of the occurrence of standing waves. If the concentration of dissolved nitrogen is less than 10 ppm, the effect of preventing the occurrence of standing waves by the bubbles of nitrogen and hydrogen peroxide is diminished and cleaning efficiency declines. If the concentration of dissolved nitrogen is greater than 16 ppm, on the other hand, then the major part of the megasonic energy is consumed in the bubbling of nitrogen and, hence, the energy needed for the bubbling of hydrogen peroxide is inadequate.

[0020] In the substrate cleaning method set forth above, the concentration of dissolved nitrogen in pure water prior to the adjustment in the first step preferably is the concentration (about 16 ppm) of dissolved nitrogen in pure water in a state of equilibrium with the atmosphere. This is to prevent the dissolution of harmful oxygen in the process of delivering the pure water prior to adjustment.

[0021] In the substrate cleaning method set forth above, it is preferred that adjustment of the concentration of dissolved

nitrogen at the first step include measuring the concentration of dissolved nitrogen in pure water delivered through the pure-water supply line that supplies the pure water, and adjusting amount of degassing of the pure water based upon information relating to the measured concentration of the dissolved nitrogen. This is to so arrange it that pure water of a proper dissolved-nitrogen concentration can be supplied automatically.

[0022] According to a further of the present invention, the foregoing object is attained by providing a cleaning solution including pure water and hydrogen peroxide, wherein the pure water is such that concentration of dissolved nitrogen has been adjusted so as to be less than concentration of dissolved nitrogen in equilibrium with the atmosphere. Owing to the combination of the hydrogen peroxide with pure water, the hydrogen peroxide, which is vital for the cleaning process, is made to function. Preferably, the concentration of dissolved nitrogen in pure water after adjustment is 10 to 16 ppm. This is to induce bubbling of the hydrogen peroxide sufficiently without the occurrence of standing waves so that cleaning can be performed evenly and efficiently.

[0023] According to a further aspect of the present invention, the foregoing object is attained by providing a cleaning apparatus having a cleaning tank for accommodating a cleaning solution for cleaning a substrate, ultrasonics application means for applying an ultrasonic wave to the cleaning solution, a mixer for producing the cleaning solution by mixing pure water and at least hydrogen peroxide, and for supplying the produced cleaning solution to the cleaning tank directly or after being adjusted in temperature, a hydrogen-peroxide supply line for supplying the mixer with hydrogen peroxide, and a pure-water supply line for supplying the mixer with pure water, the cleaning apparatus comprising a measurement unit for measuring concentration of dissolved nitrogen in the pure water delivered through the pure-water supply line; a degassing unit for adjustably degassing the dissolved nitrogen from the pure water delivered through the pure-water supply line; and a control unit for controlling the concentration of dissolved nitrogen in pure water using the degassing unit based upon information relating to the concentration of dissolved nitrogen measured by the measurement unit.

[0024] According to a further aspect of the present invention, the foregoing object is attained by providing a cleaning apparatus having a cleaning tank for accommodating a cleaning solution for cleaning a substrate, ultrasonics application means for applying an ultrasonic wave to the cleaning solution, a mixer for producing the cleaning solution by mixing pure water, hydrogen peroxide and ammonia, and for supplying the produced cleaning solution to the cleaning tank directly or after being adjusted in temperature, a hydrogen-peroxide supply line for supplying the mixer with hydrogen peroxide, an ammonia supply line for supplying the mixer with ammonia, and a pure-water supply line for supplying the mixer with pure water, the cleaning apparatus comprising a measurement unit for measuring concentration of dissolved nitrogen in the pure water delivered through the pure-water supply line; a degassing unit for adjustably degassing the dissolved nitrogen from the pure water delivered through the pure-water supply line; and a control unit for controlling the concentration of dissolved nitrogen in pure water using the degassing unit based upon information relating to the concentration of dissolved nitrogen measured by the measurement unit.

[0025] In the cleaning apparatus described above, the measurement unit and the degassing unit preferably are placed in the pure-water supply line in close proximity to the mixer. This is to suppress the dissolution of harmful oxygen in the process of delivering the pure water after to adjustment.

[0026] Still other objects and advantages of the present invention will become readily apparent to those skilled in this art from the following detailed description in conjunction with the accompanying drawings wherein only the preferred embodiments of the invention are shown and described, simply by way of illustration of the best mode contemplated of carrying out this invention. As will be realized, the invention is capable of other and different embodiments, and its several details are capable of modifications in various obvious respects, all without departing from the invention. Accordingly, the drawing and description are to be regarded as illustrative in nature, and not as restrictive.

BRIEF DESCRIPTION OF THE DRAWINGS

[0027] **FIG. 1** is a block diagram schematically illustrating the structure of a cleaning apparatus according to a first embodiment of the present invention;

[0028] **FIG. 2** is a graph illustrating the relationship between concentration of dissolved nitrogen in pure water and particle removal rate in a case where the cleaning method of the first embodiment is used;

[0029] **FIG. 3** is a graph illustrating the relationship between concentration of dissolved nitrogen in pure water and sonic pressure in a case where the cleaning method of the first embodiment is used;

[0030] **FIG. 4** is a block diagram schematically illustrating the structure of a cleaning apparatus according to a second embodiment of the present invention;

[0031] **FIG. 5** is a graph illustrating the relationship between concentration of dissolved nitrogen in pure water and increase in number of particles in a case where the cleaning method of the second embodiment is used; and

[0032] **FIG. 6** is a block diagram schematically illustrating the structure of a cleaning apparatus according to an example of the prior art.

PREFERRED EMBODIMENTS OF THE INVENTION

[0033] Preferred embodiments of the present invention will be described.

[0034] In accordance with a preferred embodiment of the present invention, there is provided a method of cleaning a substrate that includes a first step of adjusting the concentration of dissolved nitrogen in pure water, so as to be less than or equal to the concentration of dissolved nitrogen in equilibrium with the atmosphere (about 16 ppm), in a pure-water supply line that supplies the pure water; and a second step of supplying a cleaning tank with a cleaning solution produced by mixing at least hydrogen peroxide with

the pure water adjusted at the first step, and applying an ultrasonic wave (megasonics) to the cleaning solution, in which a substrate has been immersed, to thereby clean the substrate. As a result, megasonic (ultrasonic) energy consumed in inducing bubbling of nitrogen is reduced so that sonic pressure is transferred to the semiconductor substrate more effectively.

[0035] More specifically, a semiconductor substrate is subjected to the chemical action of the cleaning solution and a thin film is formed on the substrate surface. As a result, particles adhering to the substrate surface are lifted up from the surface slightly as compared with the conditions prior to formation of the thin film. The particles that have been lifted up are physically peeled (stripped) off together with the thin film on the substrate surface by the molecular motion of the solution ascribable to the applied megasonics and the shock waves produced by the implosion of the H2O2 bubbles induced. The particles are discharged from the tank together with the waste solution. In particular, the shock waves caused by the implosion of the H_2O_2 bubbles contribute to the stripping off of particles in a state in which the thin film is thinner than that when only the motion of the solution molecules is utilized. At the same time, the occurrence of standing waves can be suppressed by the nitrogen and hydrogen peroxide bubbles induced by application of megasonics.

[0036] Preferred embodiments of the present invention will now be described in detail with reference to the accompanying drawings.

[0037] **FIG. 1** is a block diagram schematically illustrating the structure of a cleaning apparatus according to a first embodiment of the present invention

[0038] The cleaning apparatus according to the present embodiment is an ultrasonic cleaning apparatus for an APM solution (a mixture of NH_4OH, H_2O_2 and pure water) and is of the type in which the cleaning solution is disposable. The apparatus includes a cleaning tank **1**, ultrasonics application means **9**, a mixer **2**, an H_2O_2 supply line **3**, an NH_4OH supply line **4**, a pure-water supply line **5**, a measurement unit **6**, a degassing unit **7** and a control unit **8**.

[0039] The cleaning tank **1** accommodates the cleaning solution (APM cleaning fluid) and is for cleaning semiconductor substrates(not shown). The cleaning tank **1** has an inlet section, which is connected to the mixer **2** via piping, for introducing the cleaning solution, and an outlet section from which the cleaning solution flows to the outside after cleaning is performed. The cleaning tank **1** may be a single tank or may be divided into two tanks, namely a tank exclusively for cleaning and a tank for rinsing.

[0040] The ultrasonics application means **9** applies ultrasonic waves to the cleaning solution(fluid), which is contained in the cleaning tank **1**. The ultrasonics application means **9** comprises for example a ceramic piezoelectric oscillator which is excited by a high frequency AC voltage to cause the oscillator to vibrate, thereby generating an acoustic wave which is transmitted through the cleaning fluid. As a result, the cleaning fluid in the tank **1** is vibrated upward from the bottom side thereof. The ultrasonic wave used in this embodiment has a frequency of 750 kHz (which belongs to a megasonic frequency band) and an output power of 760 W.

[0041] The mixer **2** produces the cleaning solution by mixing the pure water, hydrogen peroxide and ammonium hydroxide(ammonia water) supplied at a predetermined ratio. The pure-water supply line **5**, H_2O_2 supply line **3** and NH_4OH supply line **4** are connected as flow passageways, the flow rate of the flow from each line is regulated by a flow-meter(not shown), the fluid is regulated to a fixed temperature in an isothermal tank (or the fluids are mixed directly using a mixing valve), the passageways are connected to the cleaning tank **1** via piping and the cleaning solution thus produced is supplied to the cleaning tank **1**. The compositional ratio of NH_4OH : H_2O_2 : pure water in the APM solution (the mixture of NH_4OH, H_2O_2 and pure water) typically is 1:4:20.

[0042] The H_2O_2 supply line **3** is piping that supplies the mixer **2** with the delivered hydrogen peroxide and is connected to the mixer **2** as a flow passageway. The concentration of the hydrogen peroxide supplied from the H_2O_2 supply line **3** in this embodiment is about 31 wt(weight) %.

[0043] The NH_4OH supply line **4** is piping that supplies the mixer **2** with the delivered ammonia water and is connected to the mixer **2** as a flow passageway. The concentration of the hydrogen peroxide supplied from the NH_4OH supply line **4** in this embodiment is about 29 wt %.

[0044] The pure-water supply line **5** is piping that supplies the mixer **2** with the pure water. It is connected to the mixer **2** as a flow passageway and has the degassing unit **7** and the measurement unit **6** on the secondary (downstream) side. Pure water supplied from the primary side (the side upstream of the degassing unit **7**) has a dissolved-nitrogen concentration (15 to 16 ppm) in equilibrium with an atmosphere in order to prevent oxygen from dissolving into the solution.

[0045] The degassing unit **7** is adapted to be capable of performing vacuum degassing of the pure water flowing through the pure-water supply line **5** in such a manner that the concentration of dissolved nitrogen can be adjusted. The degassing unit **7** incorporates a depressurizing pump(not shown) that is opened and closed under control of the control unit **8** to thereby regulate the degree of vacuum. Here the dissolved-nitrogen concentration is adjusted (to 12 to 13 ppm, for example) so as to be less than or equal to the dissolved-nitrogen concentration of the atmosphere and pure water in a state of equilibrium (namely an equilibrium dissolved-nitrogen concentration of 15 to 16 ppm). Here vacuum degassing is carried out quantitatively under reduced pressure of about 0.6 to 0.05 atm based upon Henry's Law. Regarding the more specific configuration the degassing unit adapted for ultrasonic cleaning, a reference may be made to such a publication as "Hitoshi Shiraishi, 'ultrasonic cleaning and degassing—MDO series adopting a degassing tower system—,' Ultrasonic TECHNO, Vol. 13, No.4, 2001, page 58".

[0046] The measurement unit **6** includes a sensor for measuring the concentration of dissolved nitrogen in the pure water on the secondary side (the side downstream of the degassing unit **7**) of the pure-water supply line **5**. The measurement unit **6** sends information relating to the measured dissolved-nitrogen concentration via a signal line **10** to the control unit **8**. As for more details of the measurement unit, a reference may be made to product information of an

off-the shelf product for measuring dissolved nitrogen(N2) concentration, such as 325X product series from Orbishere (orbishere.com web site).

[0047] In response to receipt of the information relating to the dissolved-nitrogen concentration measured by the measurement unit **6**, the control unit **8** sends a control signal II to the degassing unit **7** to control the concentration of the dissolved nitrogen in the pure water by regulating the degree of vacuum in the degassing unit **7** based upon the received information.

[0048] The operation of the cleaning apparatus according to the first embodiment will now be described.

[0049] First, the concentration of dissolved nitrogen in the pure water that flows in from the primary side of the pure-water supply line **5** is reduced (to 12 to 13 ppm, for example) by the degassing unit **7** so as to be less than the pure-water dissolved-nitrogen concentration of 15 to 16 ppm in a state of equilibrium with the atmosphere (namely the equilibrium dissolved-nitrogen concentration). At this time the concentration of dissolved nitrogen in the delivered pure water (degassed) is measured using the measurement unit **6** on the secondary side of the pure-water supply line **5** and the degree to which the vacuum valve of the degassing unit **7** is opened is regulated by the control unit **8** based upon the information relating to the measured concentration of dissolved nitrogen.

[0050] Next, the pure water of reduced dissolved-nitrogen concentration is allowed to flow to the secondary side, where the mixer **2** mixes NH_4OH, H_2O_2 and pure water of reduced dissolved-nitrogen concentration at the ratio of 1:4:20, thereby producing the APM solution. The mixer **2** supplies the resulting APM solution to the cleaning tank **1**. A semiconductor substrate to be cleaned is immersed in the APM solution contained in the cleaning tank **1**, and to the APM solution is applied ultrasonic waves (megasonics) having a frequency of several hundred kilohertz. As a result, particles are removed from the semiconductor substrate immersed in the APM solution.

[0051] Finally, in an optional step, rinsing with pure water is carried out. Specifically, after APM cleaning, the concentration of dissolved nitrogen in the pure water that flows in from the primary side of the pure-water supply line **5** is reduced (to 12 to 13 ppm, for example) by the degassing unit **7** so as to be less than the pure-water dissolved-nitrogen concentration of 15 to 16 ppm in a state of equilibrium with the atmosphere (namely the equilibrium dissolved-nitrogen concentration). The pure water of reduced dissolved-nitrogen concentration is allowed to flow to the secondary side, whence it is supplied to the cleaning tank **1** as is without being mixed with other fluids in the mixer **2**. The semiconductor substrate is immersed in this pure water of reduced dissolved-nitrogen concentration contained in the cleaning tank **1** and the pure water is subjected to megasonics having a frequency of several hundred kilohertz. At this stage the supply of ammonia water and hydrogen peroxide from the NH_4OH supply line **4** and H_2O_2 supply line **3** to the mixer **2** is halted.

[0052] According to cleaning based upon the first embodiment, the major part of the APM solution is composed of pure water. When the concentration of dissolved nitrogen in the pure water is made less than the equilibrium concentration with respect to the atmosphere, greater motion of the solution molecules is produced. At the same time, the number of volatile bubbles of dissolved hydrogen peroxide molecules increases and shock waves are produced in abundance by the implosion of these bubbles. Owing to the motion of the solution molecules and the shock waves produced by the bubble implosion phenomenon, particles on the semiconductor substrate are stripped away. As illustrated in **FIG. 2**, therefore, the rate at which particles are removed from a substrate rises sharply as the concentration of dissolved nitrogen in pure water is reduced. This is advantageous in that device yield is improved significantly.

[0053] The reason for the above is construed to be as follows: The proportion of the number of volatile bubbles of dissolved hydrogen peroxide and of the molecular motion-(vibration) thereof increases owing to a reduction in the concentration of dissolved nitrogen in pure water. The reason for the increase is that the energy propagation(sonic pressure) at application of megasonics is inhibited from being consumed for the purpose of inducing the bubbling of dissolved nitrogen, which plays no role whatsoever in the cleaning effect.

[0054] Further, as depicted in **FIG. 3**, when the concentration of dissolved nitrogen is made less than the equilibrium concentration, sonic pressure rises. This is because it becomes more difficult for the sonic pressure to be absorbed (consumed) by nitrogen bubbling. In addition, the megasonic energy (the power of acoustic waves having a megasonic frequency) is directed toward the bubbling of hydrogen peroxide. As a result, while the generation of standing waves is inhibited by the bubbles of hydrogen peroxide using the same amount of energy, shock waves ascribable to implosion of the bubbles of hydrogen peroxide are utilized without imparting energy anew (i.e., without increasing the amount of energy).

[0055] A second embodiment of the present invention will now be described.

[0056] **FIG. 4** is a block diagram illustrating a structure of a cleaning apparatus according to a second embodiment of the present invention.

[0057] The cleaning apparatus of this embodiment is an ultrasonic cleaning apparatus for an HPM solution (a mixture of HCl, H_2O_2 and pure water) and is of the type in which the cleaning solution is disposable. With the exception of the fact that the NH_4OH supply line **4** in the cleaning apparatus of **FIG. 1** is replaced by an HCl supply line **4***a*, structurally this embodiment is the same as that of the first embodiment. The HPM solution is used in a case where cleaning is applied to a semiconductor substrate that requires the removal of metallic contaminants from its surface.

[0058] The operation of the cleaning apparatus according to the second embodiment will now be described.

[0059] First, HPM cleaning (metallic cleaning) is performed. The mixer **2** is supplied with hydrogen chloride from the HCl supply line **4***a* and hydrogen peroxide from the H_2O_2 supply line **3**, and is further supplied with pure water, which has not been adjusted by degassing, from the pure-water supply line **5**. The mixer **2** mixes these at an HCl : H_2O_2 : pure water ratio of 1:1:5, thereby producing the HPM solution. The mixer **2** supplies this HPM solution to the cleaning tank **1***a*. A semiconductor substrate (one which

requires removal of metallic contaminants from its surface) is immersed in the HPM solution contained in the cleaning tank **1***a*, and HPM cleaning is carried out. As a result, metals are removed from the surface of the semiconductor substrate. At this stage the degassing unit **7** in the pure-water supply line **5** does not operate. In addition, megasonics is not applied to the HPM solution.

[**0060**] Next, primary rinsing is carried out. Specifically, after HPM cleaning, the concentration of dissolved nitrogen in the pure water that flows in from the primary side of the pure-water supply line **5** is reduced (to 12 to 13 ppm, for example) by the degassing unit **7** so as to be less than the pure-water dissolved-nitrogen concentration of 15 to 16 ppm in a state of equilibrium with the atmosphere (namely the equilibrium dissolved-nitrogen concentration). The pure water of reduced dissolved-nitrogen concentration is allowed to flow to the secondary side. Here the mixer **2** mixes hydrogen peroxide and the pure water of reduced dissolved nitrogen concentration at an H_2O_2 : pure water ratio of 1:50 to 100 and supplies the resulting PM solution (a mixture of hydrogen peroxide and pure water) to the cleaning tank **1***a*. Megasonics having a frequency of several hundred kilohertz is applied to the PM solution contained in the cleaning tank **1***a* and having the semiconductor substrate (which required removal of metallic contaminants from its surface) immersed therein. As a result, particles are removed from the surface of the semiconductor substrate immersed in the PM solution. At this stage the supply of hydrogen chloride from the HCl supply line **4***a* to the mixer **2** is halted. Further, the concentration of hydrogen peroxide supplied from the H_2O_2 supply line **3** is 31 percent by weight in this embodiment.

[**0061**] Finally, secondary rinsing is carried out. Specifically, after PM cleaning, the concentration of dissolved nitrogen in the pure water that flows in from the primary side of the pure-water supply line **5** is reduced (to 12 to 13 ppm, for example) by the degassing unit **7** so as to be less than the pure-water dissolved-nitrogen concentration of 15 to 16 ppm in a state of equilibrium with the atmosphere (namely the equilibrium dissolved-nitrogen concentration). The pure water of reduced dissolved-nitrogen concentration is allowed to flow to the secondary side, whence it is supplied to the cleaning tank **1***a* as is without being mixed with other fluids in the mixer **2**. Megasonics having a frequency of several hundred kilohertz is applied to the pure water of reduced dissolved-nitrogen concentration contained in the cleaning tank **1***a* and having the semiconductor substrate (which required removal of metallic contaminants from its surface) immersed therein. At this stage the supply of hydrogen chloride and hydrogen peroxide from the HCl supply line **4***a* and H_2O_2 supply line **3** to the mixer **2** is halted.

[**0062**] By virtue of the foregoing process, particles can be removed or prevented from re-adhering, following the removal of metal contaminants, by more active molecular motion ascribable to nitrogen degassing of the pure water and shock waves produced by implosion of hydrogen peroxide bubbles.

[**0063**] **FIG. 5** is a graph illustrating the relationship between concentration of dissolved nitrogen in pure water and increase in number of particles (in terms of a comparison before and after metal removal) in a case where the cleaning method of the second embodiment is used. It will be understood from **FIG. 5** that the total number of particles of size not less than 0.13 um(micro-meter) can be reduced so as to fall within an increase of ten particles or less per wafer (cut to an outer periphery of 3 mm) by reducing the concentration of dissolved nitrogen. In other words, a wafer contaminated with a very small number of particles can eventually be obtained by reducing the concentration of dissolved nitrogen.

[**0064**] It should be noted that the primary and secondary rinsing steps in the second embodiment can be utilized after SPM cleaning (cleaning using a solution that is a mixture of H_2SO_4 and H_2O_2) or HF cleaning (cleaning using a solution that is a mixture of HF and pure water) employed in metallic cleaning (cleaning of a naturally oxidized film). In such case also it is possible to obtain a wafer having few contaminating particles thanks to a reduction in dissolved-nitrogen concentration.

[**0065**] The meritorious effects of the present invention are summarized as follows.

[**0066**] Thus, in accordance with the present invention as described above, the generation of bubbles by dissolved nitrogen (nitrogen bubbles exhibit no cleaning effect) can be suppressed and it is possible to achieve a relative increase in the efficiency with which bubbles of hydrogen peroxide are produced (bubbles of hydrogen peroxide do exhibit a cleaning effect). That is, sonic pressure formerly used in the bubbling of dissolved nitrogen can be directed toward the bubbling of hydrogen peroxide. As a result, the implosion of bubbles of hydrogen peroxide can be promoted, thereby greatly improving the particle removal rate.

[**0067**] Further, since the sonic pressure of the cleaning solution is transmitted to a semiconductor substrate efficiently, it is possible to remove particles directly by molecular motion.

[**0068**] As many apparently widely different embodiments of the invention can be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments thereof except as defined in the appended claims.

[**0069**] It should be noted that other objects, features and aspects of the present invention will become apparent in the entire disclosure and that modifications may be done without departing the gist and scope of the present invention as disclosed herein and claimed as appended herewith.

[**0070**] Also it should be noted that any combination of the disclosed and/or claimed elements, matters and/or items may fall under the modifications aforementioned.

What is claimed is:

1. A method of cleaning a substrate comprising:

a first step of adjusting concentration of dissolved nitrogen in pure water, so as to be less than or equal to concentration of dissolved nitrogen in equilibrium with an atmosphere, in a pure-water supply line that supplies the pure water; and

a second step of supplying a cleaning tank with a cleaning solution produced by mixing at least hydrogen peroxide with the pure water having the concentration of dissolved nitrogen adjusted at the first step, and apply-

ing an ultrasonic wave to the cleaning solution in which a substrate is immersed to perform cleaning of the substrate.

2. A method of cleaning a substrate comprising:

a first step of adjusting concentration of dissolved nitrogen in pure water, so as to be less than or equal to concentration of dissolved nitrogen in equilibrium with the atmosphere, in a pure-water supply line that supplies the pure water; and

a second step of supplying a cleaning tank with a cleaning solution produced by mixing hydrogen peroxide and ammonia with the pure water having the concentration of dissolved nitrogen adjusted at the first step, and applying an ultrasonic wave to the cleaning solution in which a substrate is immersed to perform cleaning of the substrate.

3. The method according to claim 1, wherein said second step includes steps of:

inducing bubbling, by application of the ultrasonic wave, of at least the hydrogen peroxide dissolved in the cleaning solution; and

causing a bubble of the hydrogen peroxide to implode.

4. The method according to claim 1, wherein the concentration of dissolved nitrogen in the pure water after the adjustment performed at said first step is 10 to 16 ppm.

5. The method according to claim 1, wherein the first step includes steps of:

measuring the concentration of dissolved nitrogen in the pure water delivered through the pure-water supply line that supplies the pure water; and

adjusting amount of degassing the pure water based upon information relating to the measured concentration of the dissolved nitrogen.

6. The method according to claim 2, wherein said second step includes steps of:

inducing bubbling, by application of the ultrasonic wave, of at least the hydrogen peroxide dissolved in the cleaning solution; and

causing a bubble of the hydrogen peroxide to implode.

7. The method according to claim 2, wherein the concentration of dissolved nitrogen in the pure water after the adjustment performed at said first step is 10 to 16 ppm.

8. The method according to claim 2, wherein the first step includes steps of:

measuring the concentration of dissolved nitrogen in the pure water delivered through the pure-water supply line that supplies the pure water; and

adjusting amount of degassing the pure water based upon information relating to the measured concentration of the dissolved nitrogen.

9. A cleaning solution comprising pure water and hydrogen peroxide;

concentration of dissolved nitrogen in the pure water being adjusted so as to be less than or equal to concentration of dissolved nitrogen in equilibrium with the atmosphere.

10. The cleaning solution according to claim 9, wherein the concentration of dissolved nitrogen in the pure water is 10 to 16 ppm.

11. A cleaning apparatus comprising:

a cleaning tank for accommodating a cleaning solution for cleaning a substrate;

ultrasonics application means for applying an ultrasonic wave to the cleaning solution;

a mixer for producing the cleaning solution by mixing pure water and at least hydrogen peroxide, and for supplying the produced cleaning solution to said cleaning tank directly or after being adjusted in temperature;

a hydrogen-peroxide supply line for supplying said mixer with hydrogen peroxide;

a pure-water supply line for supplying said mixer with pure water;

a measurement unit for measuring concentration of dissolved nitrogen in the pure water delivered through said pure-water supply line;

a degassing unit for adjustably degassing the dissolved nitrogen in the pure water delivered through said pure-water supply line; and

a control unit for controlling the concentration of dissolved nitrogen in pure water using said degassing unit based upon information relating to the concentration of dissolved nitrogen measured by said measurement unit.

12. A cleaning apparatus comprising:

a cleaning tank for accommodating a cleaning solution for cleaning a substrate;

ultrasonics application means for applying an ultrasonic wave to the cleaning solution;

a mixer for producing the cleaning solution by mixing pure water and at least hydrogen peroxide, and for supplying the produced cleaning solution to said cleaning tank directly or after being adjusted in temperature;

a hydrogen-peroxide supply line for supplying said mixer with hydrogen peroxide;

a pure-water supply line for supplying said mixer with pure water;

a mixer for producing the cleaning solution by mixing pure water, hydrogen peroxide and ammonia, and for supplying the produced cleaning solution to said cleaning tank directly or after being adjusted in temperature;

a hydrogen-peroxide supply line for supplying said mixer with hydrogen peroxide;

an ammonia supply line for supplying said mixer with ammonia;

a pure-water supply line for supplying said mixer with pure water;

a measurement unit for measuring concentration of dissolved nitrogen in the pure water delivered through said pure-water supply line;

a degassing unit for adjustably degassing the dissolved nitrogen in the pure water delivered through said pure-water supply line; and

a control unit for controlling the concentration of dissolved nitrogen in pure water using said degassing unit

based upon information relating to the concentration of dissolved nitrogen measured by said measurement unit.

13. The apparatus according to claim 11, wherein said measurement unit and said degassing unit are disposed in said pure-water supply line in close proximity to said mixer.

14. The apparatus according to claim 12, wherein said measurement unit and said degassing unit are disposed in said pure-water supply line in close proximity to said mixer.

15. A semiconductor substrate cleaned by a cleaning method comprising a first step of adjusting concentration of dissolved nitrogen in pure water, so as to be less than or equal to concentration of dissolved nitrogen in equilibrium with an atmosphere, in a pure-water supply line that supplies the pure water; and

a second step of supplying a cleaning tank with a cleaning solution produced by mixing at least hydrogen peroxide with the pure water having the concentration of dissolved nitrogen adjusted at the first step, and applying an ultrasonic wave to the cleaning solution in which the semiconductor substrate is immersed to perform cleaning of the semiconductor substrate.

16. A semiconductor substrate cleaned by a cleaning method comprising a first step of adjusting concentration of dissolved nitrogen in pure water, so as to be less than or equal to concentration of dissolved nitrogen in equilibrium with the atmosphere, in a pure-water supply line that supplies the pure water; and

a second step of supplying a cleaning tank with a cleaning solution produced by mixing hydrogen peroxide and ammonia with the pure water having the concentration of dissolved nitrogen adjusted at the first step, and applying an ultrasonic wave to the cleaning solution in which the semiconductor substrate is immersed to perform cleaning of the semiconductor substrate.

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