DESCRIPTION

TITLE OF INVENTION: APPARATUS FOR PRODUCING PH/REDOX POTENTIAL-ADJUSTED WATER, METHOD FOR PRODUCING PH/REDOX POTENTIAL-ADJUSTED WATER, AND METHOD FOR PRODUCING SEMICONDUCTOR DEVICE

Technical Field

[0001] The present invention relates to a pH/redox potential-adjusted water production device, a production method for pH/redox potential-adjusted water, and a manufacturing method for a semiconductor device.

This application claims priority based on Japanese Patent Application No. 2024-022868, filed on February 19, 2024, in Japan, the contents of which are incorporated herein by reference.

Related Art

[0002] Among semiconductor manufacturing processes, the dicing process is one of the back-end processes for assembling semiconductor chips. The dicing process is a process in which a semiconductor substrate having a large number of integrated circuits (ICs) formed thereon is cut for each integrated circuit (IC) to be separated into IC chips. In the dicing process, for example, individual IC chips are produced by undergoing a series of stages including bonding the semiconductor substrate after integrated circuit formation to a dicing tape, cutting the semiconductor substrate for each integrated circuit, and then cleaning, removing the dicing tape, and extracting the semiconductor chips.

[0003] As methods for cutting a semiconductor substrate, techniques such as blade dicing and laser ablation dicing are known. Blade dicing is a technique in which an extremely thin blade called a dicing blade is rotated at high speed to cut the semiconductor substrate. Further, laser ablation dicing is a technique in which the semiconductor substrate is cut by irradiating it with high-energy laser light to partially vaporize and sublimate the semiconductor substrate. Among these, blade dicing is the most common method.

[0004] In blade dicing, heat generated by friction between the dicing blade and the semiconductor substrate, as well as cutting debris, are produced during the separation of integrated circuits arranged on the semiconductor substrate. For this reason, blade dicing is generally performed while spraying cooling water to prevent heat generation and remove cutting debris. Pure water or carbonated water is used as the cooling water. Among these, pure water has a high specific resistance, and may cause electrostatic charging of the substrate and electrostatic destruction of devices due to friction between the dicing blade and the semiconductor substrate. For this reason, the application of carbonated water, in which the specific resistance is reduced by dissolving carbon dioxide gas into pure water, is more commonly used.

[0005] Among the dicing blades used during blade dicing, there are blades in which diamond abrasive grains are fixed by a binder to the outer peripheral end face of a disk-shaped blade having a thickness of approximately 15 μm. Metals such as nickel, cobalt, copper, tin, silver, and tungsten are used as the binder for the diamond abrasive grains. Since the dicing blade is used repeatedly in the dicing process, the area around the outer peripheral end face of the blade physically wears with use, connecting to a decline in dicing performance; therefore, the dicing blade is periodically replaced and discarded.

[0006] However, the performance degradation of the dicing blade is not limited to physical factors such as wear. Carbonated water, which is weakly acidic and used as cooling water during dicing, dissolves the various metals that serve as the binder. For this reason, in addition to wear, degradation of dicing performance due to consumption of the binder is also a concern. Accordingly, the use of carbonated water as cooling water is one factor that enhances the replacement frequency of the dicing blade.

Prior Art Documents

Patent Documents

[0007]

Patent Document 1: Japanese Patent Application Laid-Open Publication No. 2022-78489

SUMMARY OF INVENTION

Technical Problem

[0008] The present invention has been made in view of the above circumstances, and an object of the present invention is to provide a production device for producing pH/redox potential-adjusted water capable of reducing the replacement frequency of the dicing blade when used as cooling water for blade dicing, a producing method for pH/redox potential-adjusted water, and a method for manufacturing a semiconductor device.

Solution to Problem

[0009]

In order to solve the above problems, the present invention adopts the following configurations.

[1] A pH/redox potential-adjusted water production device, including: a degassing membrane device having a degassing membrane that removes, from pure water, gas dissolved as an impurity; a pH adjustment device that adjusts a pH of pure water; and

a dissolution membrane device having a gas dissolution membrane that dissolves an inert gas into pure water,

the pH/redox potential-adjusted water production device producing pH/redox potential-adjusted water having a pH of 9 to 14 and a redox potential at 25°C of -0.40 V or more and less than +0.40 V (vs Ag/AgCl).

[2] In the pH/redox potential-adjusted water production device according to [1], the pH adjustment device, the degassing membrane device, and the dissolution membrane device are arranged in sequence along a flow direction of pure water, and

the pH adjustment device adds a liquid pH adjuster to the pure water.

[3] In the pH/redox potential-adjusted water production device according to [2], the pH adjuster is at least one aqueous solution selected from a group consisting of ammonia, sodium hydroxide, potassium hydroxide, tetrahydroammonium, choline, methylamine, dimethylamine, and trimethylamine.

[4] In the pH/redox potential-adjusted water production device according to [1], the degassing membrane device and the dissolution membrane device are arranged in sequence along a flow direction of pure water,

the pH adjustment device supplies a gaseous pH adjuster to the gas dissolution membrane of the dissolution membrane device, and

the dissolution membrane device dissolves at least the pH adjuster into the pure water.

[5] In pH/redox potential-adjusted water production device according to [4], the pH adjuster is at least one selected from a group consisting of ammonia, methylamine, dimethylamine, and trimethylamine.

[6] In the pH/redox potential-adjusted water production device according to [5], the pH adjuster further contains an inert gas.

[7] A pH/redox potential-adjusted water production device, including: a degassing membrane device including a degassing membrane that removes, from pure water, gas dissolved as an impurity; and

a pH adjustment device that adjusts a pH of pure water,

the pH/redox potential-adjusted water production device producing pH/redox potential-adjusted water having a pH of 9 to 14 and a redox potential at 25°C of -0.40 V or more and less than +0.40 V (vs Ag/AgCl).

[8] In the pH/redox potential-adjusted water production device according to [7], the degassing membrane device and the pH adjustment device are arranged in sequence along a flow direction of pure water, and

the pH adjustment device dissolves at least one pH adjuster selected from a gas and a liquid into the pure water.

[9] In the pH/redox potential-adjusted water production device according to [7], the pH adjuster is an aqueous solution containing at least one selected from a group consisting of ammonia,

sodium hydroxide, potassium hydroxide, tetrahydroammonium, choline, methylamine, dimethylamine, and trimethylamine.

[10] In the pH/redox potential-adjusted water production device according to [7], the pH adjuster contains at least one selected from a group consisting of ammonia, methylamine, dimethylamine, and trimethylamine, and an inert gas.

[11] The pH/redox potential-adjusted water production device according to any one of [1] to [10], which produces pH/redox potential-adjusted water having a pH of 9 to 14, a redox potential at 25°C of -0.40 V or more and less than +0.40 V (vs Ag/AgCl), and a dissolved oxygen concentration at 25°C of 50 ppb or less.

[12] The pH/redox potential-adjusted water production device according to any one of [1] to [10], which produces pH/redox potential-adjusted water having a pH of 9 to 14, a redox potential at 25°C of -0.40 V or more and less than +0.40 V (vs Ag/AgCl), and a hydrogen peroxide concentration of 30 ppb or less.

[13] The pH/redox potential-adjusted water production device according to any one of [1] to [10], which produces pH/redox potential-adjusted water having a pH of 9 to 14, a redox potential at 25°C of -0.40 V or more and less than +0.40 V (vs Ag/AgCl), a dissolved oxygen concentration at 25°C of 50 ppb or less, and a hydrogen peroxide concentration of 30 ppb or less.

[14] In the pH/redox potential-adjusted water production device according to any one of [1] to [10], a hydrogen peroxide removal mechanism for removing hydrogen peroxide dissolved as an impurity from the pure water is provided upstream of the degassing membrane device.

[15] The pH/redox potential-adjusted water production device according to any one of [1] to [10], including a supply flow path for supplying the produced pH/redox potential-adjusted water as cooling water to a dicing blade in which diamond abrasive grains are fixed by a binder containing at least one selected from a group consisting of nickel, cobalt, copper, tin, silver, tungsten, and iron.

[16] The pH/redox potential-adjusted water production device according to any one of [1] to [10], including a supply flow path for supplying the produced pH/redox potential-adjusted water as cooling water in a dicing process of a semiconductor manufacturing process.

[17] A production method for pH/redox potential-adjusted water, including, performing sequentially: a pH adjustment process of adjusting a pH of pure water by adding a liquid pH adjuster to pure water;

a degassing process of removing gas dissolved as an impurity from pure water by a degassing membrane; and

a gas dissolution process of dissolving an inert gas into pure water by a gas dissolution membrane, to produce pH/redox potential-adjusted water having a pH of 9 to 14 and a redox potential at 25°C of -0.40 V or more and less than +0.40 V (vs Ag/AgCl).

[18] In the production method for pH/redox potential-adjusted water according to [17], the pH adjuster is an aqueous solution containing at least one selected from a group consisting of ammonia, sodium hydroxide, potassium hydroxide, tetrahydroammonium, choline, methylamine, dimethylamine, and trimethylamine.

[19] A production method for pH/redox potential-adjusted water, including, performing sequentially: a degassing process of removing gas dissolved as an impurity in pure water from pure water by a degassing membrane; and

a process of adjusting a pH of pure water by supplying a gaseous pH adjuster to pure water by a gas dissolution membrane,

to produce pH/redox potential-adjusted water having a pH of 9 to 14 and a redox potential at 25°C of -0.40 V or more and less than +0.40 V (vs Ag/AgCl).

[20] In the production method for pH/redox potential-adjusted water according to [19], the pH adjuster is at least one selected from a group consisting of ammonia, methylamine, dimethylamine, and trimethylamine.

[21] In the production method for pH/redox potential-adjusted water according to [20], the pH adjuster further contains an inert gas.

[22] A production method for pH/redox potential-adjusted water, including, performing sequentially: a degassing process of removing gas dissolved as an impurity in pure water from pure water by a degassing membrane; and

a pH adjustment process of adjusting a pH of pure water by adding at least one pH adjuster selected from a gas and a liquid to pure water,

to produce pH/redox potential-adjusted water having a pH of 9 to 14 and a redox potential at 25°C of -0.40 V or more and less than +0.40 V (vs Ag/AgCl).

[23] In the production method for pH/redox potential-adjusted water according to [22], the pH adjuster is an aqueous solution containing at least one selected from a group consisting of ammonia, sodium hydroxide, potassium hydroxide, tetrahydroammonium, choline, methylamine, dimethylamine, and trimethylamine.

[24] In the production method for pH/redox potential-adjusted water according to [22], the pH adjuster contains at least one selected from a group consisting of ammonia, methylamine, dimethylamine, and trimethylamine, and an inert gas.

[25] The production method for pH/redox potential-adjusted water according to any one of [17] to [24], which produces pH/redox potential-adjusted water having a pH of 9 to 14, a redox potential at 25°C of -0.40 V or more and less than +0.40 V (vs Ag/AgCl), and a dissolved oxygen concentration at 25°C of 50 ppb or less.

[26] The production method for pH/redox potential-adjusted water according to any one of [17] to [24], which produces pH/redox potential-adjusted water having a pH of 9 to 14, a redox potential at 25°C of -0.40 V or more and less than +0.40 V (vs Ag/AgCl), and a hydrogen peroxide concentration of 30 ppb or less.

[27] The production method for pH/redox potential-adjusted water according to any one of [17] to [24], which produces pH/redox potential-adjusted water having a pH of 9 to 14, a redox potential

at 25°C of -0.40 V or more and less than +0.40 V (vs Ag/AgCl), a dissolved oxygen concentration at 25°C of 50 ppb or less, and a hydrogen peroxide concentration of 30 ppb or less.

[28] In the production method for pH/redox potential-adjusted water according to [17], a hydrogen peroxide removal process of removing hydrogen peroxide dissolved as an impurity in pure water from pure water is performed before the pH adjustment process.

[29] In the production method for pH/redox potential-adjusted water according to [19] or [22], a hydrogen peroxide removal process of removing hydrogen peroxide dissolved as an impurity in pure water from pure water is performed before the degassing process.

[30] A manufacturing method for a semiconductor device, including: using the pH/redox potential-adjusted water produced by the production method for pH/redox potential-adjusted water according to any one of [17] to [24] as cooling water for a dicing blade in which diamond abrasive grains are fixed by a metal layer containing at least one selected from a group consisting of nickel, cobalt, copper, tin, silver, tungsten, and iron.

[31] A manufacturing method for a semiconductor device, including using the pH/redox potential-adjusted water produced by the production method for pH/redox potential-adjusted water according to any one of [17] to [24] as cooling water in a dicing process of a semiconductor manufacturing process.

Effects of Invention

[0010] According to the pH/redox potential-adjusted water production device of the present invention, pH/redox potential-adjusted water having a low concentration of dissolved gas, a pH adjusted to 9 to 14, and a stabilized pH and redox potential through dissolution of an inert gas may be produced. Such pH/redox potential-adjusted water may prevent dissolution of various metals forming the binder of a dicing blade. Thus, according to the present invention, it is possible to provide a pH/redox potential-adjusted water production device for cooling water in blade dicing, capable of reducing the replacement frequency of the dicing blade.

[0011] The pH/redox potential-adjusted water production device of the present invention adjusts the pH of pure water by a pH adjustment device that adds a liquid pH adjuster to pure water, removes dissolved gas in the pure water by a degassing membrane device, and dissolves an inert gas in the pure water by a dissolution membrane device. By using a liquid pH adjuster, the pH does not fluctuate even in the case where the pure water after pH adjustment is degassed, and thus pH/redox potential-adjusted water having a stabilized pH and redox potential may be produced.

[0012] According to the pH/redox potential-adjusted water production device of the present invention, the pH adjustment device adds, to pure water, at least one aqueous solution selected from the group consisting of ammonia, sodium hydroxide, potassium hydroxide, tetrahydroammonium, choline, methylamine, dimethylamine, and trimethylamine as a pH adjuster, and thus the pH of the pH/redox potential-adjusted water may be adjusted to a range of 9 to 14.

[0013] The pH/redox potential-adjusted water production device of the present invention removes dissolved gas in pure water by a degassing membrane device, supplies a gaseous pH adjuster to a gas dissolution membrane device by a pH adjustment device, and adds the gaseous pH adjuster to pure water by the gas dissolution membrane device. Since pH adjustment is performed on pure water that has been degassed in advance, the pH of the pure water does not fluctuate, and thus pH/redox potential-adjusted water having a stabilized pH and redox potential may be produced.

[0014] According to the pH/redox potential-adjusted water production device of the present invention, the gas dissolution membrane device adds, to pure water, a pH adjuster that is at least one selected from the group consisting of ammonia, methylamine, dimethylamine, and trimethylamine, and thus the pH of the pH/redox potential-adjusted water may be adjusted to a range of 9 to 14.

[0015] According to the pH/redox potential-adjusted water production device of the present invention, the gas dissolution membrane device dissolves an inert gas together with a gaseous pH

adjuster in pure water, and thus the pH and redox potential of the pH/redox potential-adjusted water may be stabilized.

[0016] According to the pH/redox potential-adjusted water production device of the present invention, pH/redox potential-adjusted water having a low concentration of dissolved gas and a pH adjusted to 9 to 14 may be produced. Such pH/redox potential-adjusted water may prevent dissolution of various metals forming the binder of a dicing blade. Thus, according to the present invention, it is possible to provide a pH/redox potential-adjusted water production device for cooling water in blade dicing, capable of reducing the replacement frequency of the dicing blade.

[0017] The pH/redox potential-adjusted water production device of the present invention removes dissolved gas in pure water by a degassing membrane device and adjusts the pH of pure water by a pH adjustment device that adds at least one pH adjuster selected from a gas and a liquid. Since pH adjustment is performed on pure water that has been degassed in advance, the pH of the pure water does not fluctuate, and thus pH/redox potential-adjusted water having a stabilized pH and redox potential may be produced.

[0018] According to the pH/redox potential-adjusted water production device of the present invention, the pH adjustment device adds, to pure water, a pH adjuster that is at least one selected from the group consisting of ammonia, methylamine, dimethylamine, and trimethylamine, and thus the pH of the pH/redox potential-adjusted water may be adjusted to a range of 9 to 14.

[0019] According to the pH/redox potential-adjusted water production device of the present invention, the pH adjustment device adds, to pure water, a pH adjuster containing at least one selected from the group consisting of ammonia, methylamine, dimethylamine, and trimethylamine, and an inert gas, and thus the pH of the pH/redox potential-adjusted water may be adjusted to a range of 9 to 14, and the pH and redox potential may be stabilized.

[0020] According to the pH/redox potential-adjusted water production device of the present invention, pH/redox potential-adjusted water having a pH of 9 to 14, a redox potential at 25°C of -0.40 V or more and less than +0.40 V (vs Ag/AgCl), and a dissolved oxygen concentration at

25°C of 50 ppb or less is produced. This pH/redox potential-adjusted water may prevent dissolution of various metals forming the binder of a dicing blade, and thus pH/redox potential-adjusted water for cooling water for blade dicing that may reduce the replacement frequency of the dicing blade may be produced.

[0021] According to the pH/redox potential-adjusted water production device of the present invention, pH/redox potential-adjusted water having a pH of 9 to 14, a redox potential at 25°C of -0.40 V or more and less than +0.40 V (vs Ag/AgCl), and a hydrogen peroxide concentration of 30 ppb or less is produced. This pH/redox potential-adjusted water may prevent dissolution of various metals forming the binder of a dicing blade, and thus pH/redox potential-adjusted water for cooling water for blade dicing that may reduce the replacement frequency of the dicing blade may be produced.

[0022] According to the pH/redox potential-adjusted water production device of the present invention, pH/redox potential-adjusted water having a pH of 9 to 14, a redox potential at 25°C of -0.40 V or more and less than +0.40 V (vs Ag/AgCl), a dissolved oxygen concentration at 25°C of 50 ppb or less, and a hydrogen peroxide concentration of 30 ppb or less is produced. This pH/redox potential-adjusted water may prevent dissolution of various metals forming the binder of a dicing blade, and thus pH/redox potential-adjusted water for cooling water for blade dicing that may reduce the replacement frequency of the dicing blade may be produced.

[0023] According to the pH/redox potential-adjusted water production device of the present invention, a hydrogen peroxide removal mechanism that removes hydrogen peroxide dissolved as an impurity from pure water is provided upstream of the degassing membrane device, and thus the hydrogen peroxide concentration in pure water may be reduced, and the redox potential of the pH/redox potential-adjusted water may be stably maintained within a range of -0.40 V or more and less than +0.40 V (vs Ag/AgCl).

[0024] According to the pH/redox potential-adjusted water production device of the present invention, a supply flow path that supplies the produced pH/redox potential-adjusted water as

cooling water to a dicing blade in which diamond abrasive grains are fixed by a binder is included, and thus dissolution of the binder of the dicing blade may be prevented, and the replacement frequency of the dicing blade may be reduced.

[0025] According to the pH/redox potential-adjusted water production device of the present invention, a supply flow path that supplies the produced pH/redox potential-adjusted water as cooling water in a dicing process of a semiconductor manufacturing process is included, and thus the replacement frequency of the dicing blade may be reduced.

[0026] According to the production method for pH/redox potential-adjusted water of the present invention, the pH of pure water is adjusted by adding a liquid pH adjuster to pure water in a pH adjustment process, dissolved gas in the pure water is removed in a degassing process, and an inert gas is dissolved in the pure water in a gas dissolution process. By using a liquid pH adjuster, the pH does not fluctuate even in the case where the pure water after pH adjustment is degassed, and thus pH/redox potential-adjusted water in which the pH and redox potential are adjusted to desired ranges may be produced.

[0027] According to the production method for pH/redox potential-adjusted water of the present invention, at least one aqueous solution selected from the group consisting of ammonia, sodium hydroxide, potassium hydroxide, tetrahydroammonium, choline, methylamine, dimethylamine, and trimethylamine is added as a pH adjuster to pure water in the pH adjustment process, and thus the pH of the pH/redox potential-adjusted water may be adjusted to a range of 9 to 14.

[0028] According to the production method for pH/redox potential-adjusted water of the present invention, dissolved gas in pure water is removed in the degassing process, and then a gaseous pH adjuster is added to the pure water in the gas dissolution process, so that pH adjustment is performed on pure water that has been degassed in advance, and thus fluctuation of the pH of the pure water may be prevented.

[0029] According to the production method for pH/redox potential-adjusted water of the present invention, the pH adjuster is at least one selected from the group consisting of ammonia,

methylamine, dimethylamine, and trimethylamine, and thus the pH of the pH/redox potential-adjusted water may be adjusted to a range of 9 to 14.

[0030] According to the production method for pH/redox potential-adjusted water of the present invention, the pH adjuster contains an inert gas, and thus the pH of the pH/redox potential-adjusted water may be adjusted to a range of 9 to 14, and the pH and redox potential of the pH/redox potential-adjusted water may be stabilized.

[0031] According to the pH/redox potential-adjusted water production device of the present invention, dissolved gas in pure water is removed in the degassing process, and the pH of the pure water is adjusted by adding a liquid pH adjuster to the pure water in the pH adjustment process, and thus pH/redox potential-adjusted water in which the pH and redox potential are adjusted to desired ranges may be produced.

[0032] According to the production method for pH/redox potential-adjusted water of the present invention, at least one aqueous solution selected from the group consisting of ammonia, sodium hydroxide, potassium hydroxide, tetrahydroammonium, choline, methylamine, dimethylamine, and trimethylamine is added as a pH adjuster to pure water in the pH adjustment process, and thus the pH of the pH/redox potential-adjusted water may be adjusted to a range of 9 to 14.

[0033] According to the production method for pH/redox potential-adjusted water of the present invention, at least one selected from the group consisting of ammonia, methylamine, dimethylamine, and trimethylamine, together with an inert gas, is added as a pH adjuster to pure water in the pH adjustment process, and thus the pH of the pH/redox potential-adjusted water may be adjusted to a range of 9 to 14, and the pH and redox potential may be stabilized.

[0034] According to the production method for pH/redox potential-adjusted water of the present invention, pH/redox potential-adjusted water having a pH of 9 to 14, a redox potential at 25°C of -0.40 V or more and less than +0.40 V (vs Ag/AgCl), and a dissolved oxygen concentration at 25°C of 50 ppb or less is produced, and this pH/redox potential-adjusted water may prevent dissolution of various metals constituting the binder of the dicing blade, and thus pH/redox

potential-adjusted water for use as cooling water in blade dicing that may reduce the replacement frequency of the dicing blade may be produced.

[0035] According to the production method for pH/redox potential-adjusted water of the present invention, pH/redox potential-adjusted water having a pH of 9 to 14, a redox potential at 25°C of -0.40 V or more and less than +0.40 V (vs Ag/AgCl), and a hydrogen peroxide concentration of 30 ppb or less is produced, and this pH/redox potential-adjusted water may prevent dissolution of various metals constituting the binder of the dicing blade, and thus pH/redox potential-adjusted water for use as cooling water in blade dicing that may reduce the replacement frequency of the dicing blade may be produced.

[0036] According to the production method for pH/redox potential-adjusted water of the present invention, pH/redox potential-adjusted water having a pH of 9 to 14, a redox potential at 25°C of -0.40 V or more and less than +0.40 V (vs Ag/AgCl), a dissolved oxygen concentration at 25°C of 50 ppb or less, and a hydrogen peroxide concentration of 30 ppb or less is produced, and this pH/redox potential-adjusted water may prevent dissolution of various metals constituting the binder of the dicing blade, and thus pH/redox potential-adjusted water for use as cooling water in blade dicing that may reduce the replacement frequency of the dicing blade may be produced.

[0037] According to the production method for pH/redox potential-adjusted water of the present invention, a hydrogen peroxide removal process for removing hydrogen peroxide dissolved as an impurity from pure water is performed prior to the degassing process, and thus the hydrogen peroxide concentration in the pure water may be reduced, and the redox potential of the pH/redox potential-adjusted water may be stably maintained within a range of -0.40 V or more and less than +0.40 V (vs Ag/AgCl).

[0038] According to the manufacturing method for a semiconductor device of the present invention, the produced pH/redox potential-adjusted water is used as cooling water for a dicing blade in which diamond abrasive grains are fixed by a binder, and thus dissolution of the binder

of the dicing blade may be prevented, and the replacement frequency of the dicing blade may be reduced.

[0039] According to the manufacturing method for a semiconductor device of the present invention, the produced pH/redox potential-adjusted water is used as cooling water in the dicing process of the semiconductor manufacturing process, and thus the replacement frequency of the dicing blade may be reduced.

BRIEF DESCRIPTION OF THE DRAWINGS

[0040]

[FIG. 1] is a schematic diagram illustrating a pH/redox potential-adjusted water production device according to a first embodiment of the present invention.

[FIG. 2] is a schematic diagram illustrating a pH/redox potential-adjusted water production device according to a second embodiment of the present invention.

[FIG. 3] is a schematic diagram illustrating a pH/redox potential-adjusted water production device according to a third embodiment of the present invention.

DESCRIPTION OF EMBODIMENTS

[0041] The pH/redox potential-adjusted water production device of the present invention includes at least a degassing membrane device having a degassing membrane for removing dissolved gas as an impurity from pure water, and a pH adjustment device for adjusting a pH of pure water. The pH/redox potential-adjusted water production device of the present invention may further include a gas dissolution membrane device having a gas dissolution membrane for dissolving an inert gas into pure water. The pH adjustment device may supply a gaseous pH adjuster to the gas dissolution membrane device. The pH/redox potential-adjusted water production device of the present invention is capable of producing pH/redox potential-adjusted

water having a pH of 9 to 14 and a redox potential at 25°C of -0.40 V or more and less than +0.40 V (vs Ag/AgCl).

Hereinafter, the production device and production method for pH/redox potential-adjusted water according to embodiments of the present invention will be described in detail with reference to the drawings.

[0042] [First Embodiment]

<PH/redox potential-adjusted water production device>

FIG. 1 shows a pH/redox potential-adjusted water production device according to the first embodiment of the present invention. The pH/redox potential-adjusted water production device 1 shown in FIG. 1 is provided with a supply line 2 for pure water W, a platinum group metal-supported resin column 3 serving as a hydrogen peroxide removal mechanism, a pH adjuster injection line 4 (pH adjustment device), a degassing membrane device 5 which degasses dissolved gas in the pure water, a gas dissolution membrane device 6 which dissolves inert gas in the pure water, and a storage tank 7 which stores the pH/redox potential-adjusted water (hereinafter sometimes referred to as adjusted water).

[0043] The platinum group metal-supported resin column 3, which serves as the hydrogen peroxide removal mechanism, is provided to reduce the hydrogen peroxide concentration of the raw pure water W to 30 ppb or less. However, the hydrogen peroxide removal mechanism is not necessarily required in the present embodiment; in the case where the hydrogen peroxide concentration of the pure water W is 30 ppb or less, the hydrogen peroxide removal mechanism need not be provided.

[0044] In the present embodiment, examples of the platinum group metals supported on the platinum group metal-supported resin used in the platinum group metal-supported resin column 3 include ruthenium, rhodium, palladium, osmium, iridium, and platinum. These platinum group metals may be used individually as a single type, in combination of two or more types, as an alloy of two or more types, or as a purified product of a naturally occurring mixture without separating

it into individual components. Among these, platinum, palladium, and platinum/palladium alloys, used individually or as a mixture of two or more thereof, are preferably used because of their strong catalytic activity. Furthermore, nano-order fine particles of these metals are also particularly preferably used.

[0045] In the platinum group metal-supported resin column 3, an ion exchange resin may be used as the carrier resin for supporting the platinum group metals. Among these, an anion exchange resin is particularly preferably used. Since platinum group metals are negatively charged, they are stably supported on the anion exchange resin and are resistant to detachment. The exchange group of the anion exchange resin is preferably in the OH form. The OH-form anion exchange resin renders the resin surface alkaline, promoting the decomposition of hydrogen peroxide.

[0046] The pH adjuster injection line 4 (pH adjustment device) is not particularly limited, and a general chemical injection device may be used. For example, the pH adjuster injection line 4 shown in FIG. 1 merges into the supply line 2 and adds a liquid pH adjuster to the pure water. The pH adjuster injection line 4 includes a pH adjuster tank 4A and a liquid supply mechanism 4B communicating with the pH adjuster tank 4A.

[0047] The pH adjuster tank 4A is capable of storing a liquid pH adjuster. The pH adjuster tank 4A may include an inert gas supply mechanism. It is desirable to provide a mechanism for purging the interior of the pH adjuster tank 4A using an inert gas or for removing dissolved oxygen in the pH adjuster within the tank using a degassing membrane.

[0048] The liquid supply mechanism 4B may use a pump such as a diaphragm pump to supply the liquid pH adjuster. Further, a pressurized pump that uses the pH adjuster tank 4A as a sealed container, in which the pH adjuster is stored together with an inert gas such as N_2 gas, and pushes out the adjuster by the pressure of the inert gas, is also preferably used.

[0049] The degassing membrane device 5 is disposed downstream of the pH adjuster injection line 4. The degassing membrane device 5 is a membrane-type degassing membrane device and

includes a degassing membrane. A vacuum pump (VP) 5A is connected to the gas phase side of the degassing membrane of the degassing membrane device 5. The degassing membrane device 5 is configured to flow pure water on one side (liquid phase side) of the degassing membrane and draw air from the other side (gas phase side) using the vacuum pump (VP) 5A, thereby transferring dissolved gases such as dissolved oxygen through the degassing membrane to the gas phase chamber side for removal. The degassing membrane may be any membrane that allows gases such as oxygen, nitrogen, and vapor to pass through but does not allow water to permeate, and examples thereof include silicone rubber-based, polytetrafluoroethylene-based, polyolefin-based, and polyurethane-based membranes. Various commercially available degassing membranes may be used.

[0050] The gas dissolution membrane device 6 is disposed downstream of the degassing membrane device 5. The gas dissolution membrane device 6 includes a gas dissolution membrane, and the gas phase chamber side of the gas dissolution membrane is connected to an N_2 gas source as an inert gas. The gas dissolution membrane device 6 dissolves the inert gas into the adjusted water W1 by flowing the adjusted water W1 on one side (liquid phase side) of the gas dissolution membrane and supplying N_2 gas to the other side (gas phase side). It is noted that the inert gas is not limited to N_2 gas, and argon and helium are also preferably used.

[0051] The storage tank 7 is disposed downstream of the gas dissolution membrane device 6. The storage tank 7 is capable of storing the adjusted water W1. In the present embodiment, the storage tank 7 is purged with an inert gas.

[0052] The supply line 2 that has passed through the storage tank 7 reaches a use point UP. An example of the use point UP reached by the supply line 2 is a dicing device for dicing a semiconductor substrate. An example of the dicing device is a dicing device of a type that cuts a semiconductor substrate using a dicing blade. An example of the dicing blade is one in which diamond abrasive grains are fixed to the outer peripheral end face of a disk-shaped blade by a

binder. Examples of the binder for the diamond abrasive grains include those made of metals such as nickel, cobalt, copper, tin, silver, and tungsten.

[0053] In the present embodiment, an adjusted water quality monitoring mechanism including a pH meter as a pH measurement means and an ORP meter as a redox potential measurement means, which are not illustrated, are provided respectively at a location downstream of the gas dissolution membrane device 6 on the supply line 2, for example at the storage tank 7. Further, these pH meter and ORP meter are connected to a control device such as a personal computer. The control device is capable of controlling the amount of pH adjuster injected and controlling the platinum group metal-supported resin column 3 based on the measured values of the pH meter and ORP meter.

[0054] <Pure water>

In the present embodiment, the pure water W serving as raw water is preferably ultrapure water having, for example, a resistivity of 18.1 MΩ·cm or more, fine particles of 1,000 particles/L or less at a particle size of 50 nm or more, viable bacteria of 1 cell/L or less, TOC (Total Organic Carbon) of 1 μg/L or less, total silicon of 0.1 μg/L or less, metals of 1 ng/L or less, ions of 10 ng/L or less, hydrogen peroxide of 30 μg/L or less, and a water temperature of 25±2°C. However, in the present embodiment, the pure water W as raw water may contain hydrogen peroxide exceeding 30 ppb, dissolved oxygen of 50 ppb or more, and furthermore, may have a pH of less than 9.

[0055] <pH adjuster>

In the present embodiment, the pH adjuster injected from the pH adjuster tank 4A is not particularly limited, and at least one aqueous solution selected from the group consisting of ammonia, sodium hydroxide, potassium hydroxide, tetrahydroammonium, choline, methylamine, dimethylamine, and trimethylamine may be used to adjust the pH of the adjusted water to 9 to 14. In the case of using the adjusted water as cooling water in the dicing process, it is preferable to make the water alkaline in order to prevent dissolution of the metal of the binder; however, alkali metal solutions such as sodium hydroxide may not be suitable because they contain metal

components. Thus, in the present embodiment, it is most preferable to use ammonia, tetrahydroammonium, choline, methylamine, dimethylamine, trimethylamine, or the like.

[0056] < Producing Method for pH/Redox Potential-Adjusted Water>

The production method for pH/redox potential-adjusted water using the pH/redox potential-adjusted water production device 1 of the present embodiment having the configuration described above will be described below.

[0057] In the present embodiment, a hydrogen peroxide removal process, a pH adjustment process, a degassing process, a gas dissolution process, and a supply process are performed.

[0058] The hydrogen peroxide removal process is a process of removing hydrogen peroxide dissolved in the pure water W to reduce the hydrogen peroxide concentration to 30 ppb or less. However, the hydrogen peroxide removal process is not necessarily required in the present embodiment, and in the case of the hydrogen peroxide concentration of the pure water W being 30 ppb or less, the hydrogen peroxide removal process need not be performed. Pure water in which the hydrogen peroxide concentration is limited to 30 ppb or less has a redox potential in the range of -0.40 V or more and less than +0.40 V (vs Ag/AgCl).

Further, the pH adjustment process adjusts the pH of the pure water after the hydrogen peroxide removal process to a range of 9 to 14.

Further, the degassing process reduces the dissolved oxygen concentration to 50 ppb or less by removing dissolved gas contained in the pure water.

Furthermore, the gas dissolution process stabilizes the pH and redox potential of the adjusted water by dissolving an inert gas into the pure water.

The supply process supplies the adjusted water W1 to the semiconductor manufacturing process via the supply line 2.

Hereinafter, the details of each process are described.

[0059] Since the pure water W as the raw water generally contains hydrogen peroxide at a level of several tens of ppb, it is necessary to remove the hydrogen peroxide in the pure water W in

advance in order to accurately control the redox potential of the adjusted water. Thus, as the hydrogen peroxide removal process, the pure water W is supplied from the supply line 2 to a platinum group metal-supported resin column 3. This platinum group metal-supported resin column 3 decomposes and removes the hydrogen peroxide in the pure water W by the catalytic action of the platinum group metal, that is, functions as a hydrogen peroxide removal mechanism.

[0060] Next, in the pH adjustment process, a liquid pH adjuster is injected into the pure water W from the pH adjuster tank 4A. The addition of the pH adjuster may be set as appropriate according to the desired pH, the flow rate of the supply line 2, and the concentration of the pH adjuster. For example, in the case of making the adjusted water alkaline as cooling water for the dicing process, an amount that brings the pH of the pure water to a range of 9 to 14 may be added.

[0061] Next, in the degassing process, the adjusted water W1 after pH adjustment is degassed by the degassing membrane device 5. In the degassing membrane device 5, the adjusted water W1 is flowed through the liquid phase chamber side of a liquid phase chamber and a gas phase chamber constituted by a hydrophobic gas-permeable membrane, and the gas phase chamber is depressurized by a vacuum pump (VP) 5A, whereby dissolved gas such as dissolved oxygen contained in the adjusted water W1 is removed by being transferred through the hydrophobic gas-permeable membrane into the gas phase chamber. This reduces the dissolved oxygen concentration of the adjusted water W1 to a very low level. Further, since the liquid pH adjuster is not degassed, by degassing after forming the adjusted water W1, the risk of chemical leakage during vacuum degassing of these agents may be reduced.

[0062] Next, as the gas dissolution process, an inert gas is supplied to the adjusted water W1 after the degassing process by the gas dissolution membrane device 6 to stabilize the properties of the adjusted water W1, whereby the stabilized adjusted water W1 may be produced. The inert gas is preferably dissolved up to a saturated amount.

[0063] After the adjusted water W1 is produced in this manner, it is stored in the storage tank 7. Since the storage tank 7 is purged with an inert gas, it is possible to prevent oxygen and carbon

dioxide from dissolving into the adjusted water W1 during storage, which would cause fluctuations in the pH and redox potential. At this time, based on the measurement results of a pH meter and an ORP meter (not shown), the control device controls the amount of pH adjuster added from the pH adjuster tank 4A and controls the platinum group metal-supported resin column 3, whereby the adjusted water W1 adjusted to the desired pH and redox potential may be stably supplied.

[0064] The quality of the produced adjusted water W1 has a pH of 9 to 14 and a redox potential at 25°C of -0.40 V or more and less than +0.40 V (vs Ag/AgCl).

The produced adjusted water W1 may also have a dissolved oxygen concentration at 25°C of 50 ppb or less.

The produced adjusted water W1 may also have a hydrogen peroxide concentration of 30 ppb or less.

Furthermore, the produced adjusted water W1 may have a pH of 9 to 14, a redox potential at 25°C of -0.40 V or more and less than +0.40 V (vs Ag/AgCl), a dissolved oxygen concentration at 25°C of 50 ppb or less, and a hydrogen peroxide concentration of 30 ppb or less.

[0065] The adjusted water W1 produced in this manner is then sent to the use point UP via the supply line 2 as the supply process.

[0066] (Example of supplying pH/redox potential-adjusted water)

The following describes the case in which the adjusted water W1 produced as described above is used as cooling water in the dicing process.

[0067] In the present embodiment, the adjusted water W1 is supplied to the semiconductor manufacturing process via the supply line 2. Here, as the semiconductor manufacturing process, a dicing device of a type that cuts a semiconductor substrate with a dicing blade may be exemplified. The dicing blade has diamond abrasive grains fixed to the outer peripheral end face of a disk-shaped blade by a binder. The binder for the diamond abrasive grains is made of any one of metals such as nickel, cobalt, copper, tin, silver, and tungsten.

[0068] The adjusted water is supplied as cooling water in cutting the semiconductor substrate with the dicing blade. The water quality of the adjusted water has a pH of 9 to 14 and a redox potential at 25°C of -0.40 V or more and less than +0.40 V (vs Ag/AgCl). Furthermore, the water quality of the adjusted water satisfies either or both of a dissolved oxygen concentration at 25°C of 50 ppb or less and a hydrogen peroxide concentration of 30 ppb or less. Such adjusted water is alkaline and has a redox potential within the range of ±0.40 V, and thus does not dissolve the metal constituting the binder of the dicing blade. Accordingly, deterioration of the dicing blade may be prevented, and the replacement frequency of the dicing blade may be reduced.

[0069] [Second Embodiment]

<pH/redox potential-adjusted water production device>

FIG. 2 shows a pH/redox potential-adjusted water production device 11 according to the second embodiment of the present invention. In FIG. 2, components identical to those in the first embodiment described above are denoted by the same reference numerals, and their detailed descriptions are omitted.

[0070] The pH/redox potential-adjusted water production device 11 shown in FIG. 2 is provided with a degassing membrane device 5 for degassing dissolved gas from the pure water and a gas dissolution membrane device 16 for dissolving gas in the pure water, in addition to the supply line 2 of the pure water W. Furthermore, the pH/redox potential-adjusted water production device 11 shown in FIG. 2 is provided with a pH adjuster injection line 14 (pH adjustment device) that supplies a pH adjuster to the gas dissolution membrane device 16.

[0071] It is noted that the pH/redox potential-adjusted water production device 11 shown in FIG. 2 may include a platinum group metal-supported resin column serving as a hydrogen peroxide removal mechanism upstream of the degassing membrane device 5. Further, a storage tank for storing the adjusted pH/redox potential-adjusted water (adjusted water) may be provided downstream of the gas dissolution membrane device 16.

[0072] The platinum group metal-supported resin column, which serves as the hydrogen peroxide removal mechanism, is provided to reduce the hydrogen peroxide concentration of the raw pure water W to 30 ppb or less. However, the hydrogen peroxide removal mechanism is not necessarily required in the present embodiment; in the case where the hydrogen peroxide concentration of the pure water W is 30 ppb or less, the hydrogen peroxide removal mechanism need not be provided. The details of the platinum group metal-supported resin column are the same as those in the first embodiment.

[0073] The degassing membrane device 5 is a membrane-type degassing membrane device and includes a degassing membrane. A vacuum pump (VP) 5A is connected to the gas phase side of the degassing membrane of the degassing membrane device 5. The detailed configuration is the same as in the first embodiment.

[0074] The gas dissolution membrane device 16 is disposed downstream of the degassing membrane device 5. The gas dissolution membrane device 16 includes a gas dissolution membrane, and the gas phase chamber side of the gas dissolution membrane is connected to the pH adjuster injection line 14 (pH adjustment device). The gas dissolution membrane device 16 flows the pure water W on one side (liquid phase side) of the gas dissolution membrane and supplies a gaseous pH adjuster to the other side (gas phase side), thereby dissolving the pH adjuster into the pure water W and adjusting the pH of the pure water W to 9 to 14. It is noted that the gas dissolution membrane device 16 may also dissolve an inert gas into the pure water W together with the pH adjuster. As the inert gas, N_2 gas as well as argon and helium may be suitably used. The inert gas is preferably dissolved up to a saturated amount.

[0075] The pH adjuster injection line 14 (pH adjustment device) is not particularly limited, and any piping capable of supplying a gaseous pH adjuster may be used. The pH adjuster injection line 14 shown in FIG. 2 is connected to the gas phase chamber side of the gas dissolution membrane of the gas dissolution membrane device 16, and supplies a gaseous pH adjuster to the gas phase chamber side of the gas dissolution membrane. The pH adjuster injection line 14 may

also supply an inert gas to the gas dissolution membrane device 16 together with the gaseous pH adjuster. That is, the pH adjuster injection line 14 may supply a mixed gas of the pH adjuster and the inert gas to the gas dissolution membrane device 16. Upstream of the pH adjuster injection line 14, a pH adjuster tank filled with the pH adjuster, an inert gas source, and a gas pressurization mechanism for pressurizing and supplying the pH adjuster and the inert gas may be provided.

[0076] The storage tank is disposed downstream of the gas dissolution membrane device 16 as needed. The storage tank is capable of storing adjusted water W1. In the present embodiment, the storage tank is purged with an inert gas.

[0077] The supply line 2, having passed through the gas dissolution membrane device 16 or the storage tank, then reaches the use point UP. An example of a use point UP to which the supply line 2 reaches is a dicing device that cuts semiconductor substrates using a dicing blade. An example of the dicing blade is one in which diamond abrasive grains are fixed to the outer peripheral end face of a disk-shaped blade by a binder. Examples of the binder for the diamond abrasive grains include those made of metals such as nickel, cobalt, copper, tin, silver, and tungsten.

[0078] In the present embodiment, an adjusted water quality monitoring mechanism including a pH meter as a pH measurement means and an ORP meter as a redox potential measurement means, which are not illustrated, are provided respectively at a location downstream of the gas dissolution membrane device 6 on the supply line 2, for example at the storage tank. Further, these pH meter and ORP meter are connected to a control device such as a personal computer. The control device is capable of controlling the amount of pH adjuster injected and controlling the platinum group metal-supported resin column based on the measured values of the pH meter and ORP meter.

[0079] <Pure water>

In the present embodiment, the pure water W serving as raw water is the same as in the case of the first embodiment.

[0080] <pH adjuster>

In the present embodiment, the pH adjuster injected from the pH adjuster injection line 14 is not particularly limited as long as it is a gas, and at least one selected from the group consisting of ammonia, methylamine, dimethylamine, and trimethylamine may be used to adjust the pH of pure water to 9 to 14. Further, an inert gas such as nitrogen, argon, or helium may be mixed into the pH adjuster. All of these pH adjusters are supplied in a gaseous state.

[0081] < Producing Method for pH/Redox Potential-Adjusted Water>

The production method for pH/redox potential-adjusted water using the pH/redox potential-adjusted water production device 11 of the present embodiment having the configuration described above will be described below.

[0082] In the present embodiment, a degassing process, a gas dissolution process for dissolving a pH adjuster, and a supply process are performed. Further, a hydrogen peroxide removal process may be performed at a stage prior to the degassing process.

[0083] The hydrogen peroxide removal process is a process of removing hydrogen peroxide dissolved in the pure water W to reduce the hydrogen peroxide concentration to 30 ppb or less. However, the hydrogen peroxide removal process is not necessarily required in the present embodiment, and in the case of the hydrogen peroxide concentration of the pure water W being 30 ppb or less, the hydrogen peroxide removal process need not be performed. Pure water in which the hydrogen peroxide concentration is limited to 30 ppb or less has a redox potential in the range of -0.40 V or more and less than +0.40 V (vs Ag/AgCl).

Further, the degassing process reduces the dissolved oxygen concentration to 50 ppb or less by removing dissolved gas contained in the pure water.

Furthermore, the gas dissolution process adjusts the pH of pure water by dissolving a pH adjuster into the pure water. Further, by supplying an inert gas, the pH and redox potential of the pH-adjusted water are stabilized.

The supply process supplies the adjusted water W1 to the semiconductor manufacturing process via the supply line 2.

Hereinafter, the details of each process are described.

[0084] Since the pure water W as the raw water generally contains hydrogen peroxide at a level of several tens of ppb, it is necessary to remove the hydrogen peroxide in the pure water W in advance in order to accurately control the redox potential of the adjusted water. Thus, as the hydrogen peroxide removal process, the pure water W is supplied from the supply line 2 to a platinum group metal-supported resin column 3. This platinum group metal-supported resin column 3 decomposes and removes the hydrogen peroxide in the pure water W by the catalytic action of the platinum group metal, that is, functions as a hydrogen peroxide removal mechanism.

[0085] Next, in the degassing process, the pure water W is degassed by the degassing membrane device 5. In the degassing membrane device 5, the pure water W is flowed through the liquid phase chamber side of a liquid phase chamber and a gas phase chamber constituted by a hydrophobic gas-permeable membrane, and the gas phase chamber is depressurized by a vacuum pump (VP) 5A, whereby dissolved gas such as dissolved oxygen contained in the pure water W is transferred through the hydrophobic gas-permeable membrane into the gas phase chamber and removed. This reduces the dissolved oxygen concentration of the pure water W to a very low level, for example, to 50 ppb or less.

[0086] It is noted that in the present embodiment, the degassing process must be performed before the gas dissolution process in order to adjust the pH of the adjusted water to a range of 9 to 14. In the case of performing the degassing process after the gas dissolution process, the pH adjuster added to the pure water in the gas dissolution process may be degassed, and the pH of the adjusted water may deviate from the range of 9 to 14.

[0087] Next, as the gas dissolution process, a gaseous pH adjuster is supplied from the pH adjuster injection line 14 to a gas dissolution membrane, and the gaseous pH adjuster is dissolved into pure water via the gas dissolution membrane to adjust the pH of the pure water. The addition of the pH adjuster may be set as appropriate according to the desired pH, the flow rate of the supply line 2, and the concentration of the pH adjuster. For example, in the case of making the adjusted water alkaline as cooling water for the dicing process, an amount that brings the pH of the pure water to a range of 9 to 14 may be added. Further, an inert gas may be dissolved into the pure water W together with the pH adjuster. By dissolving the inert gas, contamination by oxygen and carbon dioxide is prevented, and the pH and redox potential may be stabilized. The inert gas is preferably dissolved up to a saturated amount.

[0088] After producing the adjusted water W1 in this manner, the adjusted water W1 may be stored in the storage tank 7. Since the storage tank 7 is purged with an inert gas, it is possible to prevent oxygen and carbon dioxide from dissolving into the adjusted water W1 during storage, which would cause fluctuations in the pH and redox potential. At this time, based on the measurement results of a pH meter and an ORP meter (not shown), the control device controls the amount of pH adjuster added from the pH adjuster injection line 14 and controls the platinum group metal-supported resin column, whereby the adjusted water W1 adjusted to the desired pH and redox potential may be stably supplied.

[0089] The water quality of the adjusted water W1 produced is the same as in the case of the first embodiment.

[0090] The adjusted water W1 produced in this manner is then sent to a use point UP via the supply line 2 as a supply process, and is utilized as cooling water for the dicing process.

[0091] [Third Embodiment]

<pH/redox potential-adjusted water production device>

FIG. 3 shows a pH/redox potential-adjusted water production device 21 according to the third embodiment of the present invention. In FIG. 3, components identical to those in the first

embodiment described above are denoted by the same reference numerals, and their detailed descriptions are omitted. The pH/redox potential-adjusted water production device 21 shown in FIG. 3 is provided with a degassing membrane device 5 for degassing dissolved gases from the pure water and a pH adjuster injection line 24 as a pH adjustment device for adjusting the pH of the pure water, in addition to the supply line 2 of the pure water W.

[0092] It is noted that the pH/redox potential-adjusted water production device 21 shown in FIG. 3 may include a platinum group metal-supported resin column serving as a hydrogen peroxide removal mechanism upstream of the degassing membrane device 5. Further, a storage tank for storing the adjusted pH/redox potential-adjusted water (adjusted water) may be provided downstream of the pH adjustment device 24.

[0093] The platinum group metal-supported resin column, which serves as the hydrogen peroxide removal mechanism, is provided to reduce the hydrogen peroxide concentration of the raw pure water W to 30 ppb or less. However, the hydrogen peroxide removal mechanism is not necessarily required in the present embodiment; in the case where the hydrogen peroxide concentration of the pure water W is 30 ppb or less, the hydrogen peroxide removal mechanism need not be provided. The details of the platinum group metal-supported resin column are the same as those in the first embodiment.

[0094] The degassing membrane device 5 is a membrane-type degassing membrane device and includes a degassing membrane. A vacuum pump (VP) 5A is connected to the gas phase side of the degassing membrane of the degassing membrane device 5. The detailed configuration is the same as in the first embodiment.

[0095] The pH adjuster injection line 24 serving as the pH adjustment device is not particularly limited, provided that it is capable of adding at least one pH adjuster selected from a gas and a liquid to the pure water. The pH adjuster injection line 24 includes a pH adjuster tank 24A and a supply mechanism 24B in communication with the pH adjuster tank 24A. The pH adjuster tank 24A may include a supply mechanism for an inert gas such as nitrogen.

[0096] The supply mechanism 24B may employ a pump such as a diaphragm pump in the case where the pH adjuster is a liquid. In this case, it is desirable to provide a mechanism for purging the interior of the pH adjuster tank 24A with an inert gas or for removing dissolved oxygen in the pH adjuster liquid in the tank using a degassing membrane. Further, a pressurized pump may also be suitably employed, in which the pH adjuster is placed in the pH adjuster tank 24A together with an inert gas such as N_2 gas, and these agents are pushed out by the pressure of the inert gas.

[0097] Further, the supply mechanism 24B may employ a gas-permeable membrane module, an ejector, or other direct gas-liquid contact device in the case where the pH adjuster is a gas.

[0098] The storage tank is disposed downstream of the pH adjuster injection line 24 as necessary. The storage tank is capable of storing adjusted water W1. In the present embodiment, the storage tank is purged with an inert gas.

[0099] The supply line 2 that has passed through the pH adjuster injection line 24 or the storage tank reaches the use point UP. An example of a use point UP to which the supply line 2 reaches is a dicing device that cuts semiconductor substrates using a dicing blade. An example of the dicing blade is one in which diamond abrasive grains are fixed to the outer peripheral end face of a disk-shaped blade by a binder. Examples of the binder for the diamond abrasive grains include those made of metals such as nickel, cobalt, copper, tin, silver, and tungsten.

[00100] In the present embodiment, an adjusted water quality monitoring mechanism, including a pH meter serving as a pH measurement means and an ORP meter serving as a redox potential measurement means, which are not illustrated, are provided respectively at a location downstream of the pH adjuster injection line 24 of the supply line 2, for example, in the storage tank. Further, these pH meter and ORP meter are connected to a control device such as a personal computer. The control device is capable of controlling the amount of pH adjuster injected and controlling the platinum group metal-supported resin column based on the measured values of the pH meter and ORP meter.

[00101] <Pure water>

In the present embodiment, the same pure water W serving as raw water as in the first embodiment may be used.

[00102] <pH adjuster>

In the present embodiment, the pH adjuster injected from the pH adjuster injection line 24 is not particularly limited, and may be at least one pH adjuster selected from gases and liquids. Specifically, as a liquid pH adjuster for adjusting the pH of pure water to 9 to 14, an aqueous solution containing at least one selected from the group consisting of ammonia, sodium hydroxide, potassium hydroxide, tetrahydroammonium, choline, methylamine, dimethylamine, and trimethylamine may be used. Further, as a gaseous pH adjuster, one containing at least one selected from the group consisting of ammonia, methylamine, dimethylamine, and trimethylamine, together with an inert gas, may be used.

[00103] < Producing Method for pH/Redox Potential-Adjusted Water>

The production method for pH/redox potential-adjusted water using the pH/redox potential-adjusted water production device 21 of the present embodiment having the configuration described above will be described below.

[00104] In the present embodiment, a degassing process for degassing pure water, a pH adjustment process for adjusting the pH of pure water, and a supply process are performed. Further, a hydrogen peroxide removal process may be performed at a stage prior to the degassing process.

[00105] The hydrogen peroxide removal process is a process of removing hydrogen peroxide dissolved in the pure water W to reduce the hydrogen peroxide concentration to 30 ppb or less. However, the hydrogen peroxide removal process is not necessarily required in the present embodiment, and in the case of the hydrogen peroxide concentration of the pure water W being 30 ppb or less, the hydrogen peroxide removal process need not be performed. Pure water in which the hydrogen peroxide concentration is limited to 30 ppb or less has a redox potential in the range of -0.40 V or more and less than +0.40 V (vs Ag/AgCl).

The degassing process reduces the dissolved oxygen concentration to 50 ppb or less by removing dissolved gas contained in the pure water.

The pH adjustment process adjusts the pH of pure water by adding at least one pH adjuster selected from gases and liquids. Further, by supplying an inert gas, the pH and redox potential of the pH-adjusted water are stabilized.

The supply process supplies the adjusted water W1 to the semiconductor manufacturing process via the supply line 2.

Hereinafter, the details of each process are described.

[00106] Since the pure water W as the raw water generally contains hydrogen peroxide at a level of several tens of ppb, it is necessary to remove the hydrogen peroxide in the pure water W in advance in order to accurately control the redox potential of the adjusted water. Thus, as the hydrogen peroxide removal process, the pure water W is supplied from the supply line 2 to a platinum group metal-supported resin column 3. This platinum group metal-supported resin column 3 decomposes and removes the hydrogen peroxide in the pure water W by the catalytic action of the platinum group metal, that is, functions as a hydrogen peroxide removal mechanism.

[00107] Next, in the degassing process, the pure water W is degassed by the degassing membrane device 5. In the degassing membrane device 5, the pure water W is flowed through the liquid phase chamber side of a liquid phase chamber and a gas phase chamber constituted by a hydrophobic gas-permeable membrane, and the gas phase chamber is depressurized by a vacuum pump (VP) 5A, whereby dissolved gas such as dissolved oxygen contained in the pure water W is transferred through the hydrophobic gas-permeable membrane into the gas phase chamber and removed. This reduces the dissolved oxygen concentration of the pure water W to a very low level, for example, to 50 ppb or less.

[00108] Next, in the pH adjustment process, at least one pH adjuster selected from gases and liquids is injected into the pure water W from the pH adjuster tank 24A. The addition of the pH adjuster may be set as appropriate according to the desired pH, the flow rate of the supply line 2,

and the concentration of the pH adjuster. For example, in the case of making the adjusted water alkaline as cooling water for the dicing process, an amount that brings the pH of the pure water to a range of 9 to 14 may be added. Further, during pH adjustment using a gaseous pH adjuster, by adding an inert gas together with the pH adjuster to pure water, contamination by oxygen and carbon dioxide is prevented, and the pH and redox potential may be stabilized.

[00109] Once the adjusted water W1 is produced in this manner, it may be stored in a storage tank. Since the storage tank is purged with an inert gas, it is possible to prevent oxygen and carbon dioxide from dissolving into the adjusted water W1 during storage, which would cause fluctuations in the pH and redox potential. At this time, based on the measurement results of a pH meter and an ORP meter (not shown), the control device controls the amount of pH adjuster added from the pH adjuster injection line 24 and controls the platinum group metal-supported resin column, whereby the adjusted water W1 adjusted to the desired pH and redox potential may be stably supplied.

[00110] The water quality of the adjusted water W1 produced is the same as in the case of the first embodiment.

[00111] The adjusted water W1 produced in this manner is then sent to a use point UP via the supply line 2 as a supply process, and is utilized as cooling water for the dicing process.

[00112] As described above, according to the pH/redox potential-adjusted water production device and production method of the present embodiment, adjusted water may be produced in which the concentration of dissolved gas is low, the pH is adjusted to 9 to 14, and the redox potential is adjusted to -0.40 V or more and less than +0.40 V (vs Ag/AgCl). Such adjusted water may prevent dissolution of various metals constituting the binder of the dicing blade. Thus, according to the present embodiment, it is possible to provide a pH/redox potential-adjusted water production device and production method for cooling water in blade dicing, capable of reducing the replacement frequency of the dicing blade.

Examples

[00113] Hereinafter, the present invention is described in further detail by way of examples.

[00114] [Production of Adjusted Water of Example 1]

Using the pH/redox potential-adjusted water production device shown in FIG. 3, the hydrogen peroxide in the pure water was reduced to 30 ppb or less by a hydrogen peroxide removal mechanism, and then the dissolved oxygen content in the pure water was reduced to 50 ppb or less by a degassing membrane device 5. Then, ammonia water was added from the pH adjuster tank 24A to produce adjusted water W1, which is an ammonia/hydrogen peroxide aqueous solution (ammonia concentration: 1 ppm, pH 9 (23°C), hydrogen peroxide concentration: 30 ppb, redox potential: +0.31 V).

[00115] [Production of Adjusted Water of Example 2]

In the same manner as in Example 1, an ammonia/hydrogen peroxide aqueous solution (ammonia concentration: 100 ppm, pH 10 (23°C), hydrogen peroxide concentration: 30 ppb, redox potential: +0.17 V) was produced as adjusted water W1.

[00116] [Production of Adjusted Water of Example 3]

In the same manner as in Example 1, an ammonia/hydrogen peroxide aqueous solution (ammonia concentration: 100 ppm, pH 10 (23°C), hydrogen peroxide concentration: less than 1 ppb, redox potential: +0.15 V) was produced as adjusted water W1.

[00117] [Production of Adjusted Water of Example 4]

Using the pH/redox potential-adjusted water production device shown in FIG. 1, the hydrogen peroxide in the pure water was reduced to 30 ppb or less by a hydrogen peroxide removal mechanism, and then the dissolved oxygen content in the pure water was reduced to 50 ppb or less by a degassing membrane device 5. Then, ammonia water was added from the pH adjuster tank 4A, and nitrogen was further dissolved using a gas dissolution membrane device to produce adjusted water W1, which is an ammonia/hydrogen peroxide aqueous solution (ammonia concentration: 100 ppm, pH 11 (23°C), hydrogen peroxide concentration: less than 1 ppb, redox potential: +0.15 V).

[00118] [Production of Adjusted Water of Example 5]

Using the pH/redox potential-adjusted water production device shown in FIG. 3, the hydrogen peroxide in the pure water was reduced to 30 ppb or less by a hydrogen peroxide removal mechanism, and then the dissolved oxygen content in the pure water was reduced to 50 ppb or less by a degassing membrane device 5. Then, a sodium hydroxide aqueous solution was added from the pH adjuster tank 24A to produce adjusted water W1, which is a sodium hydroxide/hydrogen peroxide aqueous solution (sodium hydroxide concentration: 1000 ppm, pH 12 (23°C), hydrogen peroxide concentration: 30 ppb, redox potential: +0.05 V).

[00119] [Production of Adjusted Water of Example 6]

Using the pH/redox potential-adjusted water production device shown in FIG. 3, the hydrogen peroxide in the pure water was reduced to 30 ppb or less by a hydrogen peroxide removal mechanism, and then the dissolved oxygen content in the pure water was reduced to 50 ppb or less by a degassing membrane device 5. Then, a sodium hydroxide aqueous solution was added from the pH adjuster tank 24A to produce adjusted water W1, which is a sodium hydroxide/hydrogen peroxide aqueous solution (sodium hydroxide concentration: 5%, pH 14 (23°C), hydrogen peroxide concentration: 30 ppb, redox potential: -0.20V).

[00120] [Production of Adjusted Water of Comparative Example 1]

Using the pH/redox potential-adjusted water production device shown in FIG. 3, the hydrogen peroxide in the pure water was reduced to 30 ppb or less by a hydrogen peroxide removal mechanism, and then the dissolved oxygen content in the pure water was reduced to 50 ppb or less by a degassing membrane device 5, thereby producing ultrapure water (pH 9 or less (23°C), hydrogen peroxide concentration: 30 ppb, redox potential: +0.40V) as adjusted water W1.

[00121] [Production of Adjusted Water of Comparative Example 2]

Using the pH/redox potential-adjusted water production device shown in FIG. 3, the hydrogen peroxide in the pure water was reduced to 30 ppb or less by a hydrogen peroxide removal mechanism, then the dissolved oxygen content in the pure water was reduced to 50 ppb or less by

a degassing membrane device 5, and finally, carbon dioxide was added to the pure water from the pH adjuster injection line 24 to produce adjusted water W1, which is carbonated water (carbon dioxide concentration: 30 ppm, pH 9 or less (23°C), hydrogen peroxide concentration: 30 ppb, redox potential: +0.41 V).

[00122] (Solubility with Respect to Ni Film)

A square test piece measuring 20 mm × 20 mm was cut from a substrate with a nickel film having a diameter of 300 mmΦ. This test piece was immersed in the adjusted water of Examples 1 to 6 and Comparative Examples 1 to 2, respectively, at 23°C for 20 minutes. The surface of the nickel film of the test piece after immersion was observed with an atomic force microscope (AFM) to confirm the surface roughness (root mean square surface roughness (Rms)) (the same applies hereinafter). Further, the amount of nickel eluted into the immersion liquid was analyzed by inductively coupled plasma mass spectrometry (ICP-MS), the dissolution rate of nickel was obtained from the amount of nickel eluted by immersion, and the reliability of the dicing blade was evaluated based on this dissolution rate. Furthermore, the charge potential of the test piece after immersion was measured with a surface electrometer. The results are shown in Table 1.

[00123] It is noted that the evaluation criteria for the surface roughness of the nickel film were as follows.

[00124] [Surface Roughness]

Good: The root mean square surface roughness (Rms) of the nickel film is less than 1 nm.

Acceptable: The root mean square surface roughness (Rms) of the nickel film is 1 nm or more and less than 3 nm.

Poor: The root mean square surface roughness (Rms) of the nickel film is 3 nm or more.

[00125] The reliability of the dicing blade was evaluated by estimating the blade wear amount during dicing processing using the dicing blade with the adjusted water of Examples 1 to 6 and Comparative Examples 1 to 2 from the dissolution rate of the nickel film, and the smaller the wear amount, the better the reliability was evaluated. The prerequisites for the dicing blade and dicing

processing conditions were as follows. It is noted that there is a correlation between the dissolution rate of the nickel film and the blade wear amount during dicing processing under the following conditions, and the reliability of the blade was evaluated based on the estimated blade wear amount according to the following criteria. Those evaluated as "Good" and "Acceptable" were regarded as passing.

[00126] Workpiece for dicing processing: 10 silicon wafers (wafer diameter: 12 inches, wafer thickness: 400 μm)

[00127] Dicing blade: diameter 55 mm, actual thickness 32.5 μm, diamond abrasive grain diameter 2000 nm, concentration 70, bond material: Ni.

[00128] Dicing process conditions: cutting depth 400 μm, feed rate 30 mm/s, spindle rotation speed 30,000/min, processing time 7 hours, processing water supply rate 2 L/min

[00129] [Reliability of dicing blade]

Good: blade wear amount is less than 20 μm.

Acceptable: blade wear amount is 20μm or more and less than 40 μm.

Poor: blade wear amount is 40 μm or more.

[00130] As shown in Table 1, in Examples 1 to 6, the dissolution rate of Ni was 0.002 to 0.003 nm/min, indicating low values. As a result, it was determined that the consumption of the binder in the dicing blade was small. Further, upon observing the surface roughness of the nickel film, some deterioration in surface roughness due to etching was confirmed, but it was determined that there was no problem. Furthermore, the charging potential was observed to be -1 V in all cases. This value was also within an acceptable range.

[00131] On the other hand, as shown in Table 1, in Comparative Example 1, the dissolution rate was 0.004 nm/min, indicating a somewhat high value, and it was determined that the consumption of the binder in the dicing blade was large. Further, upon observing the surface roughness of the nickel film, deterioration in surface roughness due to etching was confirmed, and it was

determined to be poor. Furthermore, the charging potential was -15 V, raising concerns about the occurrence of electrostatic breakdown of semiconductor elements.

[00132] In Comparative Example 2, the dissolution rate was 0.005 nm/min, indicating a somewhat high value, and it was determined that the consumption of the binder in the dicing blade was large. Further, upon observing the surface roughness of the nickel film, deterioration in surface roughness due to etching was confirmed, and it was determined to be poor.

[00133] [Table 1]

Name	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Comparative Example 1	Comparative Example 2
	1 ppm Ammonia/ hydrogen peroxide aqueous solution	100 ppm Ammonia/ hydrogen peroxide aqueous solution	100 ppm Ammonia/ hydrogen peroxide aqueous solution	100 ppm Ammonia/ hydrogen peroxide aqueous solution	1000 ppm Sodium hydroxide aqueous solution	5% Sodium hydroxide aqueous solution	Ultrapure water	30 ppm Carbonated water
pH	9	10	10	11	12	14	Less than 9	Less than 9
Hydrogen peroxide concentration [ppb]	30	30	< 1	< 1	30	30	30	30
Redox potential [V]	0.31	0.17	0.15	0.15	0.05	-0.2	0.4	0.41
Ni dissolution rate [nm/min]	0.003	0.003	0.002	0.002	0.003	0.003	0.004	0.005
Blade reliability	Acceptable	Acceptable	Good	Good	Acceptable	Acceptable	Poor	Poor
Wafer charging potential [V]	-1	-1	-1	-1	-1	-1	-15	-1
Surface roughness	Acceptable	Acceptable	Good	Good	Acceptable	Acceptable	Poor	Poor

[00134] (Solubility with respect to Cu film)

A square test piece measuring 20 mm × 20 mm was cut from a substrate with a Cu film having a diameter of 300 mmΦ. This test piece was immersed in the adjusted water of Examples 1 to 4 and Comparative Examples 1 to 2, respectively, at 23°C for 20 minutes. The surface of the Cu film of the test piece after immersion was observed by atomic force microscopy (AFM) to confirm the surface roughness. Further, the amount of Cu eluted into the immersion liquid was analyzed by inductively coupled plasma mass spectrometry (ICP-MS), and the dissolution rate of Cu was obtained from the amount of Cu eluted by immersion. Furthermore, the charge potential of the test piece after immersion was measured with a surface electrometer. The results are shown in Table 2.

[00135] It should be noted that the evaluation criteria for the surface roughness of the Cu film and the evaluation of the reliability of the dicing blade were assessed based on the same criteria as those for the nickel film.

[00136] As shown in Table 2, in Examples 1 to 4, the dissolution rate of Cu was 0.001 to 0.005 nm/min, indicating low values. As a result, it was determined that the consumption of the binder in the dicing blade was small. Further, upon observing the surface roughness of the Cu film, some deterioration in surface roughness due to etching was confirmed; however, it was determined to be acceptable. Furthermore, the charging potential was observed to be -1 V in all cases. This value was also within an acceptable range.

[00137] On the other hand, as shown in Table 2, in Comparative Example 1, the dissolution rate was 0.05 nm/min, indicating a considerably high value, and it was determined that the consumption of the binder in the dicing blade was extremely large. Further, upon observing the surface roughness of the Cu film, deterioration in surface roughness due to etching was confirmed, and it was determined to be poor. Furthermore, the charging potential was -15 V, raising concerns about the occurrence of electrostatic breakdown of semiconductor elements.

[00138] In Comparative Example 2, the dissolution rate was 0.1 nm/min, indicating a somewhat high value, and it was determined that the consumption of the binder in the dicing blade was large.

Further, upon observing the surface roughness of the Cu film, deterioration in surface roughness due to etching was confirmed, and it was determined to be poor.

[00139] [Table 2]

	Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2
Name	1 ppm Ammonia/ hydrogen peroxide aqueous solution	100 ppm Ammonia/ hydrogen peroxide aqueous solution	100 ppm Ammonia/ hydrogen peroxide aqueous solution	100 ppm Ammonia/ hydrogen peroxide aqueous solution	Ultrapure water	30 ppm Carbonated water
pH	9	10	10	11	9 or less	9 or less
Hydrogen peroxide concentration [ppb]	30	30	<1	<1	30	30
Redox potential [V]	0.31	0.17	0.15	0.15	0.4	0.41
Cu dissolution rate [nm/min]	0.001	0.005	0.005	0.004	0.05	0.1
Blade reliability	Acceptable	Acceptable	Good	Good	Poor	Poor
Wafer charging potential [V]	-1	-1	-1	-1	-15	-1
Surface roughness	Acceptable	Acceptable	Good	Good	Poor	Poor

[00140] (Solubility with respect to Co Film)

A square test piece measuring 20 mm × 20 mm was cut from a substrate with a Co film having a diameter of 300 mmΦ. This test piece was immersed in the adjusted water of Examples 1 to 6 and Comparative Examples 1 to 2, respectively, at 23°C for 20 minutes. The surface of the Co film of the test piece after immersion was observed by atomic force microscopy (AFM) to confirm

the surface roughness. Further, the amount of Co eluted into the immersion liquid was analyzed by inductively coupled plasma mass spectrometry (ICP-MS), and the dissolution rate of Co was obtained from the amount of Co eluted by immersion. Furthermore, the charge potential of the test piece after immersion was measured with a surface electrometer. The results are shown in Table 3.

[00141] It is noted that the evaluation criteria for the surface roughness of the Co film and the evaluation of the reliability of the dicing blade were assessed using the same criteria as those for the nickel film.

[00142] As shown in Table 3, in Examples 1 to 6, the dissolution rate of Co was 0.005 to 0.008 nm/min, indicating low values. As a result, it was determined that the consumption of the binder in the dicing blade was small. Further, upon observing the surface roughness of the Co film, some deterioration in surface roughness due to etching was confirmed; however, it was determined to be acceptable. Furthermore, the charging potential was observed to be -1 V in all cases. This value was also within an acceptable range.

[00143] On the other hand, as shown in Table 3, in Comparative Example 1, the dissolution rate was 0.3 nm/min, indicating a considerably high value, and it was determined that the consumption of the binder in the dicing blade was extremely large. Further, upon observing the surface roughness of the Co film, deterioration in surface roughness due to etching was confirmed, and it was determined to be poor. Furthermore, the charging potential was -15 V, raising concerns about the occurrence of electrostatic breakdown of semiconductor elements.

[00144] In Comparative Example 2, the dissolution rate was 0.5 nm/min, indicating a considerably high value, and it was determined that the consumption of the binder in the dicing blade was large. Further, upon observing the surface roughness of the Co film, deterioration in surface roughness due to etching was confirmed, and it was determined to be poor.

[00145] [Table 3]

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Comparative Example 1	Comparative Example 2
Name	1 ppm Ammonia/ hydrogen peroxide aqueous	100 ppm Ammonia/ hydrogen peroxide aqueous	100 ppm Ammonia/ hydrogen peroxide aqueous	100 ppm Ammonia/ hydrogen peroxide aqueous	1000 ppm Sodium hydroxide aqueous solution	5% Sodium hydroxide aqueous solution	Ultrapure water	30 ppm Carbonated water
pH	9	10	10	11	12	14	9 or less	9 or less
Hydrogen peroxide concentration [ppb]	30	30	< 1	< 1	30	30	30	30
Redox potential [V]	0.31	0.17	0.15	0.15	0.05	-0.2	0.4	0.41
Co dissolution rate [nm/min]	0.005	0.007	0.006	0.004	0.008	0.05	0.3	0.5
Blade reliability	Acceptable	Acceptable	Good	Good	Acceptable	Acceptable	Poor	Poor
Wafer charging potential [V]	-1	-1	-1	-1	-1	-1	-15	-1
Surface roughness	Acceptable	Acceptable	Good	Good	Acceptable	Acceptable	Poor	Poor

Industrial Applicability

[00146] The present invention has industrial applicability in that, as cooling water for blade dicing, it may reduce the replacement frequency of the dicing blade.

Reference Signs List

[00147] 1, 11, 21...pH/redox potential-adjusted water production device, 2...supply line, 3...platinum group metal-supported resin column (hydrogen peroxide removal mechanism), 4, 14, 24...pH adjuster injection line (pH adjustment device), 5...degassing membrane device, 6, 16...gas dissolution membrane device, 7...storage tank.