[Document Name] Specification

[Title of the Invention] Cleaning Liquid and Cleaning Method for Electronic Material

[Technical Field]

[0001]

The present invention relates to a cleaning liquid for electronic materials, particularly, silicon wafers, and a cleaning method using the same.

[Background Art]

[0002]

Recently, in manufacturing techniques of semiconductor LSIs using silicon wafers, usage of wafers having larger diameters and further fine processing techniques are required. Furthermore, solving problems such as maintenance and improvement of product quality that comes along with complexity of processes and reduction in production cost is also required.

[0003]

Particularly, in many fields of manufacturing techniques of semiconductor LSIs using silicon wafers, so-called wet treatment steps including treatment by various solutions are essential steps. A particularly important step among the wet treatment steps is a cleaning step. In conventional cleaning steps, mainly, improvements have been made in the point of selection of component compositions of cleaning liquids, concentrations thereof, cleaning temperatures, cleaning time

and the like. (for example, "New Edition, Clean Technology of Silicon Wafer Surface" written and edited by Takeshi Hattori, Realize Co. Ltd. (2000)). However, these conventional techniques were not enough for satisfying demands caused along with recent necessity of further fine processing techniques, complexity of steps, high cleanliness, and reduction in cost. Moreover, recently, dilute chemical solution cleaning, cleaning without chemical solutions and the like are desired by demands for strict environmental protection measures and reduction in cost of waste liquid processing.

[0004]

As a method for solving these problems, research and development of so-called functional water typified by ozone water or hydrogen water has been energetically carried out, and practical use thereof has been developed. Practical use of the ozone water has been developed in wide fields of semiconductor cleaning in removal of metal impurity contamination and organic substance contamination. The hydrogen water is also applied in glass substrate cleaning of liquid crystal display in order to remove particles (for example, "Functional Water Leaning From the Elements" supervised by Masayuki Toda, edited by Japan Industrial Conference on Cleaning, Kogyo Chosakai Publishing Co., Ltd. (2002)).

[0005]

The hydrogen water is expected as a substitute for ammonia

+ hydrogen peroxide (hereinafter, described as "APM") which is widely applied as a cleaning liquid for particle removal in the field of semiconductor cleaning. The hydrogen water is extremely advantageous in terms of chemical solution cost compared with APM; however, it is inferior in particle removal ability. The hydrogen water has been put into practical use since the cleaning level is enough for cleaning of glass substrates for liquid crystal display; however, it has not been put into practical use in the field of cleaning of semiconductors such as silicon wafers since the cleaning ability is insufficient.

[0006]

Therefore, the ability of the hydrogen water has to be improved so as to develop APM substituting techniques which are low cost in semiconductor cleaning.

[Disclosure of the Invention]

[Problem to be Solved by the Invention]

[0007]

The present invention provides a completely novel method which can be applied generally to cleaning treatment of silicon wafers.

[Means for Solving the Problems]

[0008]

The present inventors have carried out diligent research and development about a new cleaning liquid which can satisfy

recent strong demands for cleaning treatment of silicon wafers and a cleaning treatment method using the same and, as a result, found out that, surprisingly, the problems can be solved by using ultra-pure water or hydrogen water as raw material water and using a cleaning liquid in combination with ultrasonic irradiation in the presence of hydrogen micro-bubbles, thereby accomplishing the present invention.

[0009]

Specifically, a cleaning liquid for an electronic material of the present invention is characterized by containing micro-bubbles generated by a hydrogen gas and characterized by being an aqueous liquid to which ultrasonic oscillation is imparted.

[0010]

The cleaning liquid for the electronic material of the present invention is characterized in that the aqueous liquid is ultra-pure water or hydrogen water.

[0011]

A cleaning method of the present invention is a method characterized by using the cleaning liquid and is characterized by being carried out in an aqueous liquid in which hydrogen micro-bubbles are present and under ultrasonic irradiation.

[0012]

The cleaning method of the present invention is characterized in that the aqueous liquid is ultra-pure water.

[0013]

The cleaning method of the present invention is characterized in that the aqueous liquid is hydrogen water.

[0014]

The cleaning method of the present invention is characterized in that alkali is further added to the aqueous liquid.

[0015]

The cleaning method of the present invention is characterized in that alkali and hydrogen peroxide is added to the aqueous liquid.

[0016]

The cleaning method of the present invention is characterized in that a surfactant is added to the aqueous liquid raw material.

[0017]

The cleaning method of the present invention is characterized in that the added alkali contains at least one of sodium hydroxide, potassium hydroxide, ammonia, tetramethylammonium hydroxide (hereinafter, described as "TMAH"), and choline.

[0018]

Furthermore, the cleaning method of the present invention is characterized in that the electronic material is a silicon wafer.

[Effects of the Invention]

[0019]

When cleaning treatment is carried out by using the cleaning liquid of the present invention, particle components and the like on the wafer surface can be efficiently cleaned and removed, and re-contamination can be prevented.

[Best Modes for Carrying Out the Invention]

[0020]

A cleaning liquid for electronic materials of the present invention is an aqueous liquid containing micro-bubbles generated by a hydrogen gas and is an aqueous liquid to which ultrasonic oscillation is imparted. The aqueous liquid is characterized by being ultra-pure water or hydrogen water. Furthermore, the cleaning liquid for electronic materials of the present invention includes those to which various additives are added in order to obtain desired property. The electronic materials herein which can be cleaned by the cleaning liquid of the present invention particularly include silicon wafers.

[0021]

A cleaning method of the present invention is characterized by using the above described cleaning liquid of the present invention. Specifically, the method is characterized by treating the electronic materials in the aqueous liquid, in which hydrogen micro-bubbles are present, under ultrasonic irradiation.

[0022]

Electronic Materials

No particular limitation is imposed on the materials, shapes and the like of the electronic materials which can be cleaned by the cleaning method of the present invention. The materials include various materials used in conventional semiconductor manufacturing. Specifically, the materials include Si, Ge, As, or a composite material thereof. In the present invention, the shapes of the electronic materials include various conventionally publicly known shapes and include the shapes formed in various manufacturing steps. In the present invention, particularly the shape of a wafer can be preferably used. Particularly preferably, silicon wafers of corresponding stages used in silicon cleaning steps of the stages of normal silicon wafer manufacturing steps and steps of semiconductor manufacturing into silicon wafers.

[0023]

Aqueous Liquid

The aqueous liquid of the present invention can contain micro-bubbles generated by the hydrogen gas, is a liquid to which oscillation by ultrasonic waves can be imparted, and means a liquid which at least contains water. Preferably, it does not contain unnecessary impurities in cleaning of the electronic materials, and the liquid of conventionally used cleaning liquid for electronic materials can be used. In the

present invention, particularly, usage of ultra-pure water is preferred. Furthermore, the ultra-pure water may be subjected to degassing in advance so as to remove dissolved gasses. For example, a pressure-reduced membrane degassing method can be applied as a degassing method of the ultra-pure water.

[0024]

In the present invention, furthermore, hydrogen water is preferred to be used as the aqueous liquid. No particular limitation is imposed on the preparation method of the hydrogen water which can be used in the present invention, and hydrogen water produced by publicly known hydrogen water manufacturing apparatus can be used. Herein, the publicly known hydrogen water manufacturing apparatus specifically includes a manufacturing method in which a hydrogen gas is dissolved in ultra-pure water, which has undergone pressure-reduced membrane degassing, via a gas permeable membrane (for example, "Functional Water Leaning From the Elements" supervised by Masayuki Toda, edited by Japan Industrial Conference on Cleaning, Kogyo Chosakai Publishing Co., Ltd. (2002)).

[0025]

Furthermore, also, no particular limitation is imposed on the hydrogen concentration in the cleaning liquid of the present invention, and a concentration in a preferable range can be arbitrarily selected based on the volume, the shape, the number of silicon wafers, installation method, cleaning liquid

temperature, cleaning time, other additives of the cleaning liquid, and hydrogen micro-bubbles used at the same time or ultrasonic irradiation conditions, which will be described below, of cleaning apparatus.

[0026]

Hydrogen Micro-Bubbles

No particular limitation is imposed on the preparation method of the hydrogen micro-bubbles used in the cleaning method of the present invention, and micro-bubbles can be generated in the cleaning liquid by introducing a hydrogen gas by using a publicly known micro-bubble generation method or generation apparatus. As the publicly known micro-bubble generation method, various methods described in documents can be applied (for example, "The World of Micro-Bubbles" written by Satoshi Ueyama and Makoto Miyamoto, Kogyo Chosakai Publishing Co., Ltd. (2006)). The publicly known micro-bubble generation apparatus includes high-speed shear flow type micro-bubble generation apparatus.

[0027]

Also, no particular limitation is imposed on the generation conditions of the hydrogen micro-bubbles used in the cleaning method of the present invention and the amount of generated hydrogen micro-bubbles. The hydrogen micro-bubble generation amount of a preferable range can be arbitrarily selected based on the volume, the shape, the number of silicon

wafers, the installation method, the cleaning liquid temperature, the cleaning time, other additives of the cleaning liquid, and the ultrasonic irradiation conditions, which will be described below and used at the same time, of used cleaning apparatus.

[0028]

The hydrogen of the hydrogen micro-bubbles of the present invention includes the case in which the hydrogen includes other components other than hydrogen. Examples of the other components specifically include air, helium, nitrogen, oxygen, and argon.

[0029]

Also, no particular limitation is imposed on the positions at which the hydrogen micro-bubbles are generated, and the nozzle part of the hydrogen micro-bubbles can be provided at any position of a cleaning container. A preferable position can be arbitrarily selected based on the volume, shape, number of silicon wafers, installation method, cleaning liquid temperature, cleaning time, other additives of the cleaning liquid, and ultrasonic irradiation conditions, which will be described below and used at the same time, of the used cleaning apparatus. Specific examples include a bottom part, a side surface part, or an upper part of the cleaning container and plural parts thereof.

[0030]

Also, a method in which hydrogen micro-bubbles are generated in a container which is different from the cleaning container and then it is introduced into the cleaning container by using a water conveying pump can be employed. Also, a method in which the cleaning container and a container for hydrogen micro-bubble water manufacturing are connected to each other by circulation piping and the liquid therein is kept being circulated by a water-conveying pump can be employed. Also, a method in which a hydrogen micro-bubble generating apparatus is installed in the middle of water-conveying piping and the hydrogen micro-bubble water is introduced into the cleaning container can be employed.

[0031]

Ultrasonic irradiation

No particular limitation is imposed on an ultrasonic irradiation method and apparatus for imparting ultrasonic oscillation of the present invention, and ultrasonic waves can be radiated in the cleaning liquid by using a publicly known ultrasonic irradiation method or ultrasonic irradiation apparatus.

[0032]

Also, no particular limitation is imposed on the generation conditions of the ultrasonic waves used in the cleaning method of the present invention, for example, the frequency and generated power. Preferable ranges of the

conditions can be arbitrarily selected based on the volume, shape, number of silicon wafers, objective cleaning steps, installation method, cleaning liquid temperature, cleaning time, and other additives of the cleaning liquid of the used cleaning apparatus.

[0033]

A preferable range can be arbitrarily selected for the frequency of used ultrasonic waves depending on, for example, the used cleaning step and the particle size of a removal target. Specifically, the ultrasonic frequency is preferably in the range of 20 to 2000 kHz. When the frequency is lower than the range, it is out of the region of so-called ultrasonic waves, and the effects thereof may be deteriorated. When it is higher than the range, sufficient cleaning effects cannot be obtained. Note that, when the ultrasonic frequency is low even within the above described frequency range, damage may be generated on the cleaning target object by the ultrasonic irradiation. In a step in which damage generation due to ultrasonic irradiation is problematic, for example, in a cleaning step of a silicon wafer after polishing treatment, the frequency is preferably 700 kHz or more. The output power is for example 100 to 1000 W; however, no limitation is imposed thereon, and the number of oscillation elements to be installed can be also selected depending on the size or design of the cleaning apparatus or the object of the cleaning treatment.

[0034]

Also, no limitation is imposed on the position irradiated by the ultrasonic waves, and the generation direction of the ultrasonic waves can be provided at any position of the cleaning container. A preferable position can be arbitrarily selected based on the volume, shape, number of silicon wafers, installation method, cleaning liquid temperature, cleaning time, and other additives of the cleaning liquid of the used cleaning apparatus. Specifically, the method in which irradiation is carried out from a bottom part, side surface part, and upper part of the cleaning container or plural parts thereof can be employed.

[0035]

Other Additive Components

Other components can be further added to the cleaning liquid used in the cleaning method of the present invention. For example, alkali or a surfactant can be added. Additives particularly suitable as alkali include sodium hydroxide, potassium hydroxide, ammonia, TMAH, and choline. No particular limitation is imposed on the type of the additive agents and the addition amount thereof. They can be arbitrarily selected based on the volume, shape, number of silicon wafers, installation method, cleaning liquid temperature, cleaning time, hydrogen micro-bubbles, ultrasonic irradiation and the like of the used cleaning apparatus.

[0036]

When a proper amount of hydrogen peroxide is added to alkali, the particle removing ability can be improved, hydrophilicity can be imparted to the wafer surface, and the roughness of the surface (haze) can be prevented.

[0037]

Silicon Wafer during Cleaning

The cleaning method of the present invention can extremely efficiently remove particle contamination on the surfaces of silicon wafers, and, surprisingly, re-contamination by particles and the like can be prevented.

[0038]

Hereinafter, the cleaning method of the present invention will be described in further detail based on specific examples; however, the present invention is not limited to these examples.

[Examples]

[0039]

(Example 1-1)

Sample: A P-type mirror silicon wafer surface which had undergone dilute hydrofluoric acid cleaning and then spin drying so as to remove natural oxidation coating and had a hydrophobic surface and a diameter of 200 mm was subjected to spin coating of 10 mL of a solution containing abrasive (liquid obtained by diluting GLANZOX 3900 of Fujimi Chemical Incorporated by 10 million times), thereby contaminating it by

the abrasive. As the particle contamination amount herein, 5000 to 10000 particles having a diameter of 0.13 μm or more adhered. In measurement of the number of particles, Surfscan 6220 of KLA-Tencor Corporation was used.

[0040]

Raw Material Liquid: Ultra-pure water

Cleaning Method: The cleaning liquid was kept being introduced into a 40 L-cleaning bath at 6 L/min, thereby causing it to overflow. One nozzle part of micro-bubble generating apparatus (M2-MS/PTFE type manufactured by Nanoplanet Research Institute Corporation.) was provided at a bottom position of the cleaning bath, and micro-bubbles were kept being generated at 1 L/min. A hydrogen gas was used as the gas for bubbles. Micro-bubbles were kept being generated for five minutes before the wafer was introduced into the cleaning bath, and the micro-bubbles were kept being generated also during cleaning. The ultrasonic waves having a frequency of 1 MHz and output power of 1 kW were irradiated thoroughly during cleaning. The dissolved hydrogen concentration of the cleaning liquid during cleaning was 0.5 ppm.

[0041]

The sample was immersed therein for five minutes at 20°C. Then, the sample was removed, put into an ultra-pure water bath, and subjected to overflow rinse for five minutes at 20°C. Then, the sample was subjected to spin drying.

[0042]

In measurement of the number of the particles of the sample wafer after the cleaning, Surfscan 6220 of KLA-Tencor Corporation was used. The removal rate of the particles having a diameter of 0.13 μm or more was obtained from the number of adhering particles before and after the cleaning.

[0043]

(Example 1-2)

This is same as the example except that the raw material liquid is 1.4 ppm hydrogen water. The hydrogen water was manufactured by a method in which a hydrogen gas was dissolved in ultra-pure water, which had undergone pressure-reduced membrane degassing, via a gas permeable membrane. The dissolved hydrogen concentration of the cleaning liquid during cleaning was 1.5 ppm

[0044]

(Comparative Example 1-1)

This is same as the Example 1-2 except that the hydrogen micro-bubbles are not introduced. The dissolved hydrogen concentration in the cleaning liquid during cleaning was 1.4 ppm.

[0045]

(Comparative Example 1-2)

This is same as the Example 1-1 except that ultrasonic waves are not irradiated. The dissolved hydrogen

concentration in the cleaning liquid during cleaning was 0.5 ppm.

[0046]

(Example 2-1)

This is same as the Example 1-1 except that the raw material liquid contains 15 mM of ammonia and 30 mM of hydrogen peroxide.

[0047]

(Example 2-2)

This is same as the Example 1-2 except that the raw material liquid contains 15 mM of ammonia and 30 mM of hydrogen peroxide.

[0048]

(Comparative Example 2)

This is same as the Comparative Example 1-1 except that the raw material liquid contains 15 mM of ammonia and 30 mM of hydrogen peroxide.

[0049]

(Example 3-1)

This is same as the Example 1-1 except that the sample is a silicon wafer immediately after CMP (two millions or more particles having a diameter of 0.13 μm or more are adhering), and the raw material liquid contains 10 mM of TMAH and 30 mM of hydrogen peroxide.

[0050]

(Example 3-2)

This is same as the Example 1-2 except that the sample is a silicon wafer immediately after CMP (two millions or more particles having a diameter of 0.13 μm or more are adhering), and the raw material liquid contains 10 mM of TMAH and 30 mM of hydrogen peroxide.

[0051]

(Comparative Example 3)

This is same as the Comparative Example 1-1 except that the sample is a silicon wafer immediately after CMP (two millions or more particles having a diameter of 0.13 μm or more are adhering), and the raw material liquid contains 10 mM of TMAH and 30 mM of hydrogen peroxide.

[0052]

(Example 4-1)

In order to check the re-adhesion behavior of the removed particles, a silicon wafer having clean surfaces (dried after dilute hydrofluoric acid cleaning so as to remove natural oxidation membranes and obtain hydrophobic surfaces in advance) were put in a same cleaning carrier in the cleaning test of the Example 3-1. The number of adhered particles after cleaning was measured.

[0053]

(Example 4-2)

In order to check the re-adhesion behavior of the removed

particles, a silicon wafer having clean surfaces (dried after dilute hydrofluoric acid cleaning so as to remove natural oxidation membranes and obtain hydrophobic surfaces in advance) were put in a same cleaning carrier in the cleaning test of the Example 3-2. The number of adhered particles after cleaning was measured.

[0054]

(Comparative Example 4)

In order to check the re-adhesion behavior of the removed particles, a silicon wafer having clean surfaces (dried after dilute hydrofluoric acid cleaning so as to remove natural oxidation membranes and obtain hydrophobic surfaces in advance) were put in a same cleaning carrier in the cleaning test of the Comparative Example 3. The number of adhered particles after cleaning was measured.

[0055]

(Examples 5-1 to 5-12)

Sample: A P-type mirror silicon wafer which had undergone dilute hydrofluoric acid cleaning and then spin drying so as to remove a natural oxidation membrane and had a hydrophobic surface and a diameter of 200 mm was immersed in 1 N of hydrochloric acid solution in which silicon nitride powder (grain size distribution: 500 nm) was dispersed, thereby causing silicon nitride particles to adhere thereto.

[0056]

Herein, as the particle contamination amount, 5000 to 10000 particles having a diameter of 0.1 μm or more adhered. In measurement of the number of particles, LS 6500 produced by Hitachi High-Technologies Corporation was used.

[0057]

Cleaning Liquid: In each of the examples, the cleaning liquid prepared so as to contain TMAH and hydrogen peroxide having the concentrations shown in a table 3 was used.

[0058]

Cleaning Method: The 40 L-cleaning bath was filled with the liquid containing TMAH and hydrogen peroxide having the predetermined concentrations shown in the table 3, one nozzle part of the micro-bubble generating apparatus (M2-MS/PTFE type produced by Nanoplanet Research Institute Corporation.) was provided at a bottom position of the cleaning bath, and micro-bubbles were kept being generated at 1 L/min. A hydrogen gas was used as the gas for bubbles. Micro-bubbles were kept being generated for five minutes before the wafer was introduced into the cleaning bath, and the micro-bubbles were kept being generated also during cleaning. The dissolved hydrogen concentration in the cleaning liquid during cleaning was 0.5 ppm. The ultrasonic waves having a frequency of 1 MHz and output power of 1 kW were irradiated thoroughly during cleaning.

[0059]

The sample was immersed therein for five minutes at a

liquid temperature of 60°C. Then, the sample was removed, put into an ultra-pure water bath, and subjected to overflow rinse for five minutes at 20°C. Then, the sample was subjected to spin drying.

[0060]

In particle measurement of the sample wafer before and after cleaning, LS 6500 produced by Hitachi High-Technologies Corporation was used. The removal rate of the particles having a diameter of 0.1 μm or more was obtained from the number of adhered particles before and after the cleaning.

[0061]

(Comparative Example 5)

This is same as the examples 5-1 to 5-12 except that APM (4700 ppm of ammonia and 31000 ppm of hydrogen peroxide) was used as the cleaning liquid, and hydrogen micro-bubbles were not used.

[0062] [Table 1]

	Raw Material Liquid	Hydrogen Micro-Bubbles	Ultrasonic irradiation	Dissolved Hydrogen Concentration	Particle Removal Rate (%) 0.13 μm or more
Example 1-1	Ultra-pure Water	Yes	Yes	0.5ppm	45%
Example 1-2	Hydrogen Water	Yes	Yes	1.5ppm	47%
Comparative Example 1-1	Hydrogen Water	No	Yes	1.4ppm	40%
Comparative Example 1-2	Ultra-pure Water	Yes	No	0.5ppm	20%
Eaxmple 2-1	Ultra-pure Water NH3 H2O2	Yes	Yes	0.5ppm	69%
Example 2-2	Hydrogen Water NH3 H2O2	Yes	Yes	1.5ppm	72%
Comparative Example 2	Hydrogen Water NH3 H2O2	No	Yes	1.4ppm	61%

[0063] [Table 2]

	Raw Material Liquid	Hydrogen Micro-Bubbles	Ultra-sonic irradia-tion	Dissolved Hydrogen Concen-tration	Surface State of Test Wafer	Particle Number before Cleaning Test 0.13μm or more	Particle Number after Cleaning Test 0.13 μm or more
Ex.3-1	Ultra-pure Water TMAH H2O2	Yes	Yes	0.5 ppm	Immediately after CMP	> 2 millions	13322
Ex. 3-2	Hydrogen Water TMAH H2O2	Yes	Yes	1.5 ppm	Immediately after CMP	> 2 millions	11120
Comp. Ex. 3	Hydrogen Water TMAH H2O2	No	Yes	1.4 ppm	Immediately after CMP	> 2 millions	19023
Ex. 4-1	Ultra-pure Water TMAH H2O2	Yes	Yes	0.5 ppm	Hydro-phobic	20 - 100	4820
Ex. 4-2	Hydrogen Water NH3 H2O2	Yes	Yes	1.5 ppm	Hydro-phobic	20 - 100	3111
Comp. Ex. 4	Hydrogen Water TMAH H2O2	No	Yes	1.4 ppm	Hydro-phobic	20 - 100	17985

[0064] [Table 3]

	TMAH Concentration (ppm)	NH3 Concentration (ppm)	H2O2 Concentration (ppm)	Hydrogen Micro-Bubbles	Surface Roughness (Haze)	Particle Removal Rate (%) 65 nm or more
Ex. 5-1	800	0	500	Yes	No	35%
Ex. 5-2	800	0	1000	Yes	No	30%
Ex. 5-3	800	0	3000	Yes	No	28%
Ex. 5-4	800	0	7000	Yes	No	26%
Ex. 5-5	1600	0	500	Yes	Yes	Unmeasurable due to surface roughness
Ex. 5-6	1600	0	1000	Yes	No	53%
Ex. 5-7	1600	0	3000	Yes	No	52%
Ex. 5-8	1600	0	7000	Yes	No	45%
Ex. 5-9	3000	0	500	Yes	Yes	Unmeasurable due to surface roughness
Ex. 5-10	3000	0	1000	Yes	No	60%
Ex. 5-11	3000	0	3000	Yes	No	49%
Ex. 5-12	3000	0	7000	Yes	No	40%
Comp. Ex. 5	0	4700	31000	No	No	35%

[0065]

(Results)

Implementation conditions and obtained results are summarized in the table 1 to table 3.

[0066]

The following can be understood from the table 1 to table 3.

[0067]

It is understood that, when cleaning is carried out in the presence of hydrogen micro-bubbles and under ultrasonic irradiation, the surface contamination can be significantly removed. It can be understood that, in the Example 1-1, the effects of the micro-bubbles are exerted since the cleaning ability is high although the dissolved hydrogen concentration is lower than the Comparative Example 1-1. The removal ability is further improved when the liquid is maintained to be alkaline. It can be understood that roughness of the surface (haze) can be prevented by adding hydrogen peroxide.

[0068]

According to the Table 3, it can be understood that, when the hydrogen micro-bubbles are introduced into 800 ppm of TMAH and 500 ppm of hydrogen peroxide, the cleaning ability equivalent to that of general APM (4700 ppm of ammonia and 31000 ppm of hydrogen peroxide) without hydrogen micro-bubbles is

achieved. In other words, it can be understood that the chemical solution concentration can be largely reduced by introducing the hydrogen micro-bubbles. Also, it can be understood that the cleaning ability is also improved by increasing the TMAH concentration.

[0069]

According to the results of the Examples 4-1 and 4-2 and the Comparative Example 4, it can be understood that, when the hydrogen micro-bubbles are added, re-adhesion of the particles which are removed from the wafer surface and present in the cleaning liquid in the water bath can be significantly suppressed.

[0070]

As a result, improvement in the removal ability of the particles on the wafer surface can be expected.

[Industrial Applicability]

[0071]

The cleaning liquid and cleaning methods of silicon wafers according to the present invention can be applied generally to cleaning treatment of silicon wafers which have been conventionally carried out.

[Document Name] Claims

[Claim 1]

A cleaning liquid for an electronic material, characterized by being an aqueous liquid which contains micro-bubbles generated by a hydrogen gas and to which ultrasonic oscillation is imparted.

[Claim 2]

The cleaning liquid for the electronic material according to claim 1, wherein the aqueous liquid is ultra-pure water.

[Claim 3]

The cleaning liquid for the electronic material according to claim 1, wherein the aqueous liquid is hydrogen water.

[Claim 4]

A cleaning method of an electronic material, characterized by being carried out in an aqueous liquid in which hydrogen micro-bubbles are present and under ultrasonic irradiation.

[Claim 5]

The cleaning method of the electronic material according to claim 4, wherein the aqueous liquid is ultra-pure water.

[Claim 6]

The cleaning method of the electronic material according to claim 4, wherein the aqueous liquid is hydrogen water.

[Claim 7]

The cleaning method of the electronic material described

in any one of claims 4 to 6, wherein alkali is further added to the aqueous liquid.

[Claim 8]

The cleaning method of the electronic material described in any one of claims 4 to 6, wherein alkali and hydrogen peroxide is added to the aqueous liquid.

[Claim 9]

The cleaning method of the electronic material described in any one of claims 4 to 8, wherein a surfactant is added to the aqueous liquid.

[Claim 10]

The cleaning method of the electronic material according to claim 7 or 8, wherein the added alkali contains at least one of sodium hydroxide, potassium hydroxide, ammonia, tetramethylammonium hydroxide (TMAH), and choline.

[Claim 11]

The cleaning method of the electronic material according to claims 4 to 10, wherein the electronic material is a silicon wafer.