METHOD FOR WASHING SILICON WAFER

Background of the Invention and Related Art Statement

The present invention relates to a method for washing a silicon wafer. More specifically, the present invention relates to a method for washing a silicon wafer, in which contaminants are removed from the silicon wafer and a surface of the silicon wafer is reformed after the silicon wafer is subjected to an etching treatment.

Conventionally, three methods are used for washing a silicon wafer after an etching treatment. The method used typically depends on a kind of the silicon wafer.

In the first method, the etched wafer is subjected to spin drying, and then subjected to a pretreatment for a thermal treatment (etched slice cleaning). In the second method, the etched wafer is subjected to an ozone treatment to form an oxidized film on a surface of the silicon wafer, then subjected to spin drying which is followed by a sand blast step or an edge polish step. The wafer is then subjected to a pretreatment for a thermal treatment. The third method is one used for a specific silicon wafer, in which the silicon wafer is immersed in an inorganic basic solution after an etching step, and then subjected to a pretreatment before a thermal treatment (etched slice cleaning).

There are several problems, however in the above three methods. In the first method, the silicon wafer is prone to contamination by the atmosphere, a container, and a measuring apparatus, or the like when the silicon wafer is left as it is for a long period of time, since an oxidized film is not present on a surface of the silicon wafer.

Further, a very few fine grains present on a surface of the etched silicon wafer are sometimes fixed and cannot be removed in the subsequent pretreatment for a thermal treatment (an etched slice cleaning), and therefore remain as stains.

Furthermore, there was no means identified to counter a micro etched-nonuniformity generated after an etching treatment on a surface of the silicon wafer.

In the second method, an oxidized film was formed on a surface of a silicon wafer by an ozone treatment so as to prevent the surface of the silicon wafer from being etched and/or contaminated by a chemical agent or the like which is used in a sand blast step or an edge polish step after an etching step. However, since spin drying was required after the ozone treatment, it made the process more complex. Further, there was found no means to counter a micro etched-nonuniformity generated after an etching treatment on a surface of the silicon wafer.

In the third method, a silicon wafer was immersed in an inorganic basic solution after an etching step so as to remove a micro etched-nonuniformity and a residue of contaminants (a blue-white powder). However, since spin drying was required after the immersion step, it made the process more complex. Further, an oxidized film was not formed on a surface of the silicon wafer since the silicon wafer was not subjected to an ozone treatment, and therefore, there was a possibility of having a stain by contamination.

None of the methods described above contain both an ozone treatment and a measure to counter a micro etched-nonuniformity on a surface of a silicon wafer. Accordingly, each caused a stain and/or a nonuniformity in apparent color in the next step. Additionally, spin drying was required after the ozone treatment or immersion step, thereby making a process more complex. Accordingly, it has been desired to solve these problems with a unification and simplification of a process after an etching treatment.

The present invention provides a method for washing a silicon wafer which contributes a removal of contaminants, an improvement of a surface reforming, and a unification and simplification of a process after an etching treatment

to any kind of silicon wafer by subjecting a silicon wafer to an etching treatment, subjecting a silicon wafer to a washing and reforming treatment with a washing-reforming solution, and forming an oxidized film on a surface of the silicon wafer with a solution for forming an oxidized film.

Summary of the Invention

According to the present invention, there is provided a method for washing a silicon wafer after an etching treatment, comprising the steps of:

(a) subjecting a silicon wafer after etching to washing and reforming using a washing-reforming solution, and

(b) forming an oxidized film on a surface of the silicon wafer using a solution for forming an oxidized film.

Wherein the silicon wafer is preferably subjected to rinsing after the step (a) and before the step (b) and immersed in warm water after the step (b) and subsequently subjected to hot-air drying.

Further, the washing-reforming solution is preferably an inorganic basic solution containing hydrogen peroxide or a surface-active agent.

Other objects and features will be in part apparent and in part pointed out hereinafter.

Detailed Description of the Preferred Embodiment

In a method for washing a silicon wafer of the present invention, a silicon wafer is subjected to a washing-reforming treatment with a washing-reforming solution after an etching treatment, and then an oxidized film is formed on a surface of the silicon wafer with a solution for forming an oxidized film.

In the aforementioned method, an etching action on a surface of a silicon wafer by an inorganic basic solution which is a component constituting a washing-reforming

solution cooperates with an etching inhibitory action (surface-oxidizing action, masking action, or the like) by hydrogen peroxide and a surface-active agent. Accordingly, a contaminant residue (blue-white powder) and a micro etched-nonuniformity on a surface of a silicon wafer after etching can be securely removed, thereby greatly controlling apparent inferiority in a device process.

Further, an oxidized film can be formed on the surface of the silicon wafer with a solution for forming an oxidized film after a washing-reforming treatment, thereby avoiding contamination (stain) on a surface of a silicon wafer.

Accordingly, a method for washing a silicon wafer contributes a removal of contaminants, an improvement of a surface reforming, and a unification and simplification of a process after an etching treatment to any kind of silicon wafer.

A method for washing a silicon wafer of the present invention is hereinafter described in detail.

First, a silicon wafer is put in a washing-reforming solution after an etching treatment. A surface of the silicon wafer is washed and reformed preferably applying ultrasonic waves of 26-40 kHz and 100-600 W for 4-10 minutes.

At this time, the temperature of a washing-reforming solution is preferably maintained at about 35-70°C. This is because when the temperature is lower than 35°C, a surface-active agent in the washing-reforming solution is prone to have separation or suspension, which hinders decomposition of hydrogen peroxide and lowers reaction activity of the washing-reforming solution. On the other hand, when the temperature is higher than 70°C, hydrogen peroxide is remarkably decomposed, and a life span of the washing-reforming solution deteriorates.

Then, the silicon wafer is transferred to a rinse vessel containing super deionized water and rinsed

preferably applying ultrasonic waves of 26-40 kHz and 100-600 W for 4-10 minutes with the super deionized water (room temperature) overflowing the rinse vessel.

Subsequently, the silicon wafer is transferred to a vessel for forming an oxidized film and immersed into a solution for forming an oxidized film preferably applying ultrasonic waves of 26-40 kHz and 100-600 W for 2-10 minutes so as to uniformly form an oxidized film on a surface of the silicon wafer.

Incidentally, a temperature of the solution for forming an oxidized film is preferably maintained to be 20-25°C for an ozone water and 60-80°C for SC-1 ($H_2O+H_2O_2+NH_4OH$).

Then, the silicon wafer is transferred to a vessel containing a warm water having a temperature of 60-90°C and immersed in the warm water for 60-270 seconds.

Finally, the silicon wafer is dried with a hot air having a temperature of 70-90°C to complete a method for washing a silicon wafer of the present invention.

The washing-reforming liquid used in the present invention is an inorganic basic solution containing hydrogen peroxide or a surface-active agent, and is preferably conditioned as follows so as to etch a silicon wafer at a submicron level or lower with controlling a decrease in thickness of the silicon wafer and a surface roughness as much as possible.

An inorganic basic solution containing hydrogen peroxide preferably has a composition of hydrogen peroxide, inorganic basic solution, and water with a ratio of (1-2):(1-2):(5-50), respectively. Incidentally, NaOH or KOH can be used as an inorganic basic solution.

An inorganic basic solution containing a surface-active agent preferably has a composition of 0.01-10.00 wt% of a surface-active agent and 0.05-25.00 wt% of an inorganic basic solution.

A surface active agent is not particularly limited, and there can be used, for example,

polyoxyalkylphenylether, naphthalene sulfonate compound, etc., as a surface-active agent.

As an inorganic basic solution, there can be used NaOH, $CaCO_3$, Na_2CO_3, or K_2CO_3.

Incidentally, an inorganic basic solution containing a surface-active agent enhances an effect of removing a micro etched-nonuniformity more remarkably than an inorganic basic solution containing hydrogen peroxide.

A solution for forming an oxidized film used in the present invention is an ozone water or SC-1 ($H_2O+H_2O_2+NH_4OH$).

The ozone water preferably has an ozone concentration of 2-15 ppm so as to enhance throughput.

Incidentally, when an ozone concentration is lower than 2 ppm, an oxidized-film forming ability of the ozone water deteriorates, and a stain is prone to be generated because an oxidized film is insufficiently formed on a surface of a silicon wafer.

SC-1 preferably has a composition having a volume ratio of $(H_2O):(H_2O_2):(NH_4OH) = (1-2):(1-2):(5-10)$.

[EXAMPLES]

The present invention is further described in more detail below on the basis of Examples. However, the present invention is by no means limited to these Examples.

A silicon wafer obtained by a method for washing a silicon wafer of the present invention was evaluated by a method shown below.

(Evaluation on stain and micro etched-nonuniformity)

A silicon wafer is rotated in the direction of an observation axis with holding the silicon wafer by a vacuum pincette so that a surface of the silicon wafer meets the observation axis at 45°. A fluorescent light or a condensed light is applied to a surface of the silicon wafer at a right angle to the observation axis.

The surface of the silicon wafer was observed by eyes at a site of 30 cm from an observation point for evaluation. The surface of the silicon wafer was evaluated

for a micro etched-nonuniformity and stain by a rate (%) of a brown area under the fluorescent light and a white area under the condensed light to a surface area of the silicon wafer.

(Examples 1-14, Comparative Examples 1-9: Evaluation test of washed silicon wafer)

A silicon wafer was transferred to a washing-reforming vessel after an etching treatment and subjected to washing-reforming with applying ultrasonic waves of 26 kHz and 300 W for 4 minutes.

Incidentally, as a washing-reforming solution, one of a potassium hydroxide solution (liquid temperature: 70°C) containing hydrogen peroxide and a potassium hydroxide solution (liquid temperature: 45°C) containing a surface-active agent was used under a condition of blend shown in Table 1.

Then, the silicon wafer was transferred to a rinse vessel containing a super deionized water and rinsed with applying ultrasonic waves of 26 kHz and 300 W for 4 minutes with the super deionized water (room temperature) overflowing the rinse vessel.

Subsequently, a silicon wafer is transferred to a vessel for forming an oxidized film and immersed into a solution for forming an oxidized film with applying ultrasonic waves of 26 kHz and 300 W for 4 minutes so as to uniformly form an oxidized film on a surface of the silicon wafer.

Incidentally, ozone water (ozone concentration of 5-8 ppm, liquid temperature: 23-26°C) was used as a solution for forming an oxidized film.

Further, the silicon wafer was transferred to a vessel containing a warm water having a temperature of 60-90°C and immersed in the warm water for 270 seconds.

The silicon wafer was dried with hot air having a temperature of 70-90°C.

Subsequently, the silicon wafer was subjected to RCA washing and an annealing treatment at 1150°C for 14 hours in an oxidizing furnace. Then, a surface of the silicon wafer was evaluated for a micro etched-nonuniformity.

The results are shown in Tables 1 and 2.

TABLE 1

	Washing-reforming solution (ratio)			Micro etched-nonuniformity (%)
	KOH (wt%)	H_2O_2 (wt%)	Surface active agent (wt%)	
Example 1	0.01	0.03	-	2.5
Example 2	0.50	0.03	-	1.0
Example 3	2.00	0.03	-	0.5
Example 4	0.01	0.10	-	3.0
Example 5	0.50	0.10	-	2.0
Example 6	2.00	0.10	-	1.5
Example 7	10.00	0.10	-	1.0
Example 8	0.01	-	0.001 *1	0.3
Example 9	0.50	-	0.010 *1	0.0
Example 10	2.00	-	0.010 *1	0.0
Example 11	10.00	-	10.000 *1	0.0
Example 12	0.01	-	0.001 *2	0.0
Example 13	0.50	-	0.010 *2	0.0
Example 14	2.00	-	1.000 *2	0.0

*1: poloxyalkylphenylether

*2: naphthalene sulfonate compound

TABLE 2

	Washing-reforming solution (ratio)			Micro etched-nonuniformity (%)	
	KOH (wt%)	H_2O_2 (wt%)	Surface active agent (wt%)	(Fast)	(Slow)*
Comp. Ex. 1	0.50	-	-	55	0
Comp. Ex. 2	5.00	-	-	55	0
Comp. Ex. 3	-	0.50	-	65	
Comp. Ex. 4	-	5.00	-	55	
Comp. Ex. 5	-	-	0.01 *1	55	
Comp. Ex. 6	-	-	1.00 *1	60	
Comp. Ex. 7	-	-	0.01 *2	65	
Comp. Ex. 8	-	-	0.01 *2	60	
Comp. Ex. 9	-	-	-	65	

* : Speed of conveying cassette

*1: polyoxyalkylphenylether

*2: naphthalene sulfonate compound

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(Study: Evaluation of a micro etched-nonuniformity of a washed silicon wafer)

The results in Table 1 show that micro etched-nonuniformity can be controlled to be 3% or less when a potassium hydroxide solution containing hydrogen peroxide is used as a washing-reforming solution (Examples 1-7).

When a potassium hydroxide solution containing a surface active agent is used as a washing-reforming solution (Examples 8-14), a micro etched-nonuniformity can be controlled to be 0.3% or less.

Further, when only hydrogen peroxide or a surface active agent is used as a washing-reforming solution (Comparative Examples 3-8), a micro etched-nonuniformity is hardly solved in comparison with a case that a washing-reforming treatment is not performed (Comparative Example 9).

Incidentally, when only a potassium hydroxide solution is used as a washing-reforming solution (Comparative Examples 1 and 2), an etching force is large in comparison with the case in which a potassium hydroxide solution containing hydrogen peroxide is used (Examples 1-7) or the case in which a potassium hydroxide solution containing a surface active agent (Examples 8-14). Accordingly, it was reconfirmed that a speed of conveying a silicon wafer is too slow or an insufficient washing of a silicon wafer increases possibility of widening an area of etched-nonuniformity in a state of a liquid drop in a wide range when only a potassium hydroxide solution is used.

(Examples 15-24, Comparative Examples 10-12: Evaluation Test 2 of washed silicon wafer)

A silicon wafer was transferred to a washing-reforming vessel after an etching treatment and subjected to washing-reforming with applying ultrasonic waves of 26 kHz and 300 W for 4 minutes.

Incidentally, as a washing-reforming solution, a potassium hydroxide solution (liquid temperature: 45°C) of

0.01 wt% containing as a surface-active agent polyoxyalkylphenylether (0.001 wt%) was used.

Then, the silicon wafer was transferred to a rinse vessel containing a super deionized water and rinsed with applying ultrasonic waves of 26 kHz and 300 W for 4 minutes with the super deionized water (room temperature) overflowing the rinse vessel.

Then, the silicon wafer was immersed in a solution for forming an oxidized film so as to uniformly form an oxidized film on a surface of a silicon wafer.

Incidentally, as a solution for forming an oxidized film, one of SC-1($H_2O+H_2O_2+NH_4OH$) and ozone water was used under a condition shown in Table 3 or 4.

Further, the silicon wafer was transferred to a vessel containing a warm water having a temperature of 60-90°C and immersed in the warm water for 270 seconds. The silicon wafer was dried with a hot air having a temperature of 70-90°C. Subsequently, the silicon wafer was subjected to RCA washing and an annealing treatment at 1150°C for 14 hours in an oxidizing furnace. Then, a surface of the silicon wafer was evaluated for a stain.

The results are shown in Tables 3 and 4.

TABLE 3

	Ozone water (ppm)	Liquid temperature (°C)	Time (minute)	Stain (%)	
				Fluorescent light	Condensed light
Example 15	14.0 - 17.0	20 - 25	2	0	0
Example 16	8.0 - 10.0	20 - 25	2	0	0
Example 17	4.0 - 4.5	20 - 25	2	0	0
Example 18	1.5 - 2.5	20 - 25	5	0	0
Comp. Ex. 10	2.5 - 3.5	20 - 25	2	0	85
Comp. Ex. 11	1.5 - 2.5	20 - 25	2	0	100
Comp. Ex. 12	0.8 - 1.2	20 - 25	2	0	100

TABLE 4

	SC-1 (volume ratio)			Liquid temperature (°C)	Time (minute)	Stain (%)	
	H_2O	H_2O_2	NH_4OH			Fluorescent light	Condensed light
Example 19	1	1	5	65 - 75	4	0	0
Example 20	1	1	10	65 - 75	4	0	0
Example 21	1	1	30	65 - 75	4	0	0
Example 22	1	1	50	65 - 75	4	0	0
Example 23	1	2	50	65 - 75	4	0	0
Example 24	2	1	50	65 - 75	4	0	0

(Study: Evaluation of a stain on a washed silicon wafer)

The results in Table 3 show that a stain can be avoided by immersing a silicon wafer in an ozone water for 2 minutes with an ozone concentration of about 4 ppm or more when an ozone water is used as a solution for forming an oxidized film (Examples 15-18, Comparative Examples 10-12).

Further, a stain could be avoided by immersing a silicon wafer for 5 minutes even when an ozone concentration is about 2 ppm (Example 18).

Furthermore, the results in Table 4 show that when SC-1 ($H_2O+H_2O_2+NH_4OH$) was used as a solution for forming an oxidizing film (Examples 19-24), a stain could be prevented by immersing a silicon wafer for 4 minutes with a composition of SC-1 being within a range of $(H_2O):(H_2O_2):(NH_4OH)=(1-2):(1-2):(5-50)$ by volume.

As is apparent from the above description, in a method for washing a silicon wafer of the present invention, a silicon wafer is subjected to an etching treatment and a subsequent washing-reforming treatment with a washing-reforming solution, and then an oxidized film is formed on a surface of the silicon wafer with an oxidized film forming solution, thereby enabling to contribute to a removal of contaminants of a silicon wafer, an improvement of a surface reforming and a unification and simplification of a process after an etching treatment to any kind of silicon wafer.

As various changes could be made in the above embodiments without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.



WHAT IS CLAIMED IS:

1. A method for washing a silicon wafer after an etching treatment, comprising the steps of:

(a) subjecting a silicon wafer after etching to washing and reforming using a washing-reforming solution, and

(b) forming an oxidized film on a surface of the silicon wafer using an oxidized film forming solution.

2. A method for washing a silicon wafer according to claim 1, wherein a silicon wafer is subjected to rinsing after the step (a) and before the step (b).

3. A method for washing a silicon wafer according to claims 2, wherein the washing-reforming solution is an inorganic basic solution containing hydrogen peroxide or a surface-active agent.

4. A method for washing a silicon wafer according to claim 2, wherein a silicon wafer is immersed in warm water after the step (b) and subsequently subjected to hot-air drying.

5. A method for washing a silicon wafer according to claim 4, wherein the washing-reforming solution is an inorganic basic solution containing hydrogen peroxide or a surface-active agent.

6. A method for washing a silicon wafer according to claim 1, wherein a silicon wafer is immersed in warm water after the step (b) and subsequently subjected to hot-air drying.

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7. A method for washing a silicon wafer according to claim 6, wherein the washing-reforming solution is an inorganic basic solution containing hydrogen peroxide or a surface-active agent.

8. A method for washing a silicon wafer according to claim 1, wherein the washing-reforming solution is an inorganic basic solution containing hydrogen peroxide or a surface-active agent.