

AQUEOUS CLEANING COMPOSITION FOR SEMICONDUCTOR COPPER PROCESSING

Field of the Invention

5 [0001] The invention relates to an aqueous cleaning composition used in post chemical mechanical planarization (CMP) in integrated circuit processing.

Background of the Invention

10 [0002] Semiconductor elements nowadays are developing toward the trend of smaller line width and higher integrated density. When the minimum line width of an integrated circuit is decreased below 0.25 μm , the time delay (RC delay) caused by the resistance of the metal wire itself and the spurious capacitance of the
15 dielectric layer has become a crucial influence on the operation rate of the elements. Therefore, in order to increase the operation rate of the elements, currently copper metal wires have been gradually adopted in high-level processing below 0.13 μm to replace the traditional aluminum-copper alloy wires.

20 [0003] The application of chemical mechanical planarization technology in the copper metal wire processing may not only overcome the problem of patterns being difficult to define due to the difficulty of copper metal etching, but also form a plane with global planarity upon polishing, so that the multilayer wire
25 processing may be easily carried out. The principle of chemical

mechanical planarization is that mechanical wear is produced on the wafer surface by combining polishing particles in a polishing slurry with chemical aids, whereby the high site of the uneven surface has a high removal rate due to high pressure while the low site of the uneven surface has a low removal rate due to low pressure, and thereby the purpose of global planarity can be achieved.

[0004] Large quantities of fine polishing particles and chemical aids in the polishing slurry and the scraps peeled during

polishing may attach to the chip surface during polishing of the chemical mechanical planarization. In general, the common

contaminants found on the chips after polishing are metal ions, organic compounds and polishing particles and the like. If there is no effective cleaning procedure to remove the above-described

contaminants, the subsequent processing will be affected, and the yield and the reliability of the elements will be decreased.

Therefore, the cleaning processing after CMP polishing has become a crucial technology to determine whether CMP can be successfully applied in semiconductor processing.

[0005] In the polishing slurry used in copper processing, benzotriazole (BTA) and its derivatives and ascorbic acid are often employed as a corrosion inhibitor. In the contaminants found on the wafers after polishing in the copper processing, organic residues such as BTA, etc. are the most difficult to

remove, mainly because the BTA particles are bonded on the copper wires by chemical adsorption. Physical removal methods such as static repulsive force, ultrasonic vibration and scrubbing with a polyvinyl alcohol (PVA) brush etc., are traditionally used, but
5 it is not easy to obtain a good cleaning effect.

[0006] Traditional inter layer/metal dielectric and W plugs that have been treated by chemical mechanical planarization are usually cleaned using ammonia solution and/or fluorine-containing compounds, but the above solutions are not suitable for the
10 wafers of copper metal wires. The ammonia solution will unevenly corrode the surface of copper metal, resulting in coarsening. The fluorine-containing compounds will not only coarsen the copper surface but also cost more in terms of human safety protection and waste solution treatment in order to avoid doing harm to
15 human health and to the environment.

[0007] A polishing composition that can effectively remove tantalum metal from a substrate is disclosed in Ina et al., U.S. Patent No. 6,139,763, which consists of polishing particles, an oxidant that can oxidize tantalum metal, a reducer that can
20 reduce tantalum oxide (such as oxalic acid) and water. This polishing composition can further comprise piperazine (a nitrogen-containing heterocyclic organic base). According to Ina et al.'s teaching, the piperazine can be used on the surface of the copper layer during polishing to prevent the formation of

surface impairment, such as recesses, dishing or erosion, which also can protect the polishing surface so as to achieve a mirror-like surface. However, the use of the piperazine in an aqueous cleaning solution employed in the post chemical mechanical

5 planarization in the copper processing is not taught or suggested by Ina et al.

[0008] A method of removing chemical residues from a surface of a metal or dielectric layer is disclosed in Small, U.S. Patent No. 6,546,939 (Taiwan Patent No. 396202), wherein an aqueous
10 composition with a pH between 3.5 and 7 is placed in contact with the metal or dielectric layer for a period of time sufficient to remove the chemical residues. This aqueous composition comprises an organic acid having mono-, bi- or trifunctional groups, a buffering amount of a base of quaternary amine, ammonium
15 hydroxide, hydroxylamine, hydroxylamine salt or hydrazine salt, and a choline hydroxide.

[0009] A cleaning agent is disclosed in Small et al., U.S. Patent No. 6,498,131. The cleaning agent consists of a nonionic surfactant, amines, quaternary amines and a surface retention
20 agent selected from ethylene glycol, propylene glycol, polyethylene oxide and mixtures thereof, and is used to clean the residues of the chemical mechanical planarization processing.

[0010] A cleaning agent is disclosed in Naghshineh et al., U.S. Patent No. 6,492,308. The cleaning agent consists of

tetraalkylammonium hydroxide, polar organic amine and a corrosion inhibitor, and is used to clean a copper-containing integrated circuit.

[0011] A cleaning agent is disclosed in Nam, U.S. Patent No.

5 5,863,344. The cleaning agent consists of tetramethylammonium hydroxide, acetic acid and water, and is used to clean semiconductor elements, wherein the volume ratio of acetic acid to tetramethylammonium hydroxide is preferably 1 to about 50.

[0012] A method of cleaning a semiconductor substrate with

10 copper wires on its surface is disclosed in Masahiko et al., U.S. Patent No. 6,716,803. The cleaning agent used in this method comprises a surfactant and a nitrogen-containing alkaline substance.

[0013] A cleaning agent is disclosed in Ward et al., U.S. Patent

15 No. 5,988,186. The cleaning agent consists of a water-soluble polar solvent, an organic amine and a benzene ring corrosion inhibitor, and is used to remove organic and inorganic substances.

[0014] A tetraalkylammonium hydroxide and/or a surfactant and/or

20 a corrosion inhibitor are used as the components of the cleaning solution in the prior art as described above. Tetraalkylammonium hydroxides have a high volatility (a vapor pressure of 18 mm Hg at a temperature of 20 °C), high toxicity and strong odour. If it is not handled appropriately, it will cause damage to humans and

the environment. The cleaning effect of the cleaning composition can be enhanced by way of adding the surfactant or changing the surface electrical property of the contaminant and/or the substrate, but this cannot act on contaminants produced by

5 chemical adsorption. The corrosion inhibitor can protect the surface of copper metal during cleaning to avoid the excessive corrosion of the copper metal surface induced by the chemical substances in the cleaning composition. However, the corrosion inhibitor itself may remain on the surface of copper metal after
10 cleaning, resulting in organic residues.

[0015] Therefore, the prior art as described above cannot meet the requirements for a cleaning solution used in post chemical mechanical planarization in copper processing in the industry.

There is still a desire for an aqueous cleaning composition
15 useful for post chemical mechanical planarization in the copper processing. This ideal composition would be one which is not highly volatile, has no odour, doesn't remain on the wafers after cleaning, and can effectively remove the residual contaminants from the surfaces of the copper process chips that have been
20 treated by chemical mechanical planarization and provide the copper metal wires with a better surface roughness.

Summary Of the Invention

[0016] The main objective of the invention is to provide an aqueous cleaning composition used in post chemical mechanical

planarization in copper processing, comprising a nitrogen-containing heterocyclic organic base, an alcohol amine and water. Upon contact with copper-containing semiconductor wafers that have been treated by a chemical mechanical planarization for an effective period of time, the aqueous cleaning composition of the present invention can effectively remove residual contaminants from the surfaces of the wafers, and simultaneously provide the copper wires with a better surface roughness.

[0017] A feature of the present invention is to avoid using volatile components such as tetraalkylammonium hydroxide (e.g. tetramethylammonium hydroxide), so as to decrease the potential hazards regarding the escape of solution into the environment and to human health. Another feature of the present invention is to effectively remove the residual contaminants from the surfaces of the wafers after polishing, without using a surfactant and a corrosion inhibitor (such as BTA and/or its derivatives, ascorbic acid, and the like) used for protecting the copper surface during cleaning, and to simultaneously provide the copper wires with a better surface roughness, so as to avoid the possibility that the surfactant and the corrosion inhibitor remain on the wafers.

Brief Description of the Drawing

[0018] Figure 1 shows the atomic force microscope (AFM) image of the copper chips cleaned with the cleaning composition of the present invention (No. 1).

[0019] Figure 2 shows the atomic force microscope (AFM) image of the copper chips cleaned with an improper cleaning composition (No. 12).

Detailed Description of the Invention

5 [0020] The aqueous cleaning composition of the invention includes, based on the total weight of the composition, 0.1 to 15 wt% of a nitrogen-containing heterocyclic organic base, 0.1 to 35 wt% of an alcohol amine and water.

[0021] In the aqueous cleaning composition of the invention, the
10 nitrogen-containing heterocyclic organic base is used to increase the basicity of the composition, thereby avoiding the use of ammonia solution that can cause serious coarsening of the copper surface, volatile tetramethylammonium hydroxide, and alkali metal hydroxides that will cause metal-ion contamination. On the other
15 hand, the unshared electron pairs of the nitrogen atom on the heterocyclic ring of the nitrogen-containing heterocyclic organic base will bond with the copper wires, so as to prevent the re-adsorption of the organic contaminants that have left the copper wires .

20 [0022] The nitrogen-containing heterocyclic organic base used in the invention is preferably selected from the group consisting of piperazine, 2-(1-piperazine)ethanol, 2-(1-piperazine)ethylamine, and a combination thereof, and more preferably piperazine. The amount of the nitrogen-containing heterocyclic organic base used

in the invention ranges from 0.1 to 15 wt%, preferably 0.1 to 10 wt%, and more preferably 0.2 to 10 wt%, based on the total weight of the composition.

[0023] The alcohol amine used in the invention is preferably

5 selected from the group consisting of ethanolamine, diethanolamine, triethanolamine, propanolamine, and a combination thereof, and more preferably selected from the group consisting of diethanolamine, triethanolamine, and a combination thereof.

The amount of the alcohol amine used in the invention ranges from
10 0.1 to 35 wt%, preferably 0.1 to 30 wt%, and more preferably 0.5 to 25 wt%, based on the total weight of the composition.

[0024] As described above, the corrosion inhibitor (such as BTA or its derivatives or ascorbic acid) used in the polishing slurry for chemical mechanical planarization in copper processing may

15 remain on the surfaces of the wafers after polishing. These organic residues are difficult to remove using only commonly known physical methods such as static repulsion force, ultrasonic vibration, and scrubbing with a polyvinyl alcohol (PVA) brush.

[0025] The nitrogen-containing heterocyclic organic base and the
20 alcohol amine compounds contained in the cleaning composition of the invention can increase the saturated solubility of the organic residues (such as BTA) in the cleaning composition, so as to provide a higher driving force to dissolve the BTA particles. A better cleaning effect can be achieved by combining a

traditional physical removal method with the cleaning composition of the present invention.

[0026] The cleaning composition of the invention can be used directly, or can be used after dilution with super pure water. In order to reduce the cost of production, transportation and storage, a composition with a higher concentration is generally provided, and then used after dilution with super pure water in end use. The composition is typically diluted at a multiplication in the range of 10 and 60, depending on the practical use. In the case of special requirements, such as saving processing time, a cleaning composition stock solution with a higher concentration can be used directly to clean the wafers.

[0027] The cleaning composition of the invention can be used at room temperature. The cleaning composition is placed in contact with the copper-containing semiconductor wafers that have been treated by chemical mechanical planarization for an effective period of time, which can effectively remove the residual contaminants from the surfaces of the wafers after polishing and simultaneously provide the copper wires with a better surface roughness. In general, when a lower concentration is used, a longer contact time (e.g. 1-3 min) is needed; and when a higher concentration is used, only a short contact time (e.g. shorter than 1 min) is needed. In practical use, the optimal correlation

between the concentration of the cleaning composition and the contact time can be determined by try-and-error method.

[0028] The present invention will be further illustrated by the following examples, but is not intended to be limited by the

5 examples. Any modifications and variations that can be easily achieved by those having ordinary skill in the art are contemplated within the scope of the invention.

Example 1

[0029] Considering the factors regarding the concentrations of
10 piperazine, diethanolamine and triethanolamine, cleaning solutions with different compositions (No. 1~8) were prepared using Taguchi Method L8, and the effects of the components, i.e. water, piperazine, diethanolamine and ammonia solution (No. 9~12) were studied, and then 40 X diluted solutions of the compositions
15 were measured for the ability to dissolve copper and the saturation solubility of BTA.

[0030] The ability to dissolve copper was measured by cutting a blank copper wafer into chips each with 1.5 cm both in length and width, pretreating the chips to remove copper oxide from the
20 surfaces prior to being dipped into a 50 ml test solution, and then taking out the chips after 1 min. The concentration of copper ions in the solution was measured by ICP-MS.

[0031] The saturation solubility of BTA was measured by placing the test solution under the condition of the constant temperature

of 25 °C, adding an excessive amount of BTA while stirring the solution to dissolve BTA, and then filtering off insoluble substances from the test solution after 4 hours. The BTA concentration in the solution was analyzed by high performance
5 liquid chromatography (HPLC).

[0032] Table 1: The ability to dissolve copper and the saturation solubility of BTA for different cleaning compositions

No.	Component			Dilution Multiplication	Dissolution Ability Copper (ppb)	Saturation for Solubility of BTA (%)
	Piperazine	Diethanolamine	Triethanolamine			
1	7.2%	9.0%	13.5%	40	25.3	2.76
2	7.2%	9.0%	20.0%	40	25.7	2.86
3	10.8%	9.0%	13.5%	40	21.1	2.92
4	10.8%	9.0%	20.0%	40	23.1	3.02
5	7.2%	13.5%	13.5%	40	19.3	2.90
6	7.2%	13.5%	20.0%	40	20.6	3.02
7	10.8%	13.5%	13.5%	40	20.1	3.08
8	10.8%	13.5%	20.0%	40	22.6	3.18
	Control Examples					
9	Super pure water			-	<2	2.00
10	Piperazine 9.0%			40	<2	2.40
11	Diethanolamine 16.9%			40	16.0	2.60
12	Diethanolamine 16.9% Ammonia solution 3.0%			40	42.9	3.43

[0033] The results for the above compositions 9 and 10 show that both water and piperazine exhibit no dissolution ability for copper metal, while the addition of piperazine can increase the saturation solubility of BTA in the cleaning composition. The results for the above compositions 11 and 12 indicate that the addition of ammonia solution can significantly increase the etching dissolution rate of copper metal and can obviously increase the saturation solubility of BTA in the cleaning composition. The results for the above compositions 1~8 and 11 show that the alcohol amine has the etching dissolution ability for copper metal and also can increase the saturation solubility of BTA in the cleaning composition. With a stronger dissolution ability for copper metal and a higher saturation solubility of BTA, the cleaning composition will allow a better cleaning effect on the contaminants on copper metal and the organic contaminants such as BTA to be achieved. However, it should be noted that an improper etching dissolution ability for copper metal (e.g., too fast and/or unevenly) will adversely affect the roughness.

Example 2

[0034] The cleaning compositions shown in Example 1 were used to clean a polished blank copper wafer on Ontrak(a cleaning table). The cleaning time was two minutes and the flux of the cleaning agent was 600 ml/min. After cleaning, the surface roughness (the

average roughness Ra and the root mean square roughness Rq) of the copper wafer was measured by atomic force microscope (AFM).

[0035] Table 2: The surface roughness of the copper wafer cleaned with different cleaning compositions

No.	Component			Dilution Multiplication	Surface Roughness Ra (nm)	Surface Roughness Rq (nm)
	Piperazine	Diethanolamine	Triethanolamine			
1	7.2%	9.0%	13.5%	40	0.616	0.813
2	7.2%	9.0%	20.0%	40	0.699	0.997
3	10.8%	9.0%	13.5%	40	0.663	0.888
4	10.8%	9.0%	20.0%	40	0.842	1.153
5	7.2%	13.5%	13.5%	40	0.677	0.885
6	7.2%	13.5%	20.0%	40	0.714	0.945
7	10.8%	13.5%	13.5%	40	0.721	0.977
8	10.8%	13.5%	20.0%	40	0.763	0.986
Control Examples						
9	Super pure water			-	-	-
10	Piperazine 9.0%			40	0.590	0.732
11	Diethanolamine 16.9%			40	0.785	1.040
12	Diethanolamine 16.9% Ammonia solution 3.0%			40	9.555	15.234

[0036] Comparisons between Composition 1 (Fig. 1) and

Composition 3, Composition 1 and Composition 2, and Composition 1 and Composition 5 reveal that both a higher amount of piperazine and a higher amount of alcohol amine will increase the surface

5 roughness, but still maintain it at a good level. This shows that the cleaning compositions of the invention at a wide range of concentration may not only etch and dissolve copper metal, but also maintains a better surface roughness of copper metal. The results from Composition 12 (Fig. 2) show that ammonia solution
10 will seriously erode the copper surface, thus resulting in a very bad roughness. It has been found from the results from Composition 10 that since piperazine itself doesn't have etching dissolution ability for copper metal, the treated copper surface still exhibits an excellent roughness.

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Example 3

[0037] Blank copper wafers were dipped into a polishing slurry containing the corrosion inhibitor BTA used in copper processing for 1 min so as to be contaminated. After contamination, they were rinsed with super pure water on Ontrak (a cleaning table)

20 for 18 seconds followed by spin drying. Then, the numbers of the particles on the contaminated wafers were measured using a TOPCON WM-1700 wafer particle counter. The contaminated wafers on which the particle numbers had been determined were scrubbed on Ontrak (a cleaning table) with different cleaning compositions for 2

min, and finally rinsed with super pure water for 18 sec followed by spin drying. Again, the particle numbers on the cleaned wafers were measured using TOPCON WM-1700 wafer particle counter. The removal rate of each cleaning composition for the particulate
5 contaminants on the wafer surface was calculated.

[0038] Table 3: The removal effect of the cleaning compositions for the particles on the surface of the copper wafer

No.	Original Composition	Composition After Dilution	pH After Dilution.	Removal Rate of Contaminants
10	Piperazine 9.0%	Piperazine 0.225%	11.1	79.1%
11	Diethanolamine 16.9%	Diethanolamine 0.423%	10.7	75.0%
13	Piperazine 9.0%	Piperazine 0.225%	11.2	92.1%
14	Diethanolamine 16.9%	Diethanolamine 0.423%	11.4	87.8%
1	Piperazine 7.2%	Piperazine 0.180%	11.3	94.1%
	Diethanolamine 9.0%	Diethanolamine 0.225%		
	Triethanolamine 13.5%	Triethanolamine 0.338%		
8	Piperazine 10.8%	Piperazine 0.270%	11.4	96.7%
	Diethanolamine 13.5%	Diethanolamine 0.338%		
	Triethanolamine 20.0%	Triethanolamine 0.500%		

[0039] The results shown in the above table reveal that good cleaning results cannot be achieved by using piperazine or alcohol amine alone, while the cleaning efficacy can be significantly increased when piperazine and alcohol amine are
5 used together.

Claims

What is claimed is:

1. Use of an aqueous cleaning composition in post chemical mechanical planarization, wherein said aqueous cleaning composition comprises (a) 0.1 to 15 wt% of a nitrogen-containing heterocyclic organic base; (b) 0.1 to 35 wt% of an alcohol amine; and (c) water.
2. The use according to claim 1, wherein the organic base is selected from the group consisting of piperazine, 2-(1-piperazine)ethanol, 2-(1-piperazine)ethylamine, and a combination thereof, and wherein the alcohol amine is selected from the group consisting of ethanolamine, diethanolamine, triethanolamine, propanolamine, and a combination thereof.
3. The use according to claim 1, comprising (a) 0.1 to 15 wt% of piperazine; (b) 0.1 to 35 wt% of an alcohol amine, wherein the alcohol amine is selected from the group consisting of diethanolamine, triethanolamine and a combination thereof; and (c) water.
4. The use according to claim 1, wherein the nitrogen-containing heterocyclic organic base is used in an amount of 0.1 to 10 wt%.

5. The use according to claim 1, wherein the nitrogen-containing heterocyclic organic base is used in an amount of 0.2 to 10 wt%.

6. The use according to claim 1, wherein the alcohol amine is used in an amount of 0.1 to 30 wt%.

7. The use according to claim 1, wherein the alcohol amine is used in an amount of 0.5 to 25 wt%.

AQUEOUS CLEANING COMPOSITION FOR SEMICONDUCTOR COPPER
PROCESSING

Abstract Of the Disclosure

5 [0040] The invention relates to an aqueous cleaning composition for wafers with copper wires that have been treated by chemical mechanical planarization in an integrated circuit processing, comprising 0.1 to 15 wt% of a nitrogen-containing heterocyclic organic base, 0.1 to 35 wt% of an alcohol amine
10 and water. Upon contact with copper-containing semiconductor wafers that have been treated by chemical mechanical planarization for an effective period of time, the aqueous cleaning composition can effectively remove residual contaminants from the surfaces of the wafers, and
15 simultaneously provide the copper-containing semiconductor wafers with a better surface roughness.

(FIG. 1)