A Chemical Mechanical Polishing Slurry

Technical Field

The present invention relates to abrasive substance, in particular, to a chemical mechanical polishing slurry.

Background Art

TSV technology (Through-Silicon-Via) is a novel technology which can achieve the chip interconnection by creating a vertical access between chip and chip, and wafer and wafer. The advantage of TSV over the conventional stacking technique using bump and IC bonding packaging is that it could maximize the density of chip in a three-dimensional direction, minimize the shape of chip and shorten the interconnection so as to improve the speed of chip and low power consumption. When polishing, the backside thinning technology of TSV technology requires a fairly high polishing rate of silicon and copper at the same time.

To achieve a high polishing rate, silicon commonly is polished under an alkaline condition. For example, US2002032987 publishes slurry containing an alcohol amine as an additive so as to improve the removal rate of poly silicon, and the most preferred additive is 2-dimethylamino-2-methyl-1-propanol. US2002151252 provides a polishing composition containing a plurality of carboxylic acids as a chelating agent to improve the removal rate of poly silicon, and the chelating agent is preferably EDTA or DTPA. EP1072662 publishes a slurry having organic substances sharing a delocalization structure produced by lone-pair electrons and double-bond so that the slurry could accelerate the removal rate of poly silicon, and the organic substances are preferably guanidines and salts thereof. US2006014390 discloses one kind of polishing solution used to improve the removal rate of poly silicon, and the solution comprises 4.25 to 18.5 weight percent of an abrasive, and 0.05 to 1.5 weight percent of an additive. And the additive is selected from the group consisting of quaternary ammonium, quaternary ammonium salt, ethanol amine and the

like. In addition, the polishing solution further contains a nonionic surfactant such as homo-or co-polymers of ethylene glycol or propylene glycol. CN101497765A significantly improves the polishing rate of silicon by using the synergistic effects of biguanides and azoles.

To achieve a high polishing rate, copper commonly is polished under an acidic condition by use of high oxidation potential of oxidant (hydrogen peroxide) under an acidic condition and the property of which copper tends to complex and dissolve under an acidic condition. For example, CN1705725 publishes a slurry for polishing a copper surface, and the slurry removes the copper surface by use of an oxidant (hydrogen peroxide, etc), a chelating agent and a passivation agent at a pH between 2.5 and 4. CN1787895A discloses a CMP composition which includes a rheology agent, an oxidizing agent, a chelating agent, a passivation agent, an abrasive and a solvent. Under an acidic condition, this kind of CMP composition advantageously improves material selectivity, and it could be used for polishing semiconductor substrates having copper thereon without dishing into the polished copper or other unfavorable planarization defects. CN01818940A discloses a copper-polishing slurry which could significantly improves the removal rate of copper by further combination with an oxidant agent such as hydrogen peroxide and/ or a corrosion inhibitor such as benzotriazole. And high polish rate is achieved while maintaining local pH stability and substantially reducing global and local corrosion.

Sometimes copper is polished under an alkaline condition. For example, CN1644640A discloses an aqueous composition useful for polishing copper under an alkaline condition. Said composition comprises weight percent 0.001 to 6 an inhibitor for a nonferrous metal, 0.05 to 10 a complexing agent for the metal, 0.01 to 25 a copper removal agent for accelerating the removal of the copper, 0.5 to 40 an abrasive, etc and accelerates the removal rate of copper by interaction of imidazoles for accelerating the polishing of the copper and BTA. CN1398938A discloses global planarization CMP slurry for multilayer copper wire in large scale integrated circuit, used for improving the removal rate of copper. Said slurry comprises the following ingredients: 18 to 50 weight percent of an abrasive,

0.1 to 10 weight percent of a chelating agent, 0.005 to 25 weight percent of a complexing agent, 0.1 to 10 weight percent of an active agent, 1 to 20 weight percent of an oxidant agent and de-ionized water.

In the prior art, although the polishing rate of copper would be high under an acidic condition, the polishing rate of silicon usually is low. The reason is that under an acidic condition, a silicon surface oxidizes to form silicon dioxide because of the effect of oxidant, and compared with the silicon, silicon dioxide is more difficult to remove. Although the polishing rate of silicon would be high without oxidant under an alkaline condition, the polishing rate of copper usually is low. Because copper needs to be oxidized so that could be easily removed. However, if an oxidant, such as hydrogen peroxide, is added, a silicon surface will oxidize to form silicon dioxide because of the effect of oxidant. In addition, an oxidant, such as hydrogen peroxide, is unstable and decomposes rapidly under an alkaline condition.

Summary of Invention

The object of the present invention is to provide chemical mechanical polishing slurry which can accelerate the polishing rate of copper and silicon at the same time under an alkaline condition.

The chemical mechanical polishing slurry of the present application includes abrasive particles, oxidants, amino acids, quaternary ammonium bases and water, and the pH of the chemical mechanical polishing slurry is alkaline.

In the present invention, wherein said abrasive particles may be one or more selected from a group consisting of SiO_2、Al_2O_3、ZrO_2、CeO_2、SiC、Fe_2O_3、TiO_2 and /or Si_3N_4. And the concentration of the abrasive particles may be in the range of 1-30% (weight percent).

In the present invention, said oxidants may be one or more selected from a group consisting of bromate, chlorate, iodate, periodic acid and/or periodate. Said bromate may be potassium bromate, said chlorate may be potassium chlorate, said iodate may be potassium iodate, and said periodate may be ammonium periodate. And the concentration

of said oxidants may be in the range of 0.5-4% (weight percent).

In the present invention, said amino acids may be selected from glycine and/ or L-glutamic acid. And the concentration of said amino acids may be in the range of 1-8% (weight percent).

In the present invention, said quaternary ammonium bases could be tetramethylammonium hydroxide (TMAH). And the concentration of said quaternary ammoniums may be in the range of 5-12% (weight percent).

In the present invention, the pH of said chemical mechanical polishing slurry may be in the range from 8.00 to 13.00.

The beneficial effects according to the present invention lie in that the polishing slurry according to the present invention could significantly accelerates the polishing rate of Cu and silicon under an alkaline condition.

Mode for Carrying Out the Invention

The following examples further illustrate the invention but, of course, should not be construed as in any way limiting its scope. And in the following examples, % stands for weight percent.

Table 1 provides compositions that were homogeneously mixed with de-ionized water to prepare chemical mechanical polishing slurry according to each of Examples 1-23 and Comparative Examples 1-4. And pH was adjusted to the desired value using a pH adjuster (50% KOH).

Table 1 Examples 1-23 of the chemical mechanical polishing slurry for present invention and comparative examples 1-4

	abrasive particles		oxidants		polyhydroxy compounds		quaternary ammonium bases		PH
	Kind	concentration	Kind	concentration	Kind	concentration	Kind	concentration	
Comparative Example 1	SiO_2	1%					TMAH	0.10%	10.5
Comparative Example 2	SiO_2	2%					TMAH	0.10%	10.5
Comparative Example 3	SiO_2	5%					TMAH	0.10%	10.5
Comparative Example 4	SiO_2	15%					TMAH	0.10%	10.5
Example 1	SiO_2	1%	potassium bromate	0.50%	glycine	2%	TMAH	8.00%	11.46
Example 2	SiO_2	1%	potassium bromate	1%	glycine	2%	TMAH	8.00%	11.51
Example 3	SiO_2	2%	potassium bromate	2%	glycine	2%	TMAH	8.00%	10.603
Example 4	SiO_2	2%	potassium bromate	2%	glycine	4%	TMAH	10.00%	10.8
Example 5	SiO_2	2%	potassium bromate	4%	glycine	4%	TMAH	10.00%	11.4
Example 6	SiO_2	2%	potassium iodate	2%	glycine	4%	TMAH	10.00%	10.894
Example 7	SiO_2	2%	periodic acid	1%	glycine	4%	TMAH	10.00%	10.8

Example 8	SiO_2	2%	periodic acid	2%	glycine	4%	TMAH	10.00%	10.592
Example 9	SiO_2	2%	periodic acid	1%	L-glutamic acid	4%	TMAH	10.00%	10.8
Example 10	SiO_2	2%	periodic acid	1%	L-glutamic acid	2%	TMAH	8.00%	10.8
Example 11	SiO_2	5%	periodic acid	1%	glycine	2%	TMAH	8.00%	10.593
Example 12	SiO_2	15%	periodic acid	1%	glycine	1%	TMAH	6.00%	10.373
Example 13	SiO_2	15%	potassium chlorate	1%	glycine	1%	TMAH	6.00%	10.5
Example 14	SiO_2	30%	periodic acid	1%	glycine	8%	TMAH	12.00%	11.35
Example 15	Fe_2O_3	5%	potassium bromate	3%	glycine	2%	TMAH	8.00%	10
Example 16	TiO_2	5%	periodic acid	3%	glycine	1%	TMAH	5.00%	11.13
Example 17	SiO_2	15%	potassium bromate	3%	glycine	4%	TMAH	10.00%	10.63
Example 18	Al_2O_3	15%	potassium iodate	3%	glycine	8%	TMAH	12.00%	13
Example 19	Si_3N_4	15%	potassium bromate	1%	L-glutamic acid	6%	TMAH	11.00%	10.44
Example 20	SiC	15%	ammonium periodate	0.50%	L-glutamic acid	6%	TMAH	11.00%	12

Example 21	SiO_2	25%	potassium bromate	3%	glycine	2%	TMAH	8.00%	8
Example 22	CeO_2	25%	ammoniu m periodate	0.50%	glycine	2%	TMAH	8.00%	10.54
Example 23	ZrO_2	30%	potassium bromate	4%	L-glutami c acid	1%	TMAH	5.00%	10.2

Effect Example

To further observe the polishing effect of the present invention, the polishing was performed according to the following conditions: Logitech (UK) 1PM 52 polishing machine, polytex polishing pad, 4cm*4cm square wafer, downward pressure = 3 psi; rotating speed of the polishing plate=70rpm, rotating speed of the polishing head = 150rpm; flow rate of the polishing slurry = 100 mL/min. The results are shown in Table 2.

Table 2 the polishing effect of Examples 1-23 of the chemical mechanical polishing slurry for present invention and comparative examples 1-4

	RR of Cu	RR of POLY
	A/min	A/min
Comparative Example 1	130	1455
Comparative Example 2	224	1581.6
Comparative	376	1704

Example 3		
Comparative Example 4	392	1904.4
Example 1	1715	3610
Example 2	1908	3795.6
Example 3	4049	4227.2
Example 4	4604	4754.8
Example 5	6010	4850
Example 6	1520	3453.6
Example 7	4520	4933.2
Example 8	6044	4511
Example 9	3284	3421
Example 10	1550	3204
Example 11	4719	5216
Example 12	4135	3365.5
Example 13	1245	2591
Example 14	4601	5010

From the results of Comparative Examples 1-4, it indicates that the slurry rate of silicon and copper are very low under an alkaline condition when the slurry only contains abrasive particles.

Compared the Examples 1-2 with Comparative Example 1, it indicates that under same concentration of abrasive particles, the slurry rate of silicon and copper significantly increases when the alkaline slurry contains a specific oxidant, amino acid and quaternary ammonium base of the present application.

Compared the Examples 3-10 with Comparative Example 2, it indicates that under same concentration of abrasive particles, the slurry rate of silicon and copper significantly increases when the alkaline slurry contains a specific oxidant, amino acid and quaternary

ammonium base of the present application.

Compared the Example 11 with Comparative Example 3, it indicates that under same concentration of abrasive particles, the slurry rate of silicon and copper significantly increases when the alkaline slurry contains a specific oxidant, amino acid and quaternary ammonium base of the present application.

Compared the Examples 12-13 with Comparative Example 4, it indicates that under same concentration of abrasive particles, the slurry rate of silicon and copper significantly increases when the alkaline slurry contains a specific oxidant, amino acid and quaternary ammonium base of the present application.

Compared the Example 1 with Example 2, Example 4 with Example 5, Example 7 with Example 8, it indicates that under same concentration of amino acid, by changing the concentration of oxidants in alkaline slurry, the slurry rate of copper significantly increases with the increase of the concentration of oxidants, and the slurry rate of silicon is not suppressed at the same time.

Compared the Example 3 with Comparative Example 4, Example 9 with Example 10, it indicates that the slurry rate of copper and silicon significantly increases with the increase of the concentration of amino acids.

Compared the Example 7 with Comparative Example 11, it indicates that the slurry rate of copper and silicon significantly increases with the increase of the concentration of abrasive particles.

CLAIMS

1. A chemical mechanical polishing slurry, comprising abrasive particles, oxidants, amino acids, quaternary ammonium bases and water, and the pH of said chemical mechanical polishing slurry is alkaline.
2. A chemical mechanical polishing slurry of Claim 1, wherein said abrasive particles are one or more selected from a group consisting of SiO_2、Al_2O_3、ZrO_2、CeO_2、SiC、Fe_2O_3、TiO_2 and /or Si_3N_4.
3. A chemical mechanical polishing slurry of Claim 1, wherein the weight concentration of said abrasive particles is in the range of 1-30%.
4. A chemical mechanical polishing slurry of Claim 1, wherein said oxidants are one or more selected from a group consisting of bromate, chlorate, iodate, periodic acid and/or periodate.
5. A chemical mechanical polishing slurry of Claim 4, wherein said bromate is potassium bromate, said chlorate is potassium chlorate, said iodate is potassium iodate, and said periodate is ammonium periodate.
6. A chemical mechanical polishing slurry of Claim 1, wherein the weight concentration of said oxidants is in the range of 0.5-4%.
7. A chemical mechanical polishing slurry of Claim 1, wherein said amino acids are selected from glycine and/ or L- glutamic acid.
8. A chemical mechanical polishing slurry of Claim 1, wherein the weight concentration of said amino acids is in the range of 1-8%.
9. A chemical mechanical polishing slurry of Claim 1, wherein said quaternary ammonium bases are tetramethylammonium hydroxide.
10. A chemical mechanical polishing slurry of Claim 1 wherein the weight concentration of said quaternary ammonium bases is in the range of 5-12%.
11. A chemical mechanical polishing slurry of Claim 1, wherein the pH of said chemical mechanical polishing slurry ranges from 8.00-13.00.