A TSV Barrier Layer Polishing Slurry

Technical field

This invention relates to polishing slurry, especially chemical mechanical polishing slurry for TSV barrier layer.

Technical Background

See Figures 5 -7, the small-scale 3D TSV (TSV, Through-Silicon-Via) packaging technology has been applied to improve IC performance, and to reduce the size and cost. The 3D TSV is one lasted technology aims to provide the vertical connections between chip or wafer layers. Different from IC wire-bonding and stud-bump bonding technology, the TSV technology maximizes the density of stacked chips in three dimensional directions, minimizes overall area, and significantly improves the chip interconnect speed and power consumption performance. The main advantages of the TSV are that (1)the size and weight of the wafer will be minimized;(2)different wafer with different technology will be integrated into one package;(3)instead of long 2D interconnection, short vertical interconnection will be applied;(4)the parasitics effect and power consumption will be reduced.

There are various integration ways for TSV processes. However, all these ways share a common problem, i.e. how to make openings through several layers of different material, including silicon layer, insulating film layer or electro-conductive film layer in IC. For example, copper, tantalum barrier layer, silicon dioxide insulating layer and silicon nitride stop layer etc. Because the thickness of each layer is great, a high polishing rate and suitable selectivity ratio are needed during CMP. Therefore, a desired correction of the defections of previous processes is achieved. Meanwhile, the process will be stopped on the silicon nitride layer, without metal erosion and defects. And the particulate matter on the outside surface would be limited so that a constraint for process is satisfied. Therefore there is a higher requirement for the CMP of TSV barrier layer. There has not been a report about commercial polishing slurry for TSV barrier layer so far.

Summary of the Invention

The purpose of the present invention is to solve the problem mentioned in the above prior art and provide a chemical mechanical polishing slurry, which has a higher silicon dioxide removal rate and a higher polishing selectivity ratio to silicon nitride. By providing the present invention, a desired correction of the defections of previous processes is achieved. Meanwhile, the process will not cause metal erosion and defects, and the polishing slurry is stable.

Hereinafter are the technical solutions of the present invention:

TSV barrier layer polishing slurry, wherein characterized in that it comprises abrasives, combination metal corrosion inhibitors, chelating agents, oxidizing agents, silicon nitride inhibitors and pH regulators.

Wherein, the abrasives are silica sols or the fumed silica. The particle size of the abrasives is 20-200nm, and 40-120nm is preferred. The amount is 10-50%, and 20-30% is preferred.

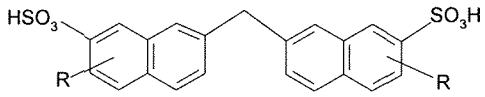
Wherein, the metal corrosion inhibitors contain azoles and water-soluble polymers.

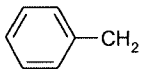
Wherein, the azoles are benzotriazole and its derivatives; the water-soluble polymers are the polyacrylic acid and co-polymers thereof.

Wherein, the concentration of the azoles is 0.01-0.5%; the concentration of the water-soluble polymers is 0.005-0.1%. Preferably, the concentration of the azoles is 0.05-0.2%; the concentration of the water-soluble polymer is 0.01-0.05%.

Wherein, the chelating agents are one or more of the organic phosphonic acids, PBTCA, HPAA, HEDP, EDTMP and ATMP. The concentration of the chelating agents is 0.05%-1%, and 0.1-0.5% is preferred.

Wherein, the silicon nitride inhibitors are naphthalene sulfonate -formaldehyde condensates, which has the following form:



R: CH_3 

Wherein, , the concentration of the silicon nitride inhibitor is from 50ppm to 0.1%.

Wherein, the silicon nitride inhibitors are disodium methylenebisnaphthalenesulphonate, methyl naphthalene sulfonate formaldehyde condensates and/or benzyl naphthalene sulfonate formaldehyde condensates. .

Wherein, the pH regulators are organic carboxylic acids.

Wherein, the organic carboxylic acids are one or more of oxalic acid, malonic acid, succinic acid, citric acid and tartaric acid.

Wherein, the oxidizing agents are peroxide or persulfide. The oxidizing agents are one or more of the hydrogen peroxide, the sodium peroxide, the potassium peroxide, the benzoyl peroxide, the sodium persulfate, the potassium persulfate and the ammonium persulfate.

Wherein, the polishing slurry also includes anti-mold and anti-bacteria agents. The anti-mold and anti-bacteria agent is quaternary ammonium salt.

Wherein, the pH of the said polishing slurry is 2-5, and 3-4 is preferred.

The present invention possesses the following advantages:

The invention has a higher Ta and SiO_2 removal rate, and the removal rate of silicon nitride is less than 100 Å/min. It increases the SiO_2: Si_3N_4 selectivity ratio to about 15-20. Desirably, the process will stop on Si_3N_4 layer. The chelating agents and metal corrosion inhibitors protect the copper and other metals from erosion. The metal removal rate varies linearly (and slowly) with the variation in the concentration of hydrogen peroxide. The thin line zone is clear and sharp after polishing without contaminants such as granular materials, organic residue etc. Furthermore, a desired correction of the defections of previous processes and polishing processes is achieved. It exhibits desirable planarization efficiency. After soaking in the polishing slurry, it has a better erosion-resistant performance.

Brief description

Figures 1, 2 show the surface topography of the wafers after polishing.

Figures 3, 4 show the surface pictures of the wafers after soaking in the polishing slurry.

Figures 5-7 schematically show the polished surface of the TSV barrier layer before and after

polishing respectively, wherein:
Figure 5 schematically shows the polished surface sketch of the TSV before the polishing
Figure 6 schematically shows the polished surface sketch of the TSV after the polishing of copper.
Figure 7 schematically shows the polished surface sketch of the TSV after the polishing of barrier layer.

The following embodiments are included to further illustrate the invention by means of certain embodiments of the invention, and are not to be construed to limit the scope of the present invention in any way.

Polishing conditions:
Polishing pad: IC pad
Polishing condition: 70/90rpm
The flux of polishing slurry: 100ml/min
The corrosion rate: socking the just-polished slurry into the slurry for 15 minutes and measuring the thickness before and after soaking.
Butterfly depressions: measuring the butterfly depressions of an 80um metal with the Semitech 854 wafers.
The polishing homogeneity of the section: measuring the butterfly depressions with different line width in a die.
Blank chips: PETEOS, Ta, Cu, Si_3N_4.

Table1 the formulas of Examples 1-7and the Comparative Example

	SiO_2	BTA	PAA	pH Regulator	chelating agents	Si_3N_4 Inhibitors	oxidizing agents	pH
Comparative Example								
Example 1	SiO_2:100nm, 25%	0.10%	0.0150%	Malonic acid				
Example 2	SiO_2:100nm, 25%	0.10%	0.0150%	Malonic acid	PBTCA 0.2%			
Example 3	SiO_2:100nm, 25%	0.10%	0.0150%	Malonic acid	PBTCA 0.2%	DISN1 200ppm	H_2O_2 0.1%	3
Example 4							H_2O_2 0.3%	3
Example 5							H_2O_2 0.5%	3
Example 6	SiO2:100n, 25%	0.10%	0.0150%	Oxalic acid	PBTCA 0.2%	DISN1 200ppm	Ammonium persulfate 0.1%	3
Example 7	SiO_2:20nm, 50%	0.50%	0.0050%	Oxalic acid	EDTMP 0.01%	DISN2 200ppm	H_2O_2 0.1%	2
Example 8	SiO_2:200nm, 10%	0.01%	0.1000%	Succinic acid	ATMP 1%	DISN3 50ppm	H_2O_2 0.1%	5

Example 9	SiO_2(Fumed silica):100nm,10%	0.10%	0.1000%	Tartaric acid	HPAA 0.2%	DISN1 0.1%	H_2O_2 0.1%	3
Example 10	SiO_2:100nm, 20%	0.10%	0.0150%	Malonic acid	PBTCA 0.2%	DISN2 200ppm	H_2O_2 0.3%	3
Example 11	SiO_2:100nm, 20%	0.10%	0.0150%	Malonic acid	HPAA 0.2%	DISN1 200ppm	Sodium peroxide 0.3%	3
Example 12	SiO_2:100nm, 20%	0.10%	0.0150%	Malonic acid	HPAA 0.2%	DISN1 200ppm	Potassium peroxide 0.3%	2
Example 13	SiO_2:100nm, 30%	0.10%	0.0150%	Oxalic acid	HEDP 0.2%	DISN1 200ppm	H2O2 0.3%	5
Example 14	SiO_2:40nm, 30%	0.20%	0.010%	Oxalic acid	HEDP 0.2%	DISN2 100ppm	Sodium peroxide 0.3%	3
Example 15	SiO_2:120nm, 20%	0.05%	0.005%	Malonic acid	PBTCA 0.2%	DISN2 100ppm	Benzoyl peroxide 0.2%	3

BTA: benzotriazole,

PAA: polyacrylic acid,

PBTCA: 2-phosphonobutane-1,2,4-tricarboxylic acid,

$DISN_1$, disodium methylenebisnaphthalenesulphonate,

$DISN_2$, methyl naphthalene sulfonate formaldehyde condensates,

$DISN_3$, benzyl naphthalene sulfonate formaldehyde condensates,

HPAA: 2-hydroxyphosphonocarboxylic acid,

HEDP: hydroxyethylidene diphosphonate.

The comparative example is the barrier layer polishing slurry available in the market.

Table 2 Results of Examples 1-7and the Comparative Example

	TEOS	Si_3N_4	Cu	Ta	SER (static etch rate)	Pre (pre-dishing)	Pos (post-dishing)	Def.
Comparative Example	1523	456		1023	5			
Example 1	1956	652	387	1523	3			
Example 2	1935	635	442	1495	3			
Example 3	1869	52	585	1552	3	1500	350	No corrosion, no residue
Example 4			675		1			
Example 5			784		5			
Example 6	1823	74	620	1487	3	1856	285	No corrosion, no organic residue
Example 7	2855	142	523	1496	2	2000	485	
Example 8	1952	51	505	1208	3			
Example 9	1855	62	485	1186	3			
Example 10	1924	60	792	1488	3	1653	400	No corrosion, no organic residue
Example 11	1825	62	452	1505	3	1753	368	No corrosion, no organic residue
Example 12	2125	58	411	1253	2			
Example 13	1785	80	385	1438	5			
Example 14	1985	95	450	1523	3			
Example 15	1825	65	423	1468	10			

As shown in Figures 1-4, compared with the comparative example, the polishing slurry of the present invention has a higher Ta and SiO_2 removal rate, and the removal rate of silicon nitride is less than 100 Å/min. It increases the SiO_2: Si_3N_4 selectivity ratio to about 15-20. Desirably, the process will stop on Si_3N_4 layer. The chelating agents and metal corrosion inhibitors act together so as to protect the copper and other metals from erosion. The metal removal rate varies linearly (and slowly) with the variation in the concentration of hydrogen peroxide. The thin line zone is clear and sharp after polishing without contaminants such as granular materials, organic residue etc. Furthermore, a desired correction of the defections of previous processes and polishing processes is achieved. It exhibits desirable planarization efficiency. After soaking in the polishing slurry, it has a better erosion-resistant performance.

Wherein, the polishing slurry also includes anti-mold and anti-bacteria agents. The anti-mold and anti-bacteria agent is quaternary ammonium salt.

Wherein, the pH of the said polishing slurry is 2-5, and 3-4 is preferred.

Claims:

1. TSV barrier layer polishing slurry, wherein characterized in that it comprises abrasives, combination metal corrosion inhibitors, chelating agents, oxidizing agents, silicon nitride inhibitors and pH regulators.

2. The TSV barrier layer polishing slurry of claim 1, wherein said abrasives are silica sols or the fumed silica.

3. The TSV barrier layer polishing slurry of claim 1 or 2, wherein the particle size of said abrasives is 20-200nm.

4. The TSV barrier layer polishing slurry of claim 3, wherein the particle size of said abrasives is 40-120nm.

5. The TSV barrier layer polishing slurry of claim 1 or 2, wherein the amount of said abrasives is 10-50%.

6. The TSV barrier layer polishing slurry of claim 5, wherein the amount of said abrasives is 20-30%.

7. The TSV barrier layer polishing slurry of claim 1, wherein said combination metal corrosion inhibitors contain azoles and water-soluble polymers.

8. The TSV barrier layer polishing slurry of claim 7, wherein said azoles are benzotriazole and its derivatives, and said water-soluble polymers are the polyacrylic acid and co-polymers thereof.

9. The TSV barrier layer polishing slurry of claim 7, wherein the concentration of said azoles is 0.01-0.5%, and the concentration of said water-soluble polymers is 0.005-0.1%.

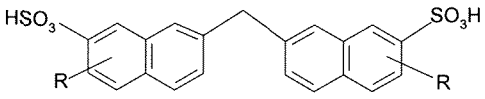
10. The said TSV barrier layer polishing slurry of claim 9, wherein the concentration of said azoles is 0.05-0.2%, and the concentration of said water-soluble polymers is 0.01-0.05%.

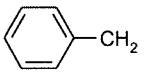
11. The TSV barrier layer polishing slurry of claim 1, wherein said chelating agents are one or more of the organic phosphonic acids, PBTCA, HPAA, HEDP, EDTMP and ATMP.

12. The TSV barrier layer polishing slurry of claim 1, wherein the concentration of said chelating agents is 0.05%-1%.

13. The TSV barrier layer polishing slurry of claim 12, wherein the concentration of said chelating agents is 0.1-0.5%.

14. The TSV barrier layer polishing slurry of claim 1, wherein said silicon nitride inhibitors are naphthalene sulfonate -formaldehyde condensates , which has the following form:



Wherein, R: CH_3 

,

15. The TSV barrier layer polishing slurry of claim 14, wherein said silicon nitride inhibitors are disodium methylenebisnaphthalenesulphonate, methyl naphthalene sulfonate formaldehyde condensates and/or benzyl naphthalene sulfonate formaldehyde condensates .

16. The TSV barrier layer polishing slurry of claim 1, wherein the said pH regulators are organic carboxylic acids.

17. The TSV barrier layer polishing slurry of claim 16, wherein said organic carboxylic acids are one or more of oxalic acid, malonic acid, succinic acid, citric acid and tartaric acid.

18. The TSV barrier layer polishing slurry of claim 1, wherein said oxidizing agents are peroxide or persulfide.

19. The TSV barrier layer polishing slurry of claim 18, where said oxidizing agents are one or more of the hydrogen peroxide, the sodium peroxide, the potassium peroxide, the benzoyl peroxide, the sodium persulfate, the potassium persulfate and the ammonium persulfate. (please make sure each oxidizing agent should be mentioned in the examples)

20. The TSV barrier layer polishing slurry of claim 1, wherein said polishing slurry also includes anti-mold and anti-bacteria agents.

21. The TSV barrier layer polishing slurry of claim 20, wherein said anti-mold and anti-bacteria agent is quaternary ammonium salt.

22. The TSV barrier layer polishing slurry of claim 1, wherein the pH of said polishing slurry is 2-5.

23. The TSV barrier layer polishing slurry of claim 22, wherein the pH of said polishing slurry is 3-4.

24. The TSV barrier layer polishing slurry of claim 1, wherein concentration of said silicon nitride inhibitors is from 50ppm to 0.1%.