CHEMICAL-MECHANICAL POLISHING LIQUID

Technical Field

[001] The invention relates to a chemical mechanical polishing slurry composition.

Background of the invention

[002] With the development of semiconductor technology and increasing interconnected layers in large-scale integrated circuits, the planarization of conductive and insulation layers are becoming more vital. Chemical mechanical polishing (CMP) process established by IBM in 1980s is currently the most effective way for global planarization process.

[003] CMP combined chemical and mechanical functions. Its device generally contains a polishing table with pad and a carrier for holding wafer, wherein the carrier secures the wafer and press the desired side of wafer to the pad. During chemical mechanical polishing process, the carrier moves linearly on the pad or rotates in same direction as polishing table. Meanwhile, slurry containing abrasive is dipped onto the pad and flattens and spreads out due to centrifugation. The surface of wafer achieves global planarization using a combination of chemical and mechanical action.

[004] In the emerging through silicon via (TSV) technology, practically, in backside thinning, high polishing rate for silicon is required. There are multiple factors involving in increasing polishing rate, and generally, using chemical action.

[005] US2002032987 discloses a polishing composition with alcohol amine as additive to im-prove removal rate of poly silicon, wherein additive is preferably 2-dimethylamino-2-methyl-1-propanol.

[006] US2002151252 discloses a polishing composition containing a chelating agent having multiple carboxylic acid structural groups, in order to improve the removal rate of poly-crystal silicon, wherein the preferable chelating agent is EDTA (propanediaminetetraacetic acid) and DTPA (diethylenetriaminepentaacetic acid).

[007] EP1072662 discloses a polishing composition containing an organic substance with conjugated effect arising from lone-pair electrons and double bond, so as to enhance the removal rate of poly-crystal silicon, and preferably compound is selected from guanidine compound and/or the salt thereof.

[008] US2006014390 discloses a polishing composition for improving removal rate of poly silicon, comprising 4.25 to 18.5 weight percent of an abrasive and 0.05 to 1.5 weight percent of an additive, wherein the additive is mainly selected from organic bases, such as quaternary ammonium, quaternary ammonium salt and ethanol amine. Besides, the polishing composition further includes non-ionic surfactant, such as homopolymer and copolymer of glycol and/or propylene glycol.

[009] US7452481B2 discloses a method for improving the polishing rate with a polishing slurry containing ZrO_2, a carboxylic acid having four or more carboxyl groups in the molecule and at least one quaternary alkylammonium hydroxide.

[010] CN101492592A discloses a method with azole for enhancing polishing rate of silicon. Since the salts of azole are sodium and potassium, the stability of the polishing system is poor. In order to adjust the pH value of acidic azole (e.g. TAZ) to alkaline, the pH value is adjusted with KOH or NaOH, and introduced Na or K ion will decrease the stability of the slurry. Meanwhile, these metal ions will contaminate the semiconductor which is polished, and thereby decreasing the reliability

of the element.

[011] The methods above are limited in improving the polishing rate of silicon, practically, in the emerging TSV technology, it hardly achieves the high polishing rate of silicon.

Summary of the invention

[012] The present invention provides a chemical mechanical polishing slurry composition for enhancing polishing rate of silicon.

[013] The present invention relates to a chemical mechanical polishing composition containing abrasive particles, water, azole compounds and piperazine. It is found that the combination of azole compounds and piperazine leads to a high polishing rate for silicon (either single-crystal or poly-crystal silicon). Moreover, colloids in the said polishing composition are also very stable. The polishing composition may futher include tetramethylammonium hydroxide (TMAH), further improving the polishing rate.

[014] In the present invention, azole compound may be one or more selected from triazole, tetrazole and derivatives thereof.

[015] In the present invention, azole compound may be one or more selected from 1,2,4-triazole, 3-amino-1,2,4-triazole, 5-amino-1,2,4-triazole, 5-carboxy-3-amino-1,2,4-triazole, benzotriazole, 1-H-tetrazole, and 5-aminotetrazole.

[016] In the present invention, the azole compound is present in an amount ranging from 1-8 weight percent

[017] In the present invention, the abrasive particle may be one or more selected from SiO_2, Al_2O_3, CeO_2, SiC and Si_3N_4.

[018] In the present invention, the abrasive particle is present in an amount ranging from 1-20 weight percent

[019] In the present invention, the piperazine is present in an amount ranging from 1-10 weight percent.

[020] In the present invention, the TMAH is present in an amount ranging from 1-10 weight percent.

[021] In the present invention, the pH value of the polishing slurry is 9-12.

[022] All chemicals and raw materials used in the present invention are all commercially available.

[023] The present invention aims to provide a polishing slurry composition for,

[024] (1) Solving the problem relating to the low polishing rate of silicon and the instability of colloids in the slurry.

[025] (2) Achieving the high polishing rate of silicon, greatly increasing the polishing ability of silicon and thereby increasing the productivity in TSV technology.

[026] (3) Reducing the overall cost of semiconductor process.

Examples

[027] The present invention will be further described by, but not limited to, the following examples. And in the following examples, % stands for weight percent.

Examples for preparation

[028] Table 1 gives the composition of the chemical mechanical polishing slurry in example 1-13.

[029] The chemical mechanical polishing slurry is prepared by mixing the materials listed in Table 1 in deionized water, and adjusting to the desired pH value with pH adjuster.

Table 1 The composition of the chemical mechanical polishing slurry in example 1-13.

No.	Abrasive	Concentration of abrasive (%)	Azole	Concentration of azole (%)	Concentration of piperazine (%)	Concentration of TMAH (%)	pH
Comparative example 1	SiO_2	5	/	/	/	/	11 (adjusted with KOH)
Comparative example 2	SiO_2	5	1,2,4-triazole	4	/	/	11 (adjusted with KOH)
Example 1	SiO_2	5	1,2,4-triazole	4	8	0	11
Example 2	SiO_2	5	1,2,4-triazole	4	10	0	11
Example 3	SiO_2	5	1,2,4-triazole	4	10	4	11
Example 4	SiO_2	5	1,2,4-triazole	4	10	8	11
Example 5	SiO_2	10	3-amino-1,2,4-triazole	8	6	0	9
Example 6	SiO_2	10	3-amino-1,2,4-triazole	6	10	0	10
Example 7	SiO_2	20	4-amino-1,2,4-triazole	1	5	10	12
Example 8	CeO_2	1	5-amino-1,2,4-triazole	4	6	2	11
Example 9	Al_2O_3	1	5-carboxy-3-amino-1,2,4-triazole	4	1	5	11
Example 10	Si_3N_4	1	benzotriazole	4	6	0	11
Example 11	SiC	1	benzotriazole	4	6	1	11
Example 12	SiO_2	5	1-H-tetrazole,	2	4	6	11
Example 13	SiO_2	5	5-aminotetrazole	2	4	6	11

Example

[030] Conditions for polishing: polishing machine: Logitech (Britain) 1PM52; Pad type: polytex; wafter dimension: 4 cm × 4 cm square wafer; Pressure: 3 psi; rotating speed of polishing table =70 rpm; rotating speed of carrier = 150 rpm; flow rate of slurry 100 ml/min.

Table 2 The polishing results of comparative example 1 and 2, and example 1-13.

No.	Abrasive	Concentration of abrasive (%)	Azole	Concentration of azole (%)	Concentration of piperazine (%)	Concentration of TMAH (%)	pH	Polishing rate of silicon (A/min)	Average increment of diameter of abrasive particle within 30 days (A)
Comparative example 1	SiO_2	5	/	/	/	/	11 (adjusted with KOH)	2100	20
Comparative example 2	SiO_2	5	1,2,4-triazole	4	/	/	11 (adjusted with KOH)	4200	Stratified, precipitated after 15 mins
Example 1	SiO_2	5	1,2,4-triazole	4	8	0	11	9000	0
Example 2	SiO_2	5	1,2,4-triazole	4	10	0	11	9500	0
Example 3	SiO_2	5	1,2,4-triazole	4	10	4	11	9700	0
Example 4	SiO_2	5	1,2,4-triazole	4	10	8	11	11000	0
Example 5	SiO_2	10	3-amino-1,2,4-triazole	8	6	0	9	7730	0
Example 6	SiO_2	10	3-amino-1,2,4-triazole	6	10	0	10	7000	0
Example 7	SiO_2	20	4-amino-1,2,4-triazole	1	5	10	12	9100	0
Example 8	CeO_2	1	5-amino-1,2,4-triazole	4	6	2	11	8400	0
Example 9	Al_2O_3	1	5-carboxy-3-amino-1,2,4-tria	4	1	5	11	7200	0

			zole						
Example 10	Si_3N_4	1	benzotriazole	4	6	0	11	8800	0
Example 11	SiC	1	benzotriazole	4	6	1	11	9600	0
Example 12	SiO_2	5	1-H-tetrazole,	2	4	6	11	7010	0
Example 13	SiO_2	5	5-aminotetrazole	2	4	6	11	7350	0

[031] Comparative example 1 indicates that polishing rate of silicon with SiO_2 particle is not very high and the polishing rate is only 2100 A/min. Comparative example 2 indicates that at the same condition, polishing rate can be increased by 2 times by adding TAZ (1,2,4-triazole) in the polishing slurry. However, since the system contains metal ion (i.e.,K ion), the polishing slurry is not stable. After 15 min, the slurry is stratified and particles are precipitated. Thereafter, the polishing slurry loses efficacy.

[032] In comparison to comparative example 2, example 2 indicates that after adding piperazine, the polishing rate can be increased by 2 times.

[033] Example 3 and 4 indicate that polishing rate can be further increased when the polishing slurry includes TMAH.

[034] Example 1-7 indicate that when SiO_2 is used as abrasive agent, the polishing rate can be significantly enhanced by using different combinations of azole and piperazine.

[035] Example 8-13 indicate that when Al_2O_3, CeO_2, SiC or Si_3N_4 is used as abrasive agent, the polishing rate can also be significantly enhanced by using different combinations of azole and piperazine.

[036] Example 1-13 further indicate that the polishing system becomes stable (with no change in average diameter of abrasive particles within 30 days) from the previous instable state (having stratified and precipitated after 5 min) by using combination of azole and piperazine. The effect on stability is significant.

[037] According to the above data, the chemical mechanical polishing slurry of the present invention has the following advantages:

[038] (1) (1) Solving the problem relating to the low polishing rate of silicon and the instability of colloids in the slurry.

[039] (2) Achieving the high polishing rate of silicon, greatly increasing the polishing ability of silicon and thereby increasing the productivity in TSV technology.

[040] (3) Reducing the overall cost of semiconductor process.

[041] Exemplary embodiments of the present invention have been disclosed herein and, although specific terms are employed, they are used and are to be interpreted in a generic and descriptive sense only and not for purpose of limitation. Accordingly, it will be understood by those of ordinary skill in the art that various changes in form and details may be made without departing from the spirit and scope of the present invention as set forth in the following claims.

CLAIMS

1. A chemical mechanical slurry composition comprising: abrasive particles, water, azole compounds and piperazine.
2. The slurry composition according to claim 1, wherein the abrasive particle is one or more selected from SiO_2, Al_2O_3, CeO_2, SiC and Si_3N_4.
3. The slurry composition according to claim 1 or 2, wherein the abrasive particle is present in an amount ranging from 1-20 weight percent.
4. The slurry composition according to claim 1, wherein the azole compound is one or more selected from triazole, tetrazole and derivatives thereof.
5. The slurry composition according to claim 4, wherein the azole compound is one or more selected from 1,2,4-triazole, 3-amino-1,2,4-triazole, 5-amino-1,2,4-triazole, 5-carboxy-3-amino-1,2,4-triazole and benzotriazole, 1-H-tetrazole, 5-aminotetrazole.
6. The slurry composition according to claim 1, wherein the azole compound is present in an amount ranging from 1-8 weight percent.
7. The slurry composition according to claim 1, wherein the piperazine is present in an amount ranging from 1-10 weight percent.
8. The slurry composition according to claim 1, further comprising tetramethylammonium hydroxide.
9. The slurry composition according to claim 8, wherein the tetramethylammonium hydroxide is present in an amount ranging from 1-10 weight percent.
10. The slurry composition according to claim 1, having a pH value equal to 9-12.
11. The slurry composition according to claim 1-10, providing slurry composition for polishing single-crystal or poly-crystal silicon.