

SPECIFICATIONS

A CHEMICAL MECHANICAL POLISHING COMPOSITION

TECHNICAL FIELD

This invention relates to a ceria-based chemical mechanical polishing composition, and more specifically, to a polishing composition in which the addition of a quaternary ammonium compound into the ceria slurry significantly enhances the polishing rate of SiN while maintaining the polishing rate of TEOS unchanged.

BACKGROUND

Chemical mechanical polishing (CMP) has become the most effective and mature planarization technique in the manufacturing of semiconductor devices. Among CMP slurries based on different abrasive particles, ceria particles offer high polishing rates even at lower concentrations and enable higher selectivity, making them highly valuable in CMP applications. Typically, most CMP slurries aim to reduce the removal rate of silicon nitride (SiN) while achieving relatively higher removal rates for other materials. For example, in the widely used shallow trench isolation (STI) process, where SiN serves as the stop layer, the CMP slurry requires a high removal rate of tetraethyl orthosilicate (TEOS).

However, with advances in semiconductor etching technology, the oxide linewidth has gradually decreased, thereby increasing the demand for chemical mechanical polishing (CMP) slurries that exhibit a high polishing rate for silicon nitride (SiN), which differs from the traditional selectivity requirements in STI processes. By tuning the selectivity ratio between SiN and TEOS, defects in the oxide lines on the substrate surface can be reduced. To achieve this goal, several studies (e.g., CN102046743B, US200690047870A1) have proposed adding certain polymers or copolymers to ceria-based slurries to enhance the SiN polishing rate; however, these polymer additives significantly suppress the polishing rate of TEOS. This invention introduces a quaternary ammonium compound into the ceria slurry, which effectively increases the SiN polishing rate while having almost no impact on the TEOS polishing rate.

DESCRIPTION

This invention discloses a chemical mechanical polishing composition, comprising: water; ceria abrasive particles; and a quaternary ammonium compound.

Further, the quaternary ammonium compound is selected from one or more of tetrabutylammonium hydroxide, benzyltriethylammonium chloride, betaine.

Further, the concentration of the quaternary ammonium compound ranges from 200 ppm to 1000 ppm.

Further, the mass percentage of the ceria abrasive particles ranges from 0.1 wt% to 0.5 wt%.

Further, the polishing composition further comprises a pH adjuster, which is selected from inorganic acids or inorganic bases. HNO_3 or KOH is preferred.

Further, the pH of the polishing composition ranges from 4.0 to 6.0.

This invention adds a quaternary ammonium compound (including but not limited to tetrabutylammonium hydroxide, benzyltriethylammonium chloride, and betaine) to a ceria-based polishing slurry, which can enhance the polishing rate of SiN by more than 1.5 times while having almost no effect on the polishing rate of TEOS. For example, with tetrabutylammonium hydroxide and benzyltriethylammonium chloride, at concentrations ranging from 200 to 1000 ppm and within a slurry pH range of 4.0 to 6.0, the increased polishing rate for SiN is consistently achieved.

EMBODIMENTS

To better understand the technical solution of this invention, the following examples will further illustrate the method provided by this invention, but this invention is not limited to the listed examples and should also include any other known modifications within the scope of the claims of this invention.

Embodiment 1

All raw materials used in this example are commercially available. According to the component ratios listed in Table 1, each component was dissolved in deionized water, with deionized water added to bring the total to 100 wt%, and the pH was adjusted to 4.5 using HNO_3 or KOH , yielding the polishing slurries of Comparative Embodiments 1A–1C and Embodiments 1D–1F of the present invention.

Table 1: Composition and content of polishing compositions for Comparative Embodiments 1A–1C and Embodiments 1D–1F

Polishing solution	Cerium oxide (wt%)	Metal ion salt	
		Specific Compounds	Concentration (ppm)
Comparative Embodiment 1A	0.1%	/	/
Comparative Embodiment 1B	0.2%	/	/
Comparative Embodiment 1C	0.1%	Polyquaternium-37	200
Embodiment 1D	0.1%	Tetrabutylammonium Hydroxide	500
Embodiment 1E	0.1%	Benzyltriethylammonium Chloride	500
Embodiment 1F	0.2%	Betaine	500

To further evaluate the polishing performance of the Polishing solutions from Embodiments 1D–1F and Comparative Embodiments 1A–1C listed in Table 1, the polishing rates on TEOS wafers and SiN wafers were measured, with results presented in Table 2.

Polishing conditions: A Mirra polisher was used with an IC1000 pad. The platen and head rotation speeds were 93 rpm and 87 rpm, respectively. The polishing pressure was set to 1.5

psi, 2.0 psi, or 3.0 psi, the polishing solution flow rate was 150 mL/min, and the polishing time was 60 seconds.

Polishing procedure: The prepared polishing solutions were separately used to polish blank TEOS and SiN wafers under the above-mentioned polishing equipment and conditions. Film thickness measurements were performed using a NanoSpec film thickness measurement system (NanoSpec6100-300, Shanghai Nanospec Technology Corporation). The measurement starts from 3 mm away from the wafer edge, taking 49 equally spaced points along a diameter line to determine the polishing rate at each point. The reported polishing rate for each polishing solution is the average of the 49 measured points.

Table 2: Polishing rates of the polishing solutions for Comparative Embodiments 1A–1C and Embodiments 1D–1F

polishing pressure	1.5 psi		2.0 psi		3.0 psi	
	SiN RR (Å/min)	TEOS RR (Å/min)	SiN RR (Å/min)	TEOS RR (Å/min)	SiN RR (Å/min)	TEOS RR (Å/min)
Comparative Embodiment 1A	334	2090	462	2662	712	3466
Comparative Embodiment 1B	198	840	338	1079	586	1424
Comparative Embodiment 1C	8	18	774	17	1072	18
Embodiment 1D	530	2051	760	2620	1011	3555
Embodiment 1E	456	1938	722	2420	1224	3428
Embodiment 1F	398	787	532	1001	756	1549

From the polishing results of Comparative Embodiment 1A and 1C, it can be observed that although adding polyquaternium-37 can enhance the SiN polishing rate at certain pressures (2.0 psi and 3.0 psi), it significantly suppresses the TEOS polishing rate. In contrast, the results of Comparative Embodiment 1A and Embodiment 1D and 1E show that both tetrabutylammonium hydroxide and benzyltriethylammonium chloride effectively increase the SiN polishing rate—by more than 1.5 times—while having minimal impact on the TEOS polishing rate.

The polishing results of Comparative Example 1B and Example 1F show that betaine, as a zwitterionic compound containing a quaternary ammonium cation, can also effectively enhance the silicon nitride (SiN) polishing rate while having almost no effect on the TEOS polishing rate. This indicates that although betaine is zwitterionic, the quaternary ammonium

cation plays the dominant role, and the carboxylate anion on the other end does not adsorb onto the SiN surface to inhibit its polishing rate.

In summary, adding a quaternary ammonium compound to the ceria-based polishing solution can effectively enhance the SiN polishing rate without suppressing the TEOS polishing rate.

Embodiment 2

The polishing solutions of Comparative Embodiments 2A–2C and Embodiments 2D–2Q were prepared by dissolving the components according to the ratios in Table 3 into deionized water, with deionized water added to reach a total of 100 wt%, and the pH was adjusted to 4.5 using HNO₃ or KOH. Each prepared solution was then used for chemical mechanical polishing (CMP) on blank TEOS and SiN wafers, and the polishing performance was compared, with results shown in Table 3.

Polishing conditions: The polishing tool was a Mirra polisher with an IC1000 pad. The platen and head rotation speeds were 93 rpm and 87 rpm, respectively. The polishing pressure was 2.0 psi, the solution flow rate was 150 mL/min, and the polishing time was 60 seconds. The film thickness measurement was performed using a NanoSpec film thickness measurement system.

Table 3: Effect of adding different concentrations of quaternary ammonium compounds on polishing performance

Polishing solution	Cerium oxide (wt%)	Quaternary Ammonium Compound		2.0 psi	
		Specific Compounds	Concentration (ppm)	SiN RR (Å/min)	TEOS RR (Å/min)
Comparative Embodiment 2A	0.1%	/	/	462	2662
Comparative Embodiment 2B	0.2%	/	/	338	1079
Comparative Embodiment 2C	0.5%	/	/	1044	3376
Embodiment 2D	0.1%	Tetrabutylammonium Hydroxide	100	468	2829
Embodiment 2E	0.1%	Tetrabutylammonium Hydroxide	200	798	2796
Embodiment 2F	0.1%	Tetrabutylammonium Hydroxide	500	760	2620

Embodiment 2G	0.5%	Tetrabutylammonium Hydroxide	500	1070	3001
Embodiment 2H	0.1%	Tetrabutylammonium Hydroxide	800	694	2770
Embodiment 2I	0.1%	Tetrabutylammonium Hydroxide	1000	800	2662
Embodiment 2J	0.1%	Benzyltriethylammonium Chloride	200	606	2525
Embodiment 2K	0.1%	Benzyltriethylammonium Chloride	500	722	2420
Embodiment 2L	0.1%	Benzyltriethylammonium Chloride	1000	1304	2441
Comparative Embodiment 2M	0.1%	Benzyltriethylammonium Chloride	1500	580	2415
Embodiment 2N	0.1%	Betaine	500	672	2802
Embodiment 2O	0.1%	Betaine	1000	640	2791
Embodiment 2P	0.2%	Betaine	500	532	1001

Table 3 shows the effect of adding different concentrations of quaternary ammonium compounds on the polishing performance of ceria-based polishing solutions. It can be observed that when the concentration of tetrabutylammonium hydroxide is 100 ppm, the enhancement in SiN polishing rate is not significant. However, when the concentration exceeds 200 ppm, a noticeable increase in SiN polishing rate is achieved. Moreover, the SiN polishing rate does not continuously increase with higher additive concentrations. Within the 200–1000 ppm range, the rate stabilizes between 700–800 Å/min, indicating that a concentration as low as 200 ppm is sufficient to achieve optimal enhancement. Meanwhile, even at 1000 ppm, the TEOS polishing rate remains almost unaffected.

Similarly, when benzyltriethylammonium chloride is added, compared to Comparative Embodiment 2A, its concentration in the range of 200–1000 ppm can effectively enhance the SiN polishing rate without significantly suppressing the TEOS polishing rate. However, when the concentration is further increased to 1500 ppm, the SiN polishing rate becomes suppressed. When betaine is added at 500 or 1000 ppm, the SiN polishing rate is also enhanced while the TEOS rate remains largely unchanged. In summary, unlike polyquaternary compounds, the addition of quaternary ammonium compounds effectively boosts the SiN polishing rate without significantly inhibiting the TEOS polishing rate.

Embodiment 3

The polishing solutions of the corresponding comparative and experimental embodiments were prepared by dissolving the components according to the ratios in Table 4 into deionized water, with deionized water added to reach 100 wt%, and the pH was adjusted to different values using HNO₃ or KOH. Each prepared polishing solution was then used for chemical mechanical polishing (CMP) on blank TEOS and SiN wafers, and the polishing performance was compared, with results presented in Table 4.

Polishing conditions: The polishing tool was a Mirra polisher with an IC1000 pad. The platen and head rotation speeds were 93 rpm and 87 rpm, respectively. The polishing pressure was 2.0 psi, the slurry flow rate was 150 mL/min, and the polishing time was 60 seconds. The film thickness measurement was performed using a NanoSpec film thickness measurement system.

Table 4: Effect of adding quaternary ammonium compounds on polishing performance under different pH conditions

Polishing solution	Cerium oxide (wt%)	Quaternary Ammonium Compound		pH	2.0 psi	
		Specific Compounds	Concentration (ppm)		SiN RR (Å/min)	TEOS RR (Å/min)
Comparative Embodiment 3A	0.1%			3.5	28	864
Comparative Embodiment 3B	0.1%	Tetrabutylammonium Hydroxide	200	3.5	24	994
Comparative Embodiment 3C	0.1%	Benzyltriethylammonium Chloride	1000	3.5	12	68
Comparative Embodiment 3D	0.1%			4.0	392	3085
Embodiment 3E	0.1%	Tetrabutylammonium Hydroxide	200	4.0	628	2846
Embodiment 3F	0.1%	Benzyltriethylammonium Chloride	1000	4.0	574	3059
Comparative Embodiment 3G	0.1%			4.5	458	2691

Embodiment 3H	0.1%	Tetrabutylammonium Hydroxide	200	4.5	798	2796
Embodiment 3I	0.1%	Benzyltriethylammonium Chloride	1000	4.5	1304	2441
Comparative Embodiment 3J	0.1%			6.0	566	2513
Embodiment 3K	0.1%	Tetrabutylammonium Hydroxide	200	6.0	682	2707
Embodiment 3L	0.1%	Benzyltriethylammonium Chloride	1000	6.0	646	2740

Table 4 shows the effect of adding tetrabutylammonium hydroxide or benzyltriethylammonium chloride on the polishing performance of ceria-based slurries under different pH conditions. The results of Comparative Embodiments 3A–3C indicate that at pH 3.5, the SiN polishing rate is suppressed. When the pH is adjusted to 4.0 or 4.5, the addition of tetrabutylammonium hydroxide or benzyltriethylammonium chloride effectively enhances the SiN polishing rate. As the pH increases further to 6.0, the enhancement effect of these compounds on the SiN polishing rate gradually weakens. In summary, using tetrabutylammonium hydroxide and benzyltriethylammonium chloride as examples, they can boost the SiN polishing rate within the pH range of 4.0 to 6.0.

In summary, this invention adds a quaternary ammonium compound to the ceria-based polishing solution, effectively enhancing the polishing rate for SiN while having almost no impact on the TEOS polishing rate, thereby overcoming the issue associated with polyquaternary compounds that typically suppress the TEOS polishing rate.

It should be noted that the embodiments of this invention are preferred implementations and do not constitute any form of limitation on the invention. Any skilled person in the field may modify or alter the disclosed technical content into equivalent effective embodiments. However, any modification, equivalent variation, or adaptation made to the above embodiments based on the technical essence of this invention, without departing from the scope of the invention's technical solution, still falls within the protection scope of this invention.

CLAIMS

1. A chemical-mechanical polishing composition comprising: water; ceria abrasive particles; a quaternary ammonium compound.
2. The chemical-mechanical polishing composition according to claim 1, wherein the quaternary ammonium compound is selected from one or more of tetrabutylammonium hydroxide, benzyltriethylammonium chloride, betaine.
3. The chemical-mechanical polishing composition according to claim 1, wherein the concentration of the quaternary ammonium compound ranges from 200 ppm to 1000 ppm.
4. The chemical-mechanical polishing composition according to claim 1, wherein the mass percentage of the ceria abrasive particles ranges from 0.1 wt% to 0.5 wt%.
5. The chemical-mechanical polishing composition according to claim 1, wherein the polishing composition further comprises a pH adjuster, which is selected from inorganic acids or inorganic bases.
6. The chemical-mechanical polishing composition according to claim 5, wherein the pH adjuster is HNO_3 or KOH .
7. The chemical-mechanical polishing composition according to claim 1, wherein the pH of the polishing composition ranges from 4.0 to 6.0.