

SPECIFICATIONS

A CHEMICAL MECHANICAL POLISHING COMPOSITION

TECHNICAL FIELD

The present invention relates to a ceria chemical-mechanical polishing solution, and more particularly, to a chemical-mechanical polishing composition with trivalent transition metal ions as an additive effective to achieve different polishing rates SiN/TEOS selectivities.

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 preferentially polish silicon nitride (SiN) over oxide, i.e., exhibiting a selectivity opposite to that of traditional STI processes. This helps minimize defects in the oxide lines formed on the substrate surface. Therefore, developing a polishing slurry capable of enhancing the SiN polishing rate is a critical challenge. This invention addresses this issue by adding a trivalent transition metal ion to the ceria-based slurry, which effectively increases the SiN polishing rate. Moreover, by adjusting the concentration of the preferred trivalent transition metal ion, different SiN/TEOS selectivity ratios can be achieved.

DESCRIPTION

Disclosed is a chemical-mechanical polishing composition comprising: water; cerium oxide abrasive particles; a trivalent transition metal ion compound.

Further, the chemical-mechanical polishing composition wherein the trivalent transition metal ion is iron (III), lanthanum (III), or cerium (III).

Further, the trivalent transition metal ion compound is iron (III) nitrate nonahydrate, lanthanum (III) nitrate hexahydrate, or cerium (III) nitrate hexahydrate.

Further, the concentration of the trivalent transition metal ion compound ranges from 1 to 100 ppm.

Further, the cerium oxide abrasive particles are present in a mass percent content ranging from 0.02% to 0.4%.

Further, the pH value range of the polishing composition is 4.0–9.0.

Further, the polishing composition comprises a pH adjuster, which is selected from inorganic acids or inorganic bases, preferably HNO₃ or KOH.

This invention adds iron(III) nitrate nonahydrate, a preferred trivalent transition metal ion compound, to the ceria-based polishing slurry, which can effectively enhance the SiN polishing rate under various pressures (1.5 psi, 2.0 psi, and 3.0 psi), concentrations (1–100 ppm), and pH values (4.0–9.0), demonstrating a wide processing window. Moreover, by adjusting the amount of iron(III) nitrate nonahydrate added, different SiN/TEOS selectivity ratios can be achieved. Additionally, under 3.0 psi, lanthanum(III) nitrate hexahydrate and cerium(III) nitrate hexahydrate also effectively increase the SiN polishing rate within the concentration range of 20–100 ppm and pH range of 4.0–9.0.

EMBODIMENTS

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 a pH adjuster (HNO₃ 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 slurries for comparative and experimental embodiments

Polishing solution	cerium oxide (wt%)	Trivalent Transition Metal Ion Compounds	
		Specific compounds	Concentration (ppm)
Comparative Embodiment 1A	0.1%	/	/
Comparative Embodiment 1B	0.2%	/	/
Comparative Embodiment 1C	0.1%	Aluminum(III) Nitrate Nonahydrate	100
Embodiment 1D	0.1%	Lanthanum(III) Nitrate Hexahydrate	100
Embodiment 1E	0.1%	Iron(III) Nitrate Nonahydrate	50
Embodiment 1F	0.2%	Cerium(III) Nitrate Hexahydrate	80

To further measure the polishing performance of the polishing solutions in each of the Embodiments and Comparative Embodiments, the polishing rates of the polishing solutions on TEOS and SiN wafers were measured at different polishing pressures of 1.5 psi, 2.0 psi, or 3.0 psi, respectively, and the results are shown in Table 2.

Polishing conditions: The polishing tool was an Ebara F-REX-300X with an IK4350 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 slurry flow rate was 300 mL/min, and the polishing time was 60 seconds.

Polishing procedure: The prepared polishing slurries were separately used to polish blank TEOS and SiN wafers using the aforementioned 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 slurry is the average of the 49 measured points.

Table 2: Polishing rates of comparative and experimental embodiments under different polishing pressures

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	313	928	482	1041	794	1764
Comparative Embodiment 1B	219	894	338	1023	534	1308
Comparative Embodiment 1C	-2	502	9	455	-2	426
Embodiment 1D	176	485	251	608	1000	1557
Embodiment 1E	627	633	1072	906	1983	1285
Embodiment 1F	10	676	7	820	1212	1200

From the polishing results of Comparative Embodiments 1A and 1C, it can be observed that adding aluminum(III) nitrate nonahydrate significantly suppresses the SiN polishing rate. In contrast, the results of Comparative Embodiment 1A and Embodiments 1D and 1E show that under a polishing pressure of 3.0 psi, the addition of lanthanum(III) nitrate hexahydrate or iron(III) nitrate nonahydrate enhances the SiN polishing rate. However, under lower polishing pressures (1.5 psi or 2.0 psi), the addition of lanthanum(III) nitrate hexahydrate reduces the SiN polishing rate, whereas iron(III) nitrate nonahydrate still significantly boosts the SiN

polishing rate—by more than two times.

From the polishing results of Comparative Embodiment 1B and Embodiment 1F, it can be observed that under a pressure of 3.0 psi, cerium(III) nitrate hexahydrate can also enhance the SiN polishing rate by more than two times. However, at lower pressures (1.5 psi or 2.0 psi), it significantly suppresses the SiN polishing rate. In summary, adding trivalent transition metal ions to the ceria-based polishing slurry can boost the SiN polishing rate under certain pressure conditions. Notably, compared to lanthanum(III) or cerium(III), iron(III) nitrate nonahydrate in the embodiments exhibits a wider pressure processing window, effectively promoting the SiN polishing rate at 1.5 psi, 2.0 psi, and 3.0 psi.

Embodiment 2

The polishing slurries of Comparative Embodiment 2A and Embodiments 2B–2H 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 HNO_3 or KOH. Each prepared slurry 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 an Ebara F-REX-300X with an IK4350 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 300 mL/min, and the polishing time was 60 seconds. Film thickness measurements were performed using a NanoSpec film thickness measurement system.

Table 3: Effect of adding different concentrations of iron(III) nitrate nonahydrate on polishing performance

Polishing solution	cerium oxide (wt%)	Trivalent Transition Metal Ion Compounds		2.0 psi		
		Specific compounds	Concentration (ppm)	SiN RR (Å/min)	TEOS RR (Å/min)	SiN/TEOS Selectivity Ratio
Comparative Embodiment 2A	0.1%	/	/	482	1041	0.5
Embodiment 2B	0.1%	Iron(III) Nitrate Nonahydrate	1	588	967	0.6
Embodiment 2C	0.1%	Iron(III) Nitrate Nonahydrate	5	704	952	0.7
Embodiment 2D	0.1%	Iron(III) Nitrate Nonahydrate	10	796	939	0.8
Embodiment 2E	0.1%	Iron(III) Nitrate Nonahydrate	30	1002	933	1.1
Embodiment 2F	0.1%	Iron(III) Nitrate Nonahydrate	50	1072	906	1.2
Embodiment 2G	0.1%	Iron(III) Nitrate Nonahydrate	60	1006	753	1.3
Embodiment 2H	0.1%	Iron(III) Nitrate Nonahydrate	100	720	190	3.8

Table 3 shows the effect of adding different concentrations of iron(III) nitrate nonahydrate on the polishing performance of ceria-based slurries. It can be observed that even trace amounts (1 ppm, 5 ppm) of iron(III) nitrate nonahydrate can enhance the SiN polishing rate. As the concentration increases, the SiN rate gradually improves, with the optimal concentration at 50 ppm. When the concentration reaches 100 ppm, the SiN polishing rate in Embodiment 2H remains significantly higher than that of Comparative Embodiment 2A, indicating a broad effective concentration range for iron(III) nitrate nonahydrate. Compared to Comparative Embodiment 2A, the TEOS polishing rate in Embodiment 2H is notably suppressed, resulting in a significantly improved SiN/TEOS selectivity ratio. By adjusting the amount of iron(III) nitrate nonahydrate added, different SiN/TEOS selectivity ratios can be achieved.

Table 4 shows the effect of adding different concentrations of cerium(III) nitrate hexahydrate or lanthanum(III) nitrate hexahydrate on the polishing performance of ceria-based slurries. The polishing slurries 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 4.5 using HNO_3 or KOH. Each prepared slurry 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 3.0 psi, the slurry flow rate was 150 mL/min, and the polishing time was 60 seconds. Film thickness measurements were performed using a NanoSpec film thickness measurement system.

Table 4: Effect of adding different concentrations of cerium(III) nitrate hexahydrate or lanthanum(III) nitrate hexahydrate on polishing performance

Polishing solution	cerium oxide (wt%)	Trivalent Transition Metal Ion Compounds		3.0 psi		
		Specific compounds	Concentration (ppm)	SiN RR (Å/min)	TEOS RR (Å/min)	SiN/TEOS Selectivity Ratio
Comparative Embodiment 3A	0.2%	/	/	534	1308	0.4
Embodiment 3B	0.2%	Cerium(III) Nitrate Hexahydrate	20	722	1276	0.6
Embodiment 3C	0.2%	Cerium(III) Nitrate Hexahydrate	40	933	1357	0.7
Embodiment 3D	0.2%	Cerium(III) Nitrate Hexahydrate	80	1212	1200	1.0
Embodiment 3E	0.2%	Cerium(III) Nitrate Hexahydrate	100	824	871	0.9
Comparative Embodiment 3F	0.2%	Cerium(III) Nitrate Hexahydrate	300	440	751	0.6
Comparative Embodiment 3G	0.1%	/	/	568	1571	0.4
Embodiment 3H	0.1%	Lanthanum(I II) Nitrate Hexahydrate	20	762	1119	0.7
Embodiment 3I	0.1%	Lanthanum(I II) Nitrate Hexahydrate	100	958	1232	0.8
Comparative Embodiment 3J	0.1%	Lanthanum(I II) Nitrate Hexahydrate	200	120	878	0.1

From Table 4, it can be observed that as the concentration of cerium(III) nitrate hexahydrate increases from 20 ppm to 80 ppm, the SiN polishing rate gradually increases. When the concentration reaches 100 ppm, the SiN polishing rate in Embodiment 3E decreases

compared to Embodiment 3D, but remains higher than that of Comparative Embodiment 3A. When the concentration further increases to 300 ppm, the SiN polishing rate in Embodiment 3F is significantly lower than that of Comparative Embodiment 3A. When lanthanum(III) nitrate hexahydrate is added, the SiN polishing rate gradually increases as its concentration rises from 20 ppm to 100 ppm. However, when the concentration increases further to 200 ppm, the SiN polishing rate is notably lower compared to Comparative Embodiment 3G. This indicates that under a polishing pressure of 3.0 psi, both cerium(III) nitrate hexahydrate and lanthanum(III) nitrate hexahydrate can effectively enhance the SiN polishing rate within the concentration range of 20–100 ppm.

Embodiment 3

The polishing slurries of the corresponding comparative and experimental embodiments were prepared by dissolving the components according to the ratios in Table 5 and Table 6 into deionized water, with deionized water added to reach 100 wt%, and the pH was adjusted to different values using HNO_3 or KOH. Each prepared slurry 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 or 3.0 psi, the slurry flow rate was 150 mL/min, and the polishing time was 60 seconds. Film thickness measurements were performed using a NanoSpec film thickness measurement system.

Table 5: Effect of adding iron(III) nitrate nonahydrate on polishing performance under different pH conditions

Polishing solution	cerium oxide (wt%)	Trivalent Transition Metal Ion Compounds		pH	2.0 psi	
		Specific compounds	Concentration (ppm)		SiN (Å/min)	RR (Å/min)
Comparative Embodiment 4A	0.1%			3.5	8	441
Comparative Embodiment 4B	0.1%	Iron(III) Nitrate Nonahydrate	50	3.5	14	36
Comparative Embodiment 4C	0.1%			4.0	580	1031
Embodiment 4D	0.1%	Iron(III) Nitrate Nonahydrate	50	4.0	780	215
Comparative Embodiment 4E	0.1%			4.5	556	1131
Embodiment 4F	0.1%	Iron(III) Nitrate Nonahydrate	50	4.5	716	351
Comparative Embodiment 4G	0.1%			6.5	636	1393
Embodiment 4H	0.1%	Iron(III) Nitrate Nonahydrate	50	6.5	802	238
Comparative Embodiment 4I	0.1%			9.0	532	2343
Embodiment 4J	0.1%	Iron(III) Nitrate Nonahydrate	50	9.0	876	2241

Table 5 shows the effect of adding 50 ppm iron(III) nitrate nonahydrate on the polishing performance of ceria-based slurries under different pH conditions. It can be observed that within the pH range of 4.0–9.0, the addition of iron(III) nitrate nonahydrate effectively enhances the SiN polishing rate. The results of Comparative Embodiments 4A and 4B indicate that at pH 3.5, the SiN polishing rate is suppressed regardless of whether iron(III) nitrate nonahydrate is added. When the pH is adjusted to 4.0–6.5, the additive not only increases the

SiN polishing rate but also significantly reduces the TEOS polishing rate. When the pH is further increased to alkaline conditions (9.0), the addition of iron(III) nitrate nonahydrate still significantly boosts the SiN polishing rate, while having minimal impact on the TEOS polishing rate.

Table 6: Effect of adding cerium(III) nitrate hexahydrate or lanthanum(III) nitrate hexahydrate on polishing performance under different pH conditions

Polishing solution	cerium oxide (wt%)	Trivalent Transition Metal Ion Compounds		pH	3.0 psi	
		Specific compounds	Concentration (ppm)		SiN RR (Å/min)	TEOS RR (Å/min)
Comparative Embodiment 5A	0.2%	Cerium(III) Nitrate Hexahydrate	50	3.5	8	1018
Comparative Embodiment 5B	0.4%			4.0	418	765
Embodiment 5C	0.4%	Cerium(III) Nitrate Hexahydrate	40	4.0	780	820
Comparative Embodiment 5D	0.2%			4.5	562	933
Embodiment 5E	0.2%	Cerium(III) Nitrate Hexahydrate	40	4.5	684	831
Comparative Embodiment 5F	0.02%			4.5	452	1964
Embodiment 5G	0.02%	Cerium(III) Nitrate Hexahydrate	50	4.5	652	2079
Comparative Embodiment 5H	0.2%			5.5	128	3293
Embodiment 5I	0.2%	Cerium(III) Nitrate Hexahydrate	50	5.5	256	2481
Comparative Embodiment 5J	0.1%			9.0	616	2687
Embodiment 5K	0.1%	Cerium(III) Nitrate Hexahydrate	50	9.0	732	2965
Comparative Embodiment 5L	0.1%			4.0	856	1198
Embodiment 5M	0.1%	Lanthanum(III) Nitrate Hexahydrate	100	4.0	942	565

Comparative Embodiment 5N	0.1%			4.5	762	1119
Embodiment 5O	0.1%	Lanthanum(III) Nitrate Hexahydrate	100	4.5	958	1232
Comparative Embodiment 5P	0.1%			9.0	616	2687
Embodiment 5Q	0.1%	Lanthanum(III) Nitrate Hexahydrate	100	9.0	1042	836

Table 6 shows the effect of adding cerium(III) nitrate hexahydrate or lanthanum(III) nitrate hexahydrate on the polishing performance of ceria-based slurries under different pH conditions. Similarly, at pH 3.5, the SiN polishing rate is suppressed. However, within the pH range of 4.0–9.0, the addition of cerium(III) nitrate hexahydrate or lanthanum(III) nitrate hexahydrate can enhance the SiN polishing rate to some extent.

In summary, this invention adds iron(III) nitrate nonahydrate to the ceria-based polishing slurry, which can effectively enhance the SiN polishing rate under various pressures (1.5 psi, 2.0 psi, and 3.0 psi), concentration ranges (1–100 ppm), and pH values (4.0–9.0), demonstrating a wide operational window. Moreover, by adjusting the amount of iron(III) nitrate nonahydrate added, different SiN/TEOS selectivity ratios can be achieved. Additionally, under 3.0 psi, lanthanum(III) nitrate hexahydrate and cerium(III) nitrate hexahydrate also effectively increase the SiN polishing rate within the concentration range of 20–100 ppm and pH range of 4.0–9.0.

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 trivalent transition metal ion compound.
2. The chemical-mechanical polishing composition according to claim 1, the trivalent transition metal ion being iron (III), lanthanum (III), or cerium (III).
3. The chemical-mechanical polishing composition according to claim 1, the trivalent transition metal ion compound is iron (III) nitrate nonahydrate, lanthanum (III) nitrate hexahydrate, or cerium (III) nitrate hexahydrate.
4. The chemical-mechanical polishing composition according to claim 1, concentration of trivalent transition metal ion compound being in range of 1-100 ppm.
5. The chemical-mechanical polishing composition according to claim 1, the ceria abrasive particles have a mass percent content in a range of 0.02% to 0.4%.
6. The chemical-mechanical polishing composition according to claim 1, the polishing composition having a pH in the range of 4.0-9.0.
7. The chemical-mechanical polishing composition according to claim 1, comprising a pH-adjusting agent selected from an inorganic acid or an inorganic base.
8. The chemical-mechanical polishing composition according to claim 7, wherein the pH-adjusting agent is HNO₃ or KOH.