

**CHEMICAL MECHANICAL POLISHING SLURRY COMPOSITION FOR
POLISHING PHASE-CHANGE MEMORY DEVICE AND METHOD FOR
POLISHING PHASE-CHANGE MEMORY DEVICE USING THE SAME**

CROSS-REFERENCE TO RELATED APPLICATIONS

5 This non-provisional application claims priority under 35 USC Section 119 from Korean Patent Application No. 10-2007-0065872, filed on June 29, 2007, and Korean Patent Application No. 10-2007-0065874, filed on June 29, 2007, the entire disclosure of each of which is hereby incorporated by reference.

10 **FIELD OF THE INVENTION**

The present invention relates to a slurry composition for polishing a phase-change memory device used in a semiconductor manufacturing process. More specifically, the present invention relates to a slurry composition for chemical mechanical polishing (CMP) of a metal alloy or a chalcogenide included in a phase-
15 change memory device, and a method for polishing a phase-change memory device using the slurry composition.

BACKGROUND OF THE INVENTION

Demand for semiconductor memories has increased with expanding global
20 markets for electronic devices, such as digital cameras, camcorders, MP3 players, digital multimedia broadcasting (DMB) receivers, navigation systems and mobile phones. In addition, there has been an increasing demand for high-capacity memories that are driven at high speed and reduced power consumption in terms of performance characteristics as compared to conventional memories. Under such
25 circumstances, considerable research efforts have been made in developing next-generation memories that include the advantages and features inherent to dynamic random access memories (DRAMs), static random access memories (SRAMs) and flash memories. Phase-change RAMs (PRAMs), magnetoresistive RAMs (MRAMs), ferroelectric RAMs (FeRAMs) and polymer memories are currently
30 considered next-generation memories. Of these, PRAMs possess the advantages of

conventional highly integrated DRAMs, high-speed SRAMs and non-volatile NAND flash memories, and have excellent characteristics in terms of compatibility with conventional integration processes of complementary metal-oxide-semiconductor (C-MOS) field effect transistors (FETs). Based on these advantages, PRAMs have attracted more and more attention in recent years because of the greatest possibility of successful commercialization.

Since a paper reported by S. Lai (Intel) and T. Lowrey (Ovonyx) at the International Electronic Device Meeting (IEDM) in 2001, extensive research and development have been conducted on phase-change RAMs (PRAMs). Phase-change RAMs are non-volatile memories that use materials capable of inducing a reversible phase change between crystalline (low electrical resistance) and amorphous (high electrical resistance) phases due to Joule heating generated in response to an applied current or voltage to write data.

Metal alloys and chalcogenides are currently used as representative phase-change materials of PRAMs. Particularly, the composition of $\text{Ge}_x\text{Sb}_y\text{Te}_z$ (GST), a chalcogenide, is now being investigated.

In CMP processes for phase-change materials of PRAM devices that are currently being developed, silicon oxide (SiO_2) is used to form polish stop layers. Polishing uniformity and surface imperfections (*e.g.*, dishing and erosion) during polishing of patterned wafers are greatly affected by some processing factors, *e.g.*, polishing and etch rates on phase-change materials, polishing uniformity of silicon oxide films and polishing selectivity between phase-change materials and silicon oxide films.

On the other hand, slurries for polishing aluminum, copper, tungsten and other metal wires are mainly employed in semiconductor manufacturing processes. Since these metal layer materials are composed of a single element, unlike phase-change materials of PRAM devices, they induce no phase change. Therefore, the conventional metal materials cannot be used for PRAM devices and cause a significant difference in layer characteristics.

Depending on the choice of an oxidizing agent, an abrasive, and other

useful additives, a CMP slurry for polishing metal wires can be tailored to provide effective polishing on metal layers at desired polishing rates while minimizing surface imperfections, defects, corrosion, and erosion. Furthermore, the polishing slurry may be used to provide controlled polishing selectivities to other thin-film materials, such as titanium, titanium nitride, tantalum, tantalum nitride, oxides and the like.

Unlike conventional metal layers composed of a single element, such as copper (Cu) or tungsten (W), layers of phase-change memory devices to be polished are composed of materials consisting of particular elements, such as sulfur (S), selenium (Se), germanium (Ge), antimony (Sb), tellurium (Te), silver (Ag), indium (In), tin (Sn), gallium (Ga), and the like, in a specified ratio to undergo a reversible phase change between crystalline and amorphous phases. Since the characteristics of the materials to be polished are different from those of conventional metal layer materials, there exists a strong need to develop novel polishing compositions.

Ideal slurry compositions for polishing phase-change materials of phase-change memories (PRAMs) should meet the following requirements: i) the phase-change materials must be etched and polished at high rates; ii) the polishing selectivity between the phase-change materials and polish stop layers must be high; iii) dishing, erosion, pattern non-uniformity, imperfections (*e.g.*, scratches, defects and corrosion), and the like must be minimized; and iv) there must be no change in the composition and phase of elements constituting the surface of the phase-change materials after polishing.

SUMMARY OF THE INVENTION

The present invention provides a slurry composition for chemical mechanical polishing (CMP) of a phase-change memory device that can polish a phase-change memory device at a high rate, can achieve high polishing selectivity between a phase-change memory material and a polish stop layer (*e.g.*, a silicon oxide film), and can minimize the occurrence of processing imperfections (*e.g.*,

dishing and erosion) to provide a high-quality polished surface; and a method for polishing a phase-change memory device using the CMP slurry composition.

The present invention further provides a slurry composition for chemical mechanical polishing of a phase-change memory device that can cause substantially no change in the composition or phase of a phase-change material before and after polishing, can minimize the occurrence of surface imperfections (*e.g.*, scratches, defects, corrosion and polishing residues) to provide a clean polished surface, and can contain very small amounts of metal impurities to cause few or no environmental pollution problems after being disposed; and a method for polishing a phase-change memory device using the CMP slurry composition.

In accordance with one aspect of the present invention, there is provided a slurry composition for chemical mechanical polishing (CMP) of a phase-change memory device which comprises deionized water, a nitrogenous compound, and one or more additional components that can provide desired CMP characteristics to the slurry composition, such as abrasive particles, an oxidizing agent, or a combination of abrasive particles and an oxidizing agent.

The phase-change memory device can include a metal alloy or a chalcogenide.

The phase-change memory device can include at least one compound selected from InSe, Sb₂Te₃, GeTe, Ge₂Sb₂Te₅, InSbTe, GaSeTe, SnSb₂Te₄, InSbGe, AgInSbTe, (GeSn)SbTe, GeSb(SeTe) and Te₈₁Ge₁₅Sb₂S₂.

The nitrogenous compound can include at least one compound selected from an aliphatic amine, an aromatic amine, an ammonium salt and an ammonium base.

The aliphatic amine can be a primary amine, secondary amine or tertiary amine.

The aliphatic amine can have at least one alkyl or alcohol group.

The aliphatic amine can have at least one substituent containing one to seven carbon atoms.

The aliphatic amine can include a heterocyclic compound.

The heterocyclic compound can include a piperazine compound.

The ammonium salt or ammonium base can include at least one compound selected from tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, and salts derived therefrom.

5 The nitrogenous compound can be present in the slurry composition in an amount of about 0.001 to about 5% by weight, based on the total weight of the slurry composition.

 In one embodiment of this aspect of the invention, the slurry compositions can include abrasive particles. The abrasive particles can include particles of at least
10 one metal oxide selected from the group consisting of silica (SiO_2), alumina (Al_2O_3), ceria (CeO_2) and zirconia (ZrO_2), or synthetic polymer particles.

 The abrasive particles can have an average primary particle diameter of about 1 to about 200 nm and an average specific surface area of about 10 to about 500 m^2/g .

15 The abrasive particles can be present in the slurry composition in an amount of about 0.01 to about 30% by weight, based on the total weight of the slurry composition.

 In another embodiment of this aspect of the invention, the CMP slurry composition can include an oxidizing agent.

20 The oxidizing agent can have a higher standard electrochemical redox potential than a phase-change material to be polished.

 The oxidizing agent can include a per-compound, iron or an iron compound.

 The per-compound can be a compound containing one or more peroxy groups (-O-O-) or a compound containing an element in its highest oxidation state.
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 The compound containing one or more peroxy groups (-O-O-) can include at least one compound selected from hydrogen peroxide, urea hydrogen peroxide, percarbonate, benzoyl peroxide, peracetic acid, di-*t*-butyl peroxide, monopersulfate (SO_5), dipersulfate (S_2O_8), and salts derived therefrom.

30 The compound containing an element in its highest oxidation state can

include at least one compound selected from periodic acid, perbromic acid, perchloric acid, perboric acid, permanganate, and salts derived therefrom.

The iron or iron compound can include a metal iron or a compound containing iron in its molecular structure.

5 In exemplary embodiments of the invention, the oxidizing agent can include at least one compound selected from hydrogen peroxide, monopersulfates, dipersulfates, ionic iron compounds, and iron chelate compounds.

 The oxidizing agent can be present in the slurry composition of the invention in an amount of about 0.01 to about 10% by weight, based on the total
10 weight of the slurry composition.

 In yet another embodiment of this aspect of the invention, the CMP slurry composition can include both abrasive particles and an oxidizing agent.

 The slurry composition can have a pH of about 2 to about 10.

 The CMP slurry composition can further comprise a pH-adjusting agent.

15 The pH-adjusting agent can include at least one acid selected from nitric acid, phosphoric acid, sulfuric acid, hydrochloric acid, and organic carboxylic acids having a pKa of 6 or less.

 In accordance with another aspect of the present invention, there is provided a method for polishing a phase-change memory device using the CMP
20 slurry composition.

 A phase-change memory device can be fabricated by applying an insulating material to a semiconductor wafer to form an insulating layer, planarizing the insulating layer, patterning the planar insulating layer, and applying a phase-change material to the patterned insulating layer to form a phase-change material layer; and
25 the CMP slurry composition can be brought into contact with the phase-change material layer to polish the phase-change material layer until the insulating layer is exposed.

 The phase-change material layer can be polished by applying the CMP slurry composition to a rotating polishing pad and bringing the polishing pad into
30 contact with the phase-change material layer under predetermined pressure

conditions to polish portions of the phase-change material layer by a frictional force.

In yet another aspect of the present invention, there is provided a phase-change memory device polished by the polishing method.

5 DETAILED DESCRIPTION OF THE INVENTION

The present invention now will be described more fully hereinafter in the following detailed description of the invention, in which some, but not all embodiments of the invention are described. Indeed, this invention may be embodied in many different forms and should not be construed as limited to the
10 embodiments set forth herein; rather, these embodiments are provided so that this disclosure will satisfy applicable legal requirements.

The present invention provides a chemical mechanical polishing (CMP) slurry composition for polishing a phase-change memory device which comprises deionized water, a nitrogenous compound, and optionally one or more additional
15 components that can provide desired CMP characteristics to the slurry composition, such as abrasive particles, an oxidizing agent, or a combination of abrasive particles and an oxidizing agent. Accordingly, in exemplary embodiments of the invention, the CMP slurry composition can include deionized water and a nitrogenous compound. In other exemplary embodiments of the invention, the CMP slurry
20 composition can include deionized water; a nitrogenous compound; and abrasive particles. In other exemplary embodiments of the invention, the CMP slurry composition can include deionized water; a nitrogenous compound; and an oxidizing agent. In yet other exemplary embodiments of the invention, the CMP slurry composition can include deionized water; a nitrogenous compound; abrasive
25 particles; and an oxidizing agent.

The phase-change memory device typically includes a metal alloy or a chalcogenide as a phase-change material that undergoes a reversible phase change between crystalline and amorphous phases.

Examples of suitable phase-change materials for use in the present
30 invention include, but are not limited to: binary compounds, such as InSe, Sb₂Te₃

and GeTe; ternary compounds, such as $\text{Ge}_2\text{Sb}_2\text{Te}_5$, InSbTe , GaSeTe , SnSb_2Te_4 and InSbGe ; and quaternary compounds, such as AgInSbTe , $(\text{GeSn})\text{SbTe}$, $\text{GeSb}(\text{SeTe})$ and $\text{Te}_{81}\text{Ge}_{15}\text{Sb}_2\text{S}_2$.

The nitrogenous compound is a material that is effective in uniformly and rapidly polishing the phase-change material upon CMP processing and that is capable of reducing the occurrence of erosion and dishing in a pattern. The nitrogenous compound can be an aliphatic amine, an aromatic amine, an ammonium salt or an ammonium base, or a combination thereof. The nitrogenous compound can be one miscible with water.

The aliphatic amine may be a primary amine, secondary amine or tertiary amine. A mixture of two or more aliphatic amines may also be used.

The aliphatic amine may be unsubstituted or substituted and in exemplary embodiments can have at least one alkyl or alcohol group. An alkyl group can be useful in terms of polishing rate on the phase-change material. The aliphatic amine can have at least one substituent containing one to seven carbon atoms.

The aliphatic amine can be a heterocyclic compound such as piperazine. A combination of two or more aliphatic amines may be used.

There is no particular restriction on the kind of the ammonium salt or ammonium base, and at least one compound selected from tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide and salts derived therefrom, and well as combinations thereof, can be used as the ammonium salt or ammonium base.

The nitrogenous compound can be present in the slurry composition in an amount of about 0.001 to about 5% by weight, for example about 0.005 to about 3% by weight, and as another example about 0.01 to about 1% by weight, based on the total weight of the slurry composition. The amount of the nitrogenous compound used can be determined taking into consideration the stimulatory effects of the nitrogenous compound on the polishing of the phase-change material, uniform polishing rate on the phase-change material, desirable surface characteristics and optimal pH maintenance.

The abrasive particles may be particles of at least one metal oxide selected from the group consisting of silica (SiO_2), alumina (Al_2O_3), ceria (CeO_2) and zirconia (ZrO_2), and the like, or synthetic polymer particles, or combinations thereof.

5 As the synthetic polymer particles, any known polymer particles may be suitably selected according to the kind of the device to be polished. For example, such polymer particles include abrasive particles composed of polymers only, abrasive particles composed of polymer-coated metal oxides, and abrasive particles composed of metal oxide-coated polymers.

10 The abrasive particles can have an average primary particle diameter of about 1 to about 200 nm and an average specific surface area of about 10 to about 500 m^2/g . In exemplary embodiments of the invention, to provide certain dispersion stability and polishing performance, the abrasive particles can have an average primary particle diameter of about 5 to about 100 nm, for example about 10 to about
15 80 nm, and an average specific surface area of about 30 to about 300 m^2/g , for example about 40 to about 250 m^2/g .

The abrasive particles can be present in the slurry composition in an amount of about 0.01 to about 30% by weight, for example about 0.05 to about 20% by weight, and as another example about 0.1 to about 10% by weight, based on the
20 total weight of the slurry composition.

The oxidizing agent can oxidize the surface layer of the phase-change material to an oxide or ions to facilitate the removal of the surface layer and can function to uniformly polish portions of the phase-change material within a pattern region until a polish stop layer (e.g., a silicon oxide film) is exposed to improve the
25 surface roughness of the pattern. In addition, the use of the oxidizing agent can facilitate the removal of residues of the phase-change material present in the polish stop layer, thereby enabling more uniform polishing.

Any oxidizing agent may be used in the present invention so long as it has a higher standard electrochemical redox potential than the phase-change material to be
30 polished. The oxidizing agent can be, for example, a per-compound, iron or an iron

compound. The oxidizing agent may also be combined with one or more other oxidizing agents.

The term 'per-compound' as used herein refers to a compound containing one or more peroxy groups (-O-O-) or a compound containing an element in its highest oxidation state. Organic and inorganic per-compounds may be used in the present invention.

Examples of compounds containing one or more peroxy groups (-O-O-) include, but are not limited to, hydrogen peroxide, urea hydrogen peroxide, percarbonate, benzoyl peroxide, peracetic acid, di-*t*-butyl peroxide, monopersulfate (SO₅), dipersulfate (S₂O₈), and salts derived therefrom.

Examples of compounds containing an element in its highest oxidation state include, but are not limited to, periodic acid, perbromic acid, perchloric acid, perboric acid, permanganate, and salts derived therefrom.

The iron or iron compound may be metal iron or a compound containing iron in its molecular structure.

Non-limiting examples of suitable oxidizing agents for use in the present invention include hydrogen peroxide, monopersulfates, dipersulfates, ionic iron compounds, and iron chelate compounds. As used herein, the hydrogen peroxide is defined to include adducts obtained by previously reacting hydrogen peroxide with one or more other materials (*e.g.*, a radical generating catalyst).

The hydrogen peroxide or its adduct can cause no environmental pollution and advantageously can function to clean the surface state of the phase-change material without any change in the composition of the phase-change material before and after polishing. The use of a monopersulfate, a dipersulfate, an ionic iron compound or an iron chelate compound as the oxidizing agent can be advantageous in that the phase-change material can be polished at a high rate.

The oxidizing agent may be present in the slurry compositions in an amount of about 0.01 to about 10% by weight, for example about 0.05 to about 5% by weight, and as another example about 0.1 to about 2% by weight, based on the total weight of the slurry composition. An amount of the oxidizing agent within these

ranges can be useful to maintain optimal etching of the phase-change material.

The pH of the slurry composition can be adjusted to about 2 to about 10, for example about 2 to about 9, and as another example about 2 to about 5. The slurry composition of the present invention can further comprise a pH-adjusting agent to
5 adjust the pH of the slurry composition to the range defined above. The pH-adjusting agent can include an inorganic acid selected from nitric acid, phosphoric acid, sulfuric acid and hydrochloric acid, or an organic carboxylic acid having a pKa of 6 or less, as well as combinations thereof.

The present invention also provides a method for polishing a phase-change
10 memory device using the CMP slurry composition.

In exemplary embodiments of the present invention, the phase-change memory device can be fabricated by applying an insulating material to a semiconductor wafer to form an insulating layer, planarizing the insulating layer, patterning the planar insulating layer, and applying a phase-change material to the
15 patterned insulating layer to form a phase-change material layer; and the CMP slurry composition can be brought into contact with the phase-change material layer to polish the phase-change material layer until the insulating layer is exposed.

In exemplary embodiments of the present invention, the phase-change material layer can be polished by applying the CMP slurry composition to a rotating
20 polishing pad and bringing the polishing pad into contact with the phase-change material layer under predetermined pressure conditions to polish portions of the phase-change material layer by a frictional force. The pressure conditions can include those that are generally permissible in CMP applications.

The present invention also provides a phase-change memory device
25 polished by the polishing method.

Hereinafter, the present invention will be explained in more detail with reference to the following examples. However, these examples are given for the purpose of illustration only and are not to be construed as limiting the scope of the invention. Further, the following examples are provided to illustrate exemplary CMP
30 methods for planarizing a phase-change material.

EXAMPLES

[Evaluation of polishing of blanket wafers]

<Examples 1-2 and Comparative Examples 1-2>

Slurries having the compositions indicated in Table 1 are prepared. As
5 abrasive particles, fumed silica particles having an average primary particle diameter
of 15 nm and a specific surface area of 200 m²/g are used in an amount of 0.5% by
weight with respect to the total weight of each of the slurry compositions. The
fumed silica particles are homogeneously dispersed in deionized water.
Triethylamine (TEA) is used as a nitrogenous compound in Examples 1 and 2, and
10 hydrogen peroxide is used as an oxidizing agent in Example 2 and Comparative
Example 2. Nitric acid is used to adjust the final pH of all slurry compositions to
2.5.

TABLE 1

Example No.	Silica (%)	Triethylamine (%)	Hydrogen peroxide (%)	pH
Example 1	0.5	0.2	0	2.5
Example 2	0.5	0.2	1.0	2.5
Comparative Example 1	0.5	0	0	2.5
Comparative Example 2	0.5	0	1.0	2.5

15 After each of the slurry compositions is used to polish a blanket wafer
deposited with a phase-change material under the following polishing conditions,
the polishing performance of the slurry composition on the phase-change material is
evaluated. The results are shown in Table 2.

As the phase-change material, Ge₂Sb₂Te₅ (GST), whose composition is
20 germanium (Ge): antimony (Sb): tellurium (Te) (2:2:5), is used. The phase-change
material is deposited on the blanket wafer by D.C magnetron sputtering to form a
5,000 Å-thick layer. A 15,000 Å-thick PETEOS silicon oxide film is used as a
polish stop layer, and an IC1000/SubaIV CMP pad (Rodel Corp.) is used as a

polishing pad. The phase-change material layer is polished using a 200 mm MIRRA polisher (manufactured by Applied Materials (AMAT)) at a down pressure of 1.5 psi, a slurry flow rate of 200 mL/min., a table speed of 100 rpm and a spindle speed of 100 rpm for one minute.

5 **TABLE 2**

Example No.	Polishing rate (Å/min) on GST	<u>Polishing characteristics</u>		
		Polishing rate (Å/min) on SiO ₂	Polishing selectivity (GST:SiO ₂)	Polishing non- uniformity (%) on GST
Example 1	2,010	15	134:1	9
Example 2	2,181	21	104:1	4
Comparative Example 1	137	15	9:1	39
Comparative Example 2	312	15	21:1	15

As can be seen from Table 2, the slurry compositions of Examples 1 and 2 comprising the nitrogenous compound show high polishing rates on the GST layer and greatly increased selectivities in polishing rate between the GST layer and the silicon oxide film in comparison with the slurry compositions of Comparative Examples 1 and 2. The addition of the oxidizing agent did not contribute to further improvement of the polishing rate on the GST layer in the slurry composition (Example 2) comprising a combination of the nitrogenous compound and the oxidizing agent, but markedly decreased the polishing non-uniformity on the GST layer.

The polishing non-uniformity is calculated by the following equation:

$$\text{Non-uniformity (\%)} = (\text{Standard deviation of polishing rate} / \text{Average of polishing rate}) \times 100 (\%)$$

The polishing rate is measured over the entire surface from the center of the wafer using a 49-point polar map method. A lower value of the non-uniformity means that the polishing is more uniformly conducted.

<Examples 3 to 6>

Slurry compositions were prepared in the same manner as in Example 1 except that the kind and the content of the nitrogenous compound are varied as indicated in Table 3. The polishing characteristics (*i.e.* polishing rates) of the slurry compositions on the GST are compared according to the number of carbon atoms included in the alkyl groups of the substituted aliphatic amines, *i.e.* tertiary alkyl amines (trimethylamine, triethylamine and tripropylamine). The polishing rate of each of the slurry compositions on the blanket wafer deposited with the phase-change material is measured in the procedure described in Example 1. The results are shown in Table 3.

TABLE 3

Example No.	Kind of nitrogenous compound	Amount (%) of nitrogenous compound	Polishing rate (Å/min.) on GST
Example 1	Triethylamine	0.2	2,010
Example 3	Triethylamine	0.25	2,620
Example 4	Trimethylamine	0.2	1,012
Example 5	Tripropylamine	0.05	3,605
Example 6	Tripropylamine	0.1	4,960

The results of Table 3 indicate that the slurry compositions of Examples 3 to 6 show higher polishing rates on the GST layer than those of Comparative Examples 1 and 2.

The polishing rates of the slurry compositions on the GST layer increased with increasing number of carbon atoms included in the alkyl groups of the substituted aliphatic amines (*i.e.* trialkylamines) and increasing content of the trialkylamines.

<Examples 7 to 11>

Slurry compositions are prepared in the same manner as in Example 1 except that the kind and the content of the nitrogenous compound is varied as indicated in Table 4. The polishing rates of the slurry compositions on GST are compared according to the shapes of the nitrogenous compounds. The polishing rate of each of the slurry compositions on a blanket wafer deposited with GST as a phase-change material is was measured in the procedure described in Example 1. The results are shown in Table 4.

TABLE 4

Example No.	Kind of nitrogenous compound	Amount (%)	Polishing rate (Å/min.) on GST
Example 1	Triethylamine	0.2	2,010
Example 7	Diethylethanolamine	0.2	1,683
Example 8	Diethanolamine	0.2	941
Example 9	Triethanolamine	0.2	910
Example 10	Piperazine	0.2	1,007
Example 11	Tetraethylammonium hydroxide	0.2	2,589

The results of Table 4 demonstrate that the slurry compositions of Examples 7 to 11 show higher polishing rates on the GST layer than those of Comparative Examples 1 and 2. Particularly, the slurry compositions comprising the aliphatic alkylamine or the ammonium base show better polishing results.

[Evaluation of polishing on patterned wafers]

To evaluate the polishing performance of the slurry compositions on semiconductor patterns, patterned wafers are constructed by the following procedure:

Step 1: Deposition of silicon nitride (SiN) to a thickness of 850 Å

Step 2: Deposition of silicon dioxide (SiO₂) to a thickness of 1,500 Å

Step 3: Formation of pattern on the oxide film

Step 4: Deposition of phase-change material ($\text{Ge}_2\text{Sb}_2\text{Te}_3$) to a thickness of 2,000 Å

The silicon oxide film is used as a stop layer in the pattern region. The polishing performance of the compositions of Examples 1 to 3 on the patterned wafers is evaluated. The polishing rates of the compositions of Comparative Examples 1 and 2 on the GST are too low to evaluate the state of the patterns.

Evaluation is conducted on the patterned wafers under the same polishing conditions as described in Example 1 except that the polishing time is varied. After over polishing (30%) is performed following the optic end point detection (EPD) time measured using an EPD system, the pattern regions are observed for erosion, dishing and roughness. The results are shown in Table 5.

TABLE 5

Example No.	Erosion (Å)	Edge over Erosion (EOE, Å)	Dishing (Å)	Residues	Maximum Roughness (R_{max} , Å)
Example 1	50	Not observed	68	Small amounts Observed	120
Example 2	45	120	50	Not observed	20
Example 3	60	Not observed	80	Not observed	80

After pattern polishing, the composition of Example 1 shows better results in terms of erosion, EOE and dishing evaluation. Residues are observed in only small amounts, which could be sufficiently removed by controlling the over-polishing time after the EPD.

No residue is left after pattern polishing using the composition of Example 2. The composition of Example 2 shows excellent performance in terms of maximum roughness in the pattern region. The edges of the pattern are slightly eroded, which is lower than the acceptable level (200 Å) and causes no problem.

The composition of Example 3 using a bit larger amount of the nitrogenous compound than the composition of Example 1 causes slightly increased erosion and dishing, but shows better results in terms of residue and maximum roughness

evaluation.

It could be concluded from these results that the compositions of Examples 1 to 3 are suitable for GST polishing and exhibit excellent pattern polishing characteristics.

5.

[Further Evaluation of polishing of blanket wafers]

<Examples 12-16 and Comparative Examples 3-8>

Slurries having the compositions indicated in Table 1A are prepared using deionized water containing no abrasive particles. Triethylamine (TEA) is used as a nitrogenous compound in Examples 12 to 16 and Comparative Example 3. The TEA content and the kind and content of oxidizing agents used are varied in the slurry compositions. Nitric acid is used to adjust the final pH of all slurry compositions to 3.5.

TABLE 1A

Example No.	TEA Content (%)	Kind of oxidizing agent	Content of oxidizing agent (%)	pH
Example 12	0.2	H ₂ O ₂	0.5	3.5
Example 13	0.5	H ₂ O ₂	1.0	3.5
Example 14	0.2	Ammonium persulfate	1.0	3.5
Example 15	0.1	Propylenediamine tetraacetic acid-Fe	0.2	3.5
Example 16	0.1	FeCl ₃	0.2	3.5
Comparative Example 3	0.2	-	0	3.5
Comparative Example 4	0	H ₂ O ₂	0.5	3.5
Comparative Example 5	0	H ₂ O ₂	1.0	3.5
Comparative Example 6	0	Ammonium persulfate	1.0	3.5
Comparative Example 7	0	Propylenediamine tetraacetic acid-Fe	0.2	3.5

Comparative Example 8	0	FeCl ₃	0.2	3.5
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After each of the slurry compositions is used to polish a blanket wafer deposited with a phase-change material under the following polishing conditions, the polishing performance of the slurry composition on the phase-change material is evaluated. The results are shown in Table 2A.

5 As the phase-change material, Ge₂Sb₂Te₅ (GST), whose composition is germanium (Ge): antimony (Sb): tellurium (Te) (2:2:5), is used. The phase-change material is deposited on the blanket wafer by D.C magnetron sputtering to form a 2,000 Å-thick layer. A 15,000 Å-thick PETEOS silicon oxide film is used as a polish stop layer, and an IC1000/SubaIV CMP pad (Rodel Corp.) is used as a
10 polishing pad. The phase-change material layer is polished using a 200 mm MIRRA polisher (manufactured by Applied Materials (AMAT)) at a down pressure of 3.0 psi, a slurry flow rate of 200 mL/min., a table speed of 100 rpm and a spindle speed of 100 rpm for one minute.

TABLE 2A

Example No.	<u>Polishing Characteristics</u>			
	Polishing rate (Å/min) on GST	Polishing rate (Å/min) on SiO ₂	Polishing selectivity (GST:SiO ₂)	Polishing non- uniformity (%) on GST
Example 12	1,450	12	120.8	8
Example 13	1,793	16	112.1	9
Example 14	1,860	14	132.8	7
Example 15	1,653	15	124.0	6
Example 16	1,784	16	111.5	7
Comparative Example 3	601	10	60.0	21
Comparative Example 4	510	8	63.7	34
Comparative Example 5	590	9	65.6	39
Comparative Example 6	910	12	75.8	18
Comparative	1,230	16	76.8	11

Example 7

Comparative Example 8	1,312	15	87.5	12
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As can be seen from Table 2A the slurry compositions of Examples 12 to 16 comprising a combination of the nitrogenous compound and the corresponding oxidizing agent show high polishing rates on the GST layer and greatly increased selectivities (> 100) in polishing rate between the GST layer and the silicon oxide film in comparison with the slurry compositions of Comparative Examples 3 to 8. In addition, the slurry compositions of Examples 12 to 16 show lower polishing non-uniformities on the GST layer than the slurry compositions of Comparative Examples 3 to 8. Furthermore, since no abrasive particles are included in the slurry compositions of Examples 1 to 5, it is anticipated that the problem of surface contamination caused by abrasive particles can be largely avoid.

The polishing non-uniformity is calculated by the following equation:

$$\text{Non-uniformity (\%)} = (\text{Standard deviation of polishing rate} / \text{Average of polishing rate}) \times 100 (\%)$$

The polishing rate is measured over the entire surface from the center of the wafer using a 49-point polar map method. A lower value of the non-uniformity means that the polishing is more uniformly conducted.

<Examples 17 to 24>

Slurry compositions are prepared in the same manner as in Example 15 except that the kind and the content of the nitrogenous compound are varied as indicated in Table 3A. The polishing characteristics (*i.e.* polishing rates) of the slurry compositions on the GST are compared according to the kind and the content of the nitrogenous compounds. The polishing rate of each of the slurry compositions on the blanket wafer deposited with the phase-change material is measured in the procedure described in Example 15. The results are shown in Table 3A.

TABLE 3A

Example No.	Kind of nitrogenous compound	Amount (%) of nitrogenous compound	Polishing rate (Å/min.) on GST
Example 15	Triethylamine	0.1	1,653
Example 17	Diethylethanolamine	0.1	1,510
Example 18	Diethanolamine	0.1	1,200
Example 19	Diethanolamine	0.5	1,550
Example 20	Triethanolamine	0.1	1,100
Example 21	Triethanolamine	0.5	1,450
Example 22	Piperazine	0.1	1,210
Example 23	Piperazine	0.5	1,610
Example 24	Tetraethylammonium hydroxide	0.1	1,785

5 The results of Table 3A demonstrate that the slurry compositions comprising the aliphatic alkylamine or the ammonium base show higher polishing rates on the GST layer than those comprising the aliphatic amine substituted with alcohol groups.

[Further Evaluation of polishing on patterned wafers]

10 To actually evaluate the polishing performance of the slurry compositions on semiconductor patterns, patterned wafers are constructed by the following procedure:

- Step 1: Deposition of silicon nitride (SiN) to a thickness of 850 Å
- Step 2: Deposition of silicon dioxide (SiO₂) to a thickness of 1,500 Å
- Step 3: Formation of pattern on the oxide film
- 15 Step 4: Deposition of phase-change material (Ge₂Sb₂Te₃) to a thickness of 2,000 Å

The silicon oxide film is used as a stop layer in the pattern region. The polishing performance of the compositions of Examples 13 to 15 and Comparative

Examples 4 to 8 on the patterned wafers is evaluated.

Evaluation is conducted on the patterned wafers under the same polishing conditions as described in Example 12 except that the polishing time is varied. After over polishing (50%) is performed following the optic end point detection (EPD) time measured using an EPD system, the pattern regions are observed for erosion, dishing and roughness. The results are shown in Table 4A.

TABLE 4A

Example No.	Erosion (Å)	Edge over Erosion (EOE, Å)	Dishing (Å)	Residues	Maximum Roughness ($R_{\max}$, Å)
Example 13	100	20	42	Not observed	43
Example 14	150	35	50	Not observed	52
Example 15	60	10	24	Not observed	32
Comparative Example 4	300	250	180	Observed	210
Comparative Example 5	400	250	190	Observed	200
Comparative Example 6	350	200	160	Observed	180
Comparative Example 7	200	46	80	Not observed	90
Comparative Example 8	200	50	82	Not observed	100

Table 4A demonstrates that the slurry compositions of Examples 13 to 15 comprising a nitrogenous compound and an oxidizing agent show much better results in terms of erosion, EOE, dishing, residue and maximum roughness evaluations than those of Comparative Examples 4 to 8.

As apparent from the above description, the present invention provides a CMP slurry composition for polishing a phase-change memory device and a method for polishing a phase-change memory device using the CMP slurry composition.

The slurry composition of the present invention can polish a phase-change memory device at a high rate, can achieve high polishing selectivity between a phase-change memory material and a polish stop layer (e.g., a silicon oxide film), and can minimize the occurrence of processing imperfections (e.g., dishing and erosion) to provide a high-quality polished surface.

After pattern polishing, the compositions of the invention can show better results in terms of erosion, EOE and dishing evaluation. In exemplary embodiments, the resultant phase-change memory device can include a metal alloy or a chalcogenide layer exhibiting a maximum erosion of 175 Å, and/or a maximum edge over erosion of about 150 Å, and/or a dishing maximum of about 100 Å, and/or a maximum roughness ($R_{\max}$) of about 150 Å, for example, a maximum erosion of 150 Å, and/or a maximum edge over erosion of about 120 Å, and/or a dishing maximum of about 80 Å, and/or a maximum roughness ($R_{\max}$) of about 120 Å.

Many modifications and other embodiments of the invention will come to mind to one skilled in the art to which this invention pertains having the benefit of the teachings presented in the foregoing descriptions. Therefore, it is to be understood that the invention is not to be limited to the specific embodiments disclosed and that modifications and other embodiments are intended to be included within the scope of the appended claims. Although specific terms are employed herein, they are used in a generic and descriptive sense only and not for purposes of limitation, the scope of the invention being defined in the claims.

What is claimed is:

1. A slurry composition for chemical mechanical polishing (CMP) of a phase-change memory device, comprising deionized water; abrasive particles; and at least one nitrogenous compound selected from a tertiary amine substituted by an alkyl
5 group containing one to seven carbon atoms, a piperazine compound, tetramethylammonium hydroxide and a salt derived therefrom, tetraethylammonium hydroxide and a salt derived therefrom, and tetrapropylammonium hydroxide and a salt derived therefrom,
wherein the polishing selectivity of a phase-change material layer to an insulating
10 layer is more than 100, and the phase-change material layer comprises at least one compound selected from InSe, Sb₂Te₃, GeTe, Ge₂Sb₂Te₅, InSbTe, GaSeTe, SnSb₂Te₄, InSbGe, AgInSbTe, (GeSn)SbTe, GeSb(SeTe) and Te₈₁Ge₁₅Sb₂S₂.

2. The slurry composition according to claim 1, wherein the abrasive particles
15 have an average primary particle diameter of about 1 to about 200 nm and an average specific surface area of about 10 to about 500 m²/g, and the abrasive particles are present in an amount of about 0.01 to about 30% by weight, based on the total weight of the slurry composition.

3. The slurry composition according to claim 1, further comprising at least one oxidizing agent selected from hydrogen peroxide, monopersulfates, dipersulfates, ionic iron compounds, and iron chelate compounds.