

A process for the manufacture of semiconductor devices comprising the chemical mechanical polishing of elemental germanium and/or $\text{Si}_{1-x}\text{Ge}_x$ material in the presence of a CMP composition having a pH value of 3.0 to 5.5

5 Description

10 This invention essentially relates to a chemical mechanical polishing (CMP) composition and its use in polishing substrates of the semiconductor industry. The process according to the invention comprises the chemical mechanical polishing of elemental germanium in the presence of a specific CMP composition.

15 In the semiconductor industry, chemical mechanical polishing (abbreviated as CMP) is a well-known technology applied in fabricating advanced photonic, microelectromechanical, and microelectronic materials and devices, such as semiconductor wafers.

20 During the fabrication of materials and devices used in the semiconductor industry, CMP is employed to planarize metal and/or oxide surfaces. CMP utilizes the interplay of chemical and mechanical action to achieve the planarity of the to-be-polished surfaces. Chemical action is provided by a chemical composition, also referred to as CMP composition or CMP slurry. Mechanical action is usually carried out by a polishing pad which is typically pressed onto the to-be-polished surface and mounted on a moving platen. The movement of the platen is usually linear, rotational or orbital.

25 In a typical CMP process step, a rotating wafer holder brings the to-be-polished wafer in contact with a polishing pad. The CMP composition is usually applied between the to-be-polished wafer and the polishing pad.

30 In the state of the art, processes for the chemical-mechanical polishing of germanium-containing layers are known and described, for instance, in the following references.

35 US 2010/0130012 A1 discloses a method for polishing a semiconductor wafer provided with a strained-relaxed layer of $\text{Si}_{1-x}\text{Ge}_x$, comprising a first step of a mechanical machining of the $\text{Si}_{1-x}\text{Ge}_x$ layer of the semiconductor wafer in a polishing machine using a polishing pad containing fixedly bonded abrasive materials having a particle size of 0.55 μm or less, and a second step of chemo mechanical machining of the previously mechanically machined $\text{Si}_{1-x}\text{Ge}_x$ layer of the semiconductor wafer using a polishing pad and with supply of a polishing agent slurry containing abrasive materials. The polishing agent solution can contain compounds such as sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3), sodium hydroxide (NaOH), potassium hydroxide (KOH), ammonium hydroxide (NH_4OH), tetramethylammonium hydroxide (TMAH) or
40 any desired mixtures thereof.

US 2008/0265375 A1 discloses a method for the single-sided polishing of semiconductor wafers which are provided with a relaxed $\text{Si}_{1-x}\text{Ge}_x$ layer, comprising: the polishing of a multiplicity of

semiconductor wafers in a plurality of polishing runs, a polishing run comprising at least one polishing step and at least one of the multiplicity of semiconductor wafers being obtained with a polished $\text{Si}_{1-x}\text{Ge}_x$ layer at the end of each polishing run; and moving the at least one semiconductor wafer during the at least one polishing step over a rotating polishing plate provided with a polishing cloth while applying polishing pressure, and supplying polishing agent between the polishing cloth and the at least one semiconductor wafer, a polishing agent being supplied which contains an alkaline component and a component that dissolves germanium. The component that dissolves germanium can comprise hydrogen peroxide, ozone, sodium hypochlorite or a mixture thereof. The alkaline component can comprise potassium carbonate (K_2CO_3), potassium hydroxide (KOH), sodium hydroxide (NaOH), ammonium hydroxide (NH_4OH), tetramethylammonium hydroxide ($\text{N}(\text{CH}_3)_4\text{OH}$), or a mixture thereof.

FR 2876610 A1 discloses a process for the polishing of a germanium surface including a polishing operation with at least one polishing agent and a mild etching solution for germanium. The etching solution can be a solution selected from a hydrogen peroxide solution, water, a solution of H_2SO_4 solution, a solution of HCl, a solution of HF, a solution of NaOCl, a solution of NaOH, a solution of NH_4OH , a solution of KOH solution, a solution of $\text{Ca}(\text{ClO})_2$, or a mixture of two or more of these solutions.

US 2006/0218867 A1 discloses a polishing composition for use in polishing germanium or silicon-germanium single crystal, the polishing composition comprising sodium hypochlorite, colloidal silica and water, wherein the effective chlorine concentration in the polishing composition is 0.5 to 2.5%, and the content of colloidal silica in the polishing composition is 1 to 13% by weight.

US 2011/0045654 A1 discloses a method for polishing a structure (12) comprising at least one surface layer of germanium (121), characterized in that it comprises a first step of chemical-mechanical polishing of the surface (121a) of the germanium layer (121) carried out with a first polishing solution having an acidic pH, and a second step of chemical-mechanical polishing of the surface of the germanium layer (121) carried out with a second polishing solution having an alkaline pH.

In the state of the art, processes for the chemical-mechanical polishing of germanium-containing alloys, such as germanium-antimony-tellurium (GST) alloys, are known and described, for instance, in the following references.

US 2009/0057834 A1 discloses a method for chemical mechanical planarization of a surface having at least one feature thereon comprising a chalcogenide material, said method comprising the steps of: A) placing a substrate having the surface having the at least one feature thereon comprising a chalcogenide material in contact with a polishing pad; B) delivering a polishing composition comprising: b) an abrasive; and b) an oxidizing agent; and C) polishing the sub-

strate with the polishing composition. The chalcogenide material is for example an alloy of germanium, antimony, and tellurium.

5 US 2009/0057661 A1 discloses a method for chemical mechanical planarization of a surface having at least one feature thereon comprising a chalcogenide material, said method comprising the steps of: A) placing a substrate having the surface having the at least one feature thereon comprising a chalcogenide material in contact with a polishing pad; B) delivering a polishing composition comprising: a) a surface-modified abrasive having a positive zeta potential; and b) an oxidizing agent; and C) polishing the substrate with the polishing composition. The chalcogenide material is for example an alloy of germanium, antimony, and tellurium.

15 US 2009/0001339 A1 discloses a slurry composition for chemical mechanical polishing (CMP) of a phase-change memory device, comprising deionized water and a nitrogenous compound. The phase-change memory device preferably comprises at least one compound selected from InSe, Sb₂Te₃, GeTe, Ge₂Sb₂Te₅, InSbTe, GaSeTe, SnSb₂Te₄, InSbGe, AgInSbTe, (GeSn)SbTe, GeSb(SeTe) or Te₈₁Ge₁₅Sb₂S₂. The nitrogenous compound can be one compound selected from aliphatic amines, aromatic amines, ammonium salts, ammonium bases, or a combination thereof.

20 US 2007/0178700 A1 discloses a chemical-mechanical polishing (CMP) composition for polishing a phase change alloy-containing substrate, the composition comprising: (a) a particulate abrasive material in an amount of not more than about 3 percent by weight; (b) at least one chelating agent capable of chelating the phase change alloy, a component thereof, or a substance formed from the phase change alloy material during chemical-mechanical polishing; and (c) an aqueous carrier therefor. The phase change alloy is for example a germanium-antimony-tellurium (GST) alloy. The chelating agent can comprise at least one compound selected from the group consisting of a dicarboxylic acid, a polycarboxylic acid, an amino carboxylic acid, a phosphate, a polyphosphate, an amino phosphonate, and a phosphonocarboxylic acid, a polymeric chelating agent, and a salt thereof.

30 One of the objects of the present invention was to provide a CMP composition and a CMP process appropriate for the chemical-mechanical polishing of elemental germanium and showing an improved polishing performance, particularly a high material removal rate (MRR) of germanium and/or Si_{1-x}Ge_x material (with $0.1 \leq x < 1$), or a high selectivity of germanium to silicon dioxide (Ge:SiO₂ selectivity), or a low static etching rate (SER) of germanium, or the combination of high germanium MRR and high Ge:SiO₂ selectivity and/or low germanium SER. Furthermore, one of the objects of the present invention was to provide a CMP composition and a CMP process appropriate for the chemical-mechanical polishing of elemental germanium which has been filled or grown in trenches between the STI (shallow-trench isolation) silicon dioxide. A further object of the present invention was to provide a CMP composition and a CMP process appropriate for the chemical-mechanical polishing of elemental germanium which has the shape of a layer and/or overgrowth and has a germanium content of more than 98% by weight of the

corresponding layer and/or overgrowth. Moreover, a CMP process was sought that is easy to apply, requires as few steps as possible and requires a CMP composition which is as simple as possible.

- 5 Accordingly, a process for the manufacture of semiconductor devices comprising the chemical mechanical polishing of elemental germanium and/or $\text{Si}_{1-x}\text{Ge}_x$ material with $0.1 \leq x < 1$ in the presence of a chemical mechanical polishing (CMP) composition (referred to as (S) or CMP composition (S) in the following) composition having a pH value in the range of from 3.0 to 5.5 and comprising
- 10
- (A) inorganic particles, organic particles, or a mixture or composite thereof,
 - (B) at least one type of an oxidizing agent, and
 - (C) an aqueous medium.

15 was found.

Moreover, the use of the CMP composition (S) for chemical-mechanical polishing of a substrate comprising an elemental germanium layer and/or overgrowth was found.

- 20 Preferred embodiments are explained in the claims and the specification. It is understood that combinations of preferred embodiments are within the scope of the present invention.

A semiconductor device can be manufactured by the process of the invention, said process comprises the chemical mechanical polishing of elemental germanium and/or $\text{Si}_{1-x}\text{Ge}_x$ material (with $0.1 \leq x < 1$) in the presence of the CMP composition (S), preferably, said process comprises the chemical mechanical polishing of elemental germanium in the presence of the CMP composition (S). Generally, this elemental germanium can be of any type, form, or shape of elemental germanium. This elemental germanium preferably has the shape of a layer and/or overgrowth. If this elemental germanium has the shape of a layer and/or overgrowth, the germanium content is preferably more than 90%, more preferably more than 95%, most preferably more than 98%, particularly more than 99%, for example more than 99.9% by weight of the corresponding layer and/or overgrowth. Generally, this elemental germanium can be produced or obtained in different ways. This elemental germanium has been preferably filled or grown in trenches between other substrates, more preferably filled or grown in trenches between silicon dioxide, silicon, or other isolating and semiconducting material used in the semiconductor industry, most preferably filled or grown in trenches between the STI (shallow-trench isolation) silicon dioxide, particularly grown in trenches between the STI silicon dioxide in a selective epitaxial growth process. If this elemental germanium has been filled or grown in trenches between the STI silicon dioxide, the depth of said trenches is preferably from 20 to 500 nm, more preferably from 150 to 400 nm, and most preferably from 250 to 350 nm, particularly from 280 to 320 nm. In another embodiment, if this elemental germanium has been filled or grown in trenches between silicon dioxide, silicon, or other isolating and semiconducting material used in the semi-

conductor industry, the depth of said trenches is preferably from 5 to 100 nm, more preferably from 8 to 50 nm, and most preferably from 10 to 35 nm, particularly from 15 to 25 nm.

Elemental germanium is germanium in form of its chemical element and does not include germanium salts or germanium alloys with a content of less than 90% germanium by weight of the corresponding alloy.

Said $\text{Si}_{1-x}\text{Ge}_x$ material (with $0.1 \leq x < 1$) can be of any type, form, or shape of $\text{Si}_{1-x}\text{Ge}_x$ material with $0.1 \leq x < 1$. Generally, x can be any value in the range of $0.1 \leq x < 1$. Preferably, x is in the range of $0.1 \leq x < 0.8$, more preferably, x is in the range of $0.1 \leq x < 0.5$, most preferably, x is in the range of $0.1 \leq x < 0.3$, for example x is 0.2. Said $\text{Si}_{1-x}\text{Ge}_x$ material is preferably a $\text{Si}_{1-x}\text{Ge}_x$ layer, more preferably a strain-relaxed $\text{Si}_{1-x}\text{Ge}_x$ layer. This strain-relaxed $\text{Si}_{1-x}\text{Ge}_x$ layer can be the one described in paragraph [0006] of US 2008/0265375 A1.

If the process of the invention comprises the chemical mechanical polishing of a substrate comprising elemental germanium and silicon dioxide, the selectivity of germanium to silicon dioxide with regard to the material removal rate is preferably higher than 4.5:1, more preferably higher than 10:1, most preferably higher than 25:1, particularly higher than 50:1, especially higher than 75:1, for example higher than 100:1.

The CMP composition (S) is used for chemical-mechanical polishing of a substrate comprising elemental germanium and/or $\text{Si}_{1-x}\text{Ge}_x$ material (with $0.1 \leq x < 1$), preferably for chemical-mechanical polishing of a substrate comprising an elemental germanium layer and/or overgrowth. The germanium content of said elemental germanium layer and/or overgrowth is preferably more than 90%, more preferably more than 95%, most preferably more than 98%, particularly more than 99%, for example more than 99.9% by weight of the corresponding layer and/or overgrowth. The elemental germanium layer and/or overgrowth can be obtained in different ways, preferably by filling or growing in trenches between other substrates, more preferably by filling or growing in trenches between silicon dioxide, silicon, or other isolating and semiconducting material used in the semiconductor industry, most preferably by filling or growing in trenches between the STI (shallow-trench isolation) silicon dioxide, particularly by growing in trenches between the STI silicon dioxide in a selective epitaxial growth process.

If the CMP composition (S) is used for polishing a substrate comprising elemental germanium and silicon dioxide, the selectivity of germanium to silicon dioxide with regard to the material removal rate is preferably higher than 4.5:1, more preferably higher than 10:1, most preferably higher than 25:1, particularly higher than 50:1, especially higher than 75:1, for example higher than 100:1.

The CMP composition (S) has a pH value in the range of from 3.0 to 5.5 and comprises the components (A), (B), (C) as described below.

The CMP composition (S) comprises inorganic particles, organic particles, or a mixture or composite thereof (A). (A) can be

- of one type of inorganic particles,
- a mixture or composite of different types of inorganic particles,
- 5 - of one type of organic particles,
- a mixture or composite of different types of organic particles, or
- a mixture or composite of one or more types of inorganic particles and one or more types of organic particles.

10 A composite is a composite particle comprising two or more types of particles in such a way that they are mechanically, chemically or in another way bound to each other. An example for a composite is a core-shell particle comprising one type of particle in the outer sphere (shell) and another type of particle in the inner sphere (core).

15 Generally, the particles (A) can be contained in varying amounts in the CMP composition (S). Preferably, the amount of (A) is not more than 10 wt.% (wt.% stands for "percent by weight"), more preferably not more than 5 wt.%, most preferably not more than 2.5 wt.%, for example not more than 1.8 wt.%, based on the total weight of the composition (S). Preferably, the amount of (A) is at least 0.002 wt.%, more preferably at least 0.01 wt.%, most preferably at least 0.08
20 wt.%, for example at least 0.4 wt.%, based on the total weight of the composition (S). In another embodiment, the amount of (A) is preferably not more than 10 wt.%, more preferably not more than 8 wt.%, most preferably not more than 6.5 wt.%, for example not more than 5.5 wt.%, based on the total weight of the composition (S), and the amount of (A) is preferably at least 0.1 wt.%, more preferably at least 0.8 wt.%, most preferably at least 1.5 wt.%, for example at least
25 3.0 wt.%, based on the total weight of the composition (S).

Generally, the particles (A) can be contained in varying particle size distributions. The particle size distributions of the particles (A) can be monomodal or multimodal. In case of multimodal particle size distributions, bimodal is often preferred. In order to have an easily reproducible
30 property profile and easily reproducible conditions during the CMP process of the invention, a monomodal particle size distribution is preferred for (A). It is most preferred for (A) to have a monomodal particle size distribution.

The mean particle size of the particles (A) can vary within a wide range. The mean particle size
35 is the d_{50} value of the particle size distribution of (A) in the aqueous medium (C) and can be determined using dynamic light scattering techniques. Then, the d_{50} values are calculated under the assumption that particles are essentially spherical. The width of the mean particle size distribution is the distance (given in units of the x-axis) between the two intersection points, where the particle size distribution curve crosses the 50% height of the relative particle counts, where-
40 in the height of the maximal particle counts is standardized as 100% height.

Preferably, the mean particle size of the particles (A) is in the range of from 5 to 500 nm, more preferably in the range of from 5 to 250 nm, most preferably in the range of from 20 to 150 nm, and in particular in the range of from 35 to 130 nm, as measured with dynamic light scattering techniques using instruments such as High Performance Particle Sizer (HPPS) from Malvern Instruments, Ltd. or Horiba LB550.

The particles (A) can be of various shapes. Thereby, the particles (A) may be of one or essentially only one type of shape. However, it is also possible that the particles (A) have different shapes. For instance, two types of differently shaped particles (A) may be present. For example, (A) can have the shape of cubes, cubes with chamfered edges, octahedrons, icosahedrons, nodules or spheres with or without protrusions or indentations. Preferably, they are spherical with no or only very few protrusions or indentations.

The chemical nature of particles (A) is not particularly limited. (A) may be of the same chemical nature or a mixture or composite of particles of different chemical nature. As a rule, particles (A) of the same chemical nature are preferred. Generally, (A) can be

- inorganic particles such as a metal, a metal oxide or carbide, including a metalloid, a metalloid oxide or carbide, or
- organic particles such as polymer particles,
- a mixture or composite of inorganic and organic particles.

Particles (A) are preferably inorganic particles. Among them, oxides and carbides of metals or metalloids are preferred. More preferably, particles (A) are alumina, ceria, copper oxide, iron oxide, nickel oxide, manganese oxide, silica, silicon nitride, silicon carbide, tin oxide, titania, titanium carbide, tungsten oxide, yttrium oxide, zirconia, or mixtures or composites thereof. Most preferably, particles (A) are alumina, ceria, silica, titania, zirconia, or mixtures or composites thereof. In particular, (A) are silica particles. For example, (A) are colloidal silica particles. Typically, colloidal silica particles are produced by a wet precipitation process.

In another embodiment in which (A) are organic particles, or a mixture or composite of inorganic and organic particles, polymer particles are preferred as organic particles. Polymer particles can be homo- or copolymers. The latter may for example be block-copolymers, or statistical copolymers. The homo- or copolymers may have various structures, for instance linear, branched, comb-like, dendrimeric, entangled or cross-linked. The polymer particles may be obtained according to the anionic, cationic, controlled radical, free radical mechanism and by the process of suspension or emulsion polymerisation. Preferably, the polymer particles are at least one of the polystyrenes, polyesters, alkyd resins, polyurethanes, polylactones, polycarbonates, polyacrylates, polymethacrylates, polyethers, poly(N-alkylacrylamide)s, poly(methyl vinyl ether)s, or copolymers comprising at least one of vinylaromatic compounds, acrylates, methacrylates, maleic anhydride acrylamides, methacrylamides, acrylic acid, or methacrylic acid as monomeric units, or mixtures or composites thereof. Among them, polymer particles with a cross-linked structure are preferred.

The CMP composition (S) comprises at least one type of oxidizing agent (B), preferably one to two types of oxidizing agent (B), more preferably one type of oxidizing agent (B). In general, the oxidizing agent is a compound which is capable of oxidizing the to-be-polished substrate or one of its layers. Preferably, (B) is a per-type oxidizer. More preferably, (B) is a peroxide, persulfate, perchlorate, perbromate, periodate, permanganate, or a derivative thereof. Most preferably, (B) is a peroxide or persulfate. Particularly, (B) is a peroxide. For example, (B) is hydrogen peroxide.

The oxidizing agent (B) can be contained in varying amounts in the CMP composition (S). Preferably, the amount of (B) is not more than 20 wt.%, more preferably not more than 10 wt.%, most preferably not more than 5 wt.%, particularly not more than 3.5 wt.%, for example not more than 2.7 wt.%, based on the total weight of the composition (S). Preferably, the amount of (B) is at least 0.01 wt.%, more preferably at least 0.08 wt.%, most preferably at least 0.4 wt.%, particularly at least 0.75 wt.%, for example at least 1 wt.%, based on the total weight of the composition (S). If hydrogen peroxide is used as oxidizing agent (B), the amount of (B) is for instance 2.5 wt.%, based on the total weight of the composition (S).

According to the invention, the CMP composition (S) contains an aqueous medium (C). (C) can be of one type or a mixture of different types of aqueous media.

In general, the aqueous medium (C) can be any medium which contains water. Preferably, the aqueous medium (C) is a mixture of water and an organic solvent miscible with water (e.g. an alcohol, preferably a C₁ to C₃ alcohol, or an alkylene glycol derivative). More preferably, the aqueous medium (C) is water. Most preferably, aqueous medium (C) is de-ionized water.

If the amounts of the components other than (C) are in total y % by weight of the CMP composition, then the amount of (C) is (100-y) % by weight of the CMP composition.

The properties of the CMP composition (S), such as stability and polishing performance, depend on the pH of the corresponding composition. The pH value of the composition (S) used in the process of the invention is in the range of from 3.0 to 5.5. Said pH value is preferably in the range of from 3.1 to 5.1, more preferably in the range of from 3.3 to 4.8, most preferably in the range of from 3.5 to 4.5, particularly in the range of from 3.7 to 4.3, for example in the range of from 3.9 to 4.1. Said pH value is preferably at least 3.1, more preferably at least 3.3, most preferably at least 3.5, particularly at least 3.7, for example at least 3.9. Said pH value is preferably not more than 5.1, more preferably not more than 4.8, most preferably not more than 4.5, particularly not more than 4.3, for example not more than 4.1. The pH value can be measured with a pH combination electrode (Schott, blue line 22 pH).

The CMP composition (S) can contain further optionally contain at least one pH adjusting agent (D). In general, the pH adjusting agent (D) is an additive which is added to the CMP composition (S) only for the purpose of adjusting its pH value. Preferably, the CMP composition (S) con-

tains at least one pH adjusting agent (D). Preferred pH adjusting agents are inorganic acids, carboxylic acids, amine bases, alkali hydroxides, ammonium hydroxides, including tetraalkylammonium hydroxides. For example, the pH adjusting agent (D) is nitric acid, sulfuric acid, ammonia, sodium hydroxide, or potassium hydroxide.

5

If present, the pH adjusting agent (D) can be contained in varying amounts. If present, the amount of (D) is preferably not more than 10 wt.%, more preferably not more than 2 wt.%, most preferably not more than 0.5 wt.%, particularly not more than 0.1 wt.%, for example not more than 0.05 wt.%, based on the total weight of the corresponding composition. If present, the amount of (D) is preferably at least 0.0005 wt.%, more preferably at least 0.005 wt.%, most preferably at least 0.025 wt.%, particularly at least 0.1 wt.%, for example at least 0.4 wt.%, based on the total weight of the corresponding composition.

10

The CMP composition (S) may also contain, if necessary, various further additives. A further additive is an additive other than particles (A), oxidizing agent (B), or aqueous medium (C) and is not an additive which is added to the CMP composition only for the purpose of adjusting its pH value. Further additives include but are not limited to biocides, corrosion inhibitors, stabilizers, surfactants, friction reducing agents, etc. Said further additives are for instance those commonly employed in CMP compositions and thus known to the person skilled in the art. Such addition can for example stabilize the dispersion, or improve the polishing performance, or the selectivity between different layers.

15

20

If present, said further additive can be contained in varying amounts. Preferably, the total amount of said further additives is not more than 5 wt.%, more preferably not more than 1 wt.%, most preferably not more than 0.5 wt.%, particularly not more than 0.1 wt.%, for example not more than 0.01 wt.%, based on the total weight of the corresponding CMP composition.

25

The CMP composition (S) can further optionally contain at least one biocide (E), for example one biocide. In general, the biocide is a compound which deters, renders harmless, or exerts a controlling effect on any harmful organism by chemical or biological means. Preferably, (E) is a quaternary ammonium compound, an isothiazolinone-based compound, an *N*-substituted diazenium dioxide, or an *N*-hydroxy-diazenium oxide salt. More preferably, (E) is an *N*-substituted diazenium dioxide, or an *N*-hydroxy-diazenium oxide salt

30

If present, the biocide (E) can be contained in varying amounts. If present, the amount of (E) is preferably not more than 0.5 wt.%, more preferably not more than 0.1 wt.%, most preferably not more than 0.05 wt.%, particularly not more than 0.02 wt.%, for example not more than 0.008 wt.%, based on the total weight of the corresponding composition. If present, the amount of (E) is preferably at least 0.0001 wt.%, more preferably at least 0.0005 wt.%, most preferably at least 0.001 wt.%, particularly at least 0.003 wt.%, for example at least 0.006 wt.%, based on the total weight of the corresponding composition.

35

40

The CMP composition (S) can contain further optionally contain at least one corrosion inhibitor (F), for example two corrosion inhibitors. All compounds forming a protective molecular layer on the surface of Ge and/or germanium oxide can be used. Preferred corrosion inhibitors are thiols, film forming polymers, polyols, diazoles, triazoles, tetrazoles, and their derivatives, for example benzotriazole or tolyltriazole.

If present, the corrosion inhibitor (F) can be contained in varying amounts. If present, the amount of (F) is preferably not more than 10 wt.%, more preferably not more than 2 wt.%, most preferably not more than 0.5 wt.%, particularly not more than 0.1 wt.%, for example not more than 0.05 wt.%, based on the total weight of the corresponding composition. If present, the amount of (F) is preferably at least 0.0005 wt.%, more preferably at least 0.005 wt.%, most preferably at least 0.025 wt.%, particularly at least 0.1 wt.%, for example at least 0.4 wt.%, based on the total weight of the corresponding composition.

According to one preferred embodiment, a process for the manufacture of semiconductor devices comprising the chemical mechanical polishing of elemental germanium and/or $\text{Si}_{1-x}\text{Ge}_x$ material with $0.1 \leq x < 1$ was carried out in the presence of a CMP composition having a pH value of 3.0 to 5.5 and comprising

- (A) silica particles,
- (B) hydrogen peroxide, and
- (C) water,

wherein the total amount of further additives comprised in the CMP composition is not more than 1 wt.% based on the total weight of the CMP composition and wherein said further additive is an additive other than particles (A), oxidizing agent (B), or aqueous medium (C) and is not an additive which is added to the CMP composition only for the purpose of adjusting its pH value.

According to another preferred embodiment, a process for the manufacture of semiconductor devices comprising the chemical mechanical polishing of elemental germanium and/or $\text{Si}_{1-x}\text{Ge}_x$ material with $0.1 \leq x < 1$ was carried out in the presence of a CMP composition having a pH value of 3.0 to 5.5 and comprising

- (A) colloidal silica particles, in an amount of from 0.01 to 5 wt.% based on the total weight of the CMP composition,
- (B) hydrogen peroxide, in an amount of from 0.4 to 5 wt.% based on the total weight of the CMP composition, and
- (C) water,

wherein the total amount of further additives comprised in the CMP composition is not more than 1 wt.% based on the total weight of the CMP composition and wherein said further additive is an additive other than particles (A), oxidizing agent (B), or aqueous medium (C) and is not an additive which is added to the CMP composition only for the purpose of adjusting its pH value.

5

According to another preferred embodiment, a process for the manufacture of semiconductor devices comprising the chemical mechanical polishing of elemental germanium, which has been filled or grown in trenches between silicon dioxide, silicon, or other isolating and semiconducting material used in the semiconductor industry, was carried out in the presence of a CMP composition having a pH value of 3.0 to 5.5 and comprising

10

- (A) colloidal silica particles, in an amount of from 0.01 to 5 wt.% based on the total weight of the CMP composition,
- (B) hydrogen peroxide, in an amount of from 0.4 to 5 wt.% based on the total weight of the
- 15 CMP composition, and
- (C) water,

15

wherein the total amount of further additives comprised in the CMP composition is not more than 1 wt.% based on the total weight of the CMP composition and wherein said further additive is an additive other than particles (A), oxidizing agent (B), or aqueous medium (C) and is not an additive which is added to the CMP composition only for the purpose of adjusting its pH value.

20

According to another preferred embodiment, a process for the manufacture of semiconductor devices comprising the chemical mechanical polishing of elemental germanium, which has been filled or grown in trenches between silicon dioxide, silicon, or other isolating and semiconducting material used in the semiconductor industry, was carried out in the presence of a CMP composition having a pH value of 3.5 to 4.5 and comprising

25

- (A) colloidal silica particles, in an amount of from 0.01 to 5 wt.% based on the total weight of
- 30 the CMP composition,
- (B) hydrogen peroxide, in an amount of from 0.4 to 5 wt.% based on the total weight of the
- CMP composition, and
- (C) water,

30

wherein the elemental germanium has the shape of a layer and/or overgrowth and has a germanium content of more than 98% based on the total weight of the corresponding layer and/or overgrowth and wherein the total amount of further additives comprised in the CMP composition

35

is not more than 1 wt.% based on the total weight of the CMP composition and wherein said further additive is an additive other than particles (A), oxidizing agent (B), or aqueous medium (C) and is not an additive which is added to the CMP composition only for the purpose of adjusting its pH value.

5

According to another preferred embodiment, a process for the manufacture of semiconductor devices comprising the chemical mechanical polishing of elemental germanium and/or $\text{Si}_{1-x}\text{Ge}_x$ material with $0.1 \leq x < 1$ was carried out in the presence of a CMP composition having a pH value of 3.7 to 4.3 and comprising

- 10 (A) silica particles,
(B) hydrogen peroxide, and
(C) water.

Processes for preparing CMP compositions are generally known. These processes may be applied to the preparation of the CMP composition (S). This can be carried out by dispersing or dissolving the above-described components (A) and (B) in the aqueous medium (C), preferably water, and optionally by adjusting the pH value of the CMP composition through adding an acid, a base, a buffer or a pH adjusting agent. For this purpose the customary and standard mixing processes and mixing apparatuses such as agitated vessels, high shear impellers, ultrasonic mixers, homogenizer nozzles or counterflow mixers, can be used.

The CMP composition (S) is preferably prepared by dispersing the particles (A), dispersing and/or dissolving the oxidizing agent (B) in the aqueous medium (C).

25 The polishing process is generally known and can be carried out with the processes and the equipment under the conditions customarily used for the CMP in the fabrication of wafers with integrated circuits. There is no restriction on the equipment with which the polishing process can be carried out.

30 As is known in the art, typical equipment for the CMP process consists of a rotating platen which is covered with a polishing pad. Also orbital polishers have been used. The wafer is mounted on a carrier or chuck. The side of the wafer being processed is facing the polishing pad (single side polishing process). A retaining ring secures the wafer in the horizontal position.

35 Below the carrier, the larger diameter platen is also generally horizontally positioned and presents a surface parallel to that of the wafer to be polished. The polishing pad on the platen contacts the wafer surface during the planarization process.

40 To produce material loss, the wafer is pressed onto the polishing pad. Both the carrier and the platen are usually caused to rotate around their respective shafts extending perpendicular from the carrier and the platen. The rotating carrier shaft may remain fixed in position relative to the

rotating platen or may oscillate horizontally relative to the platen. The direction of rotation of the carrier is typically, though not necessarily, the same as that of the platen. The speeds of rotation for the carrier and the platen are generally, though not necessarily, set at different values. During the CMP process of the invention, the CMP composition (S) is usually applied onto the polishing pad as a continuous stream or in dropwise fashion. Customarily, the temperature of the platen is set at temperatures of from 10 to 70°C.

The load on the wafer can be applied by a flat plate made of steel for example, covered with a soft pad that is often called backing film. If more advanced equipment is being used a flexible membrane that is loaded with air or nitrogen pressure presses the wafer onto the pad. Such a membrane carrier is preferred for low down force processes when a hard polishing pad is used, because the down pressure distribution on the wafer is more uniform compared to that of a carrier with a hard platen design. Carriers with the option to control the pressure distribution on the wafer may also be used according to the invention. They are usually designed with a number of different chambers that can be loaded to a certain degree independently from each other.

For further details reference is made to WO 2004/063301 A1, in particular page 16, paragraph [0036] to page 18, paragraph [0040] in conjunction with the figure 2.

By way of the CMP process of the invention, wafers with integrated circuits comprising a dielectric layer can be obtained which have an excellent functionality.

The CMP composition (S) can be used in the CMP process as ready-to-use slurry, they have a long shelf-life and show a stable particle size distribution over long time. Thus, they are easy to handle and to store. They show an excellent polishing performance, particularly with regard to the combination of high germanium MRR and high Ge:SiO₂ selectivity, and/or the combination of high germanium MRR and low germanium SER. Since the amounts of its components are held down to a minimum, the CMP composition (S) and the CMP process according to the invention can be used or applied in a cost-effective way.

Examples and Comparative Examples

The pH value is measured with a pH electrode (Schott, blue line, pH 0-14 / -5...100 °C / 3 mol/L sodium chloride).

Ge-cSER (cold static etching rate of a germanium layer) is determined by dipping 1x1 inch germanium coupon into the corresponding composition for 5 minutes at 25°C and measuring the loss of mass before and after the dipping.

Ge-hSER (hot static etching rate of a germanium layer) is determined by dipping 1x1 inch germanium coupon into the corresponding composition for 5 minutes at 60°C and measuring the loss of mass before and after the dipping.

5 Inorganic particles (A) used in the Examples

Silica particles used as particles (A) are of NexSil™ (Nyacol) type. NexSil™ 125K are potassium-stabilized colloidal silica having a typical particle size of 85 nm and a typical surface area of 35 m²/g. NexSil™ 85K are potassium-stabilized colloidal silica having a typical particle size of 50 nm and a typical surface area of 55 m²/g. Apart from NexSil™ type particles, other commercially available colloidal silica particles such as FUSO PL3, Evonik EM5530K, Evonik EM7530K, Aerosil 90, Levasil 50CK can also be used and show comparable polishing performance compared to NexSil™ 125K or NexSil™ 85K.

15 General procedure for the CMP experiments

For the evaluation on benchtop polisher, the following parameters were chosen:

Powerpro 5000 Bühler. DF = 40 N, Table speed 150 rpm, Platen speed 150 rpm, slurry flow 200 ml/ min, 20 s conditioning, 1 min polishing time, IC1000 pad, diamond conditioner (3M).

The pad is conditioned by several sweeps, before a new type of CMP composition is used for CMP. For the determination of removal rates at least 3 wafers are polished and the data obtained from these experiments are averaged.

25 The CMP composition is stirred in the local supply station.

The germanium material removal rates (Ge-MRR) for 2 inch discs polished by the CMP composition are determined by difference of weight of the coated wafers or blanket discs before and after CMP, using a Sartorius LA310 S scale. The difference of weight can be converted into the difference of film thickness since the density (5.323 g/cm³ for germanium) and the surface area of the polished material are known. Dividing the difference of film thickness by the polishing time provides the values of the material removal rate.

35 The silicon oxide material removal rates (oxide MRR) for 2 inch discs polished by the CMP composition are determined by difference of weight of the coated wafers or blanket discs before and after CMP, using a Sartorius LA310 S scale. The difference of weight can be converted into the difference of film thickness since the density (2.648 g/cm³ for silicon oxide) and the surface area of the polished material are known. Dividing the difference of film thickness by the polishing time provides the values of the material removal rate.

Objective to be polished: unstructured germanium wafer

Standard procedure for slurry preparation:

The components (A) and (B) – each in the amounts as indicated in Table 1 – were dispersed or dissolved in de-ionized water. pH is adjusted by adding of aqueous ammonia solution (0.1% - 10%), 10% KOH solution or HNO₃ (0.1 % - 10 %) to the slurry. The pH value is measured with a pH combination electrode (Schott, blue line 22 pH).

Example 1-8 (Compositions used in the process of the invention) and Comparative Examples V1-V7 (comparative composition)

An aqueous dispersion containing the components as listed in Table 1 was prepared, furnishing the CMP compositions of the examples 1 to 8 and the comparative examples V1 to V7.

The formulation and polishing performance data and of the CMP compositions of the examples 1 to 8 and of the comparative examples V1 to V7 are given in the Table 1:

Table 1: CMP compositions of the examples 1 to 8 and of the comparative examples V1 to V7, their pH values, Ge-cSER, Ge-hSER data as well as their Ge-MRR and oxide-MRR data in the process of chemical-mechanical polishing of 2" unstructured germanium wafers using these compositions, wherein the aqueous medium (C) of the CMP compositions is de-ionized water. The concentration of the components (A) and (B) are specified in weight percent (wt.%) by weight of the corresponding CMP composition. If the amounts of the components other than (C) are in total y % by weight of the CMP composition, then the amount of (C) is (100-y) % by weight of the CMP composition.

	Comparative Example V1	Example 1	Example 2	Comparative Example V2
Particles (A)	NexSil™ 125K 5 wt. %	NexSil™ 125K 1.5 wt. %	NexSil™ 85K 5 wt. %	NexSil™ 85K 5 wt. %
Oxidizing agent (B)	H ₂ O ₂ 2.5 wt. %	H ₂ O ₂ 2.5 wt. %	H ₂ O ₂ 2.5 wt. %	H ₂ O ₂ 2.5 wt. %
pH	2	4	4	6
Ge-MRR [Å/min]	2600	859	1636	1385
Ge-cSER [Å/min]	293	135	149	189
Ge-hSER [Å/min]	1069	515	424	840
Ratio Ge-MRR to Ge-hSER	2.4	1.7	3.9	1.6
Oxide-MRR [Å/min]	-	177	-	-
Ratio Ge-MRR to Oxide-MRR	-	4.9	-	-

(Table 1: Continuation)

	Comparative Example V3	Comparative Example V4	Comparative Example V5
Particles (A)	NexSil™ 85K 5 wt. %	NexSil™ 85K 5 wt. %	NexSil™ 85K 5 wt. %
Oxidizing agent (B)	H ₂ O ₂ 2.5 wt. %	H ₂ O ₂ 2.5 wt. %	H ₂ O ₂ 2.5 wt. %
pH	8	10	12
Ge-MRR [Å/min]	1975	6510	20808
Ge-cSER [Å/min]	535	1442	2036
Ge-hSER [Å/min]	1920	6271	9928
Ratio Ge-MRR to Ge-hSER	1.0	1.0	2.1
Oxide-MRR [Å/min]	-	-	-
Ratio Ge-MRR to Oxide-MRR	-	-	-

5 (Table 1: Continuation)

	Comparative Example V6	Example 3	Example 4
Particles (A)	NexSil™ 125K 5 wt. %	NexSil™ 125K 5 wt. %	NexSil™ 85K 5 wt. %
Oxidizing agent (B)	H ₂ O ₂ 0 wt. %	H ₂ O ₂ 2.5 wt. %	H ₂ O ₂ 5 wt. %
pH	3	3	3
Ge-MRR [Å/min]	170	2388	2792
Ge-cSER [Å/min]	20	159	370
Ge-hSER [Å/min]	27	711	1379
Ratio Ge-MRR to Ge-hSER	6.3	3.4	2.0

(Table 1: Continuation)

	Comparative Example V7	Example 5	Example 6	Example 7
Particles (A)	NexSil™ 125K 0 wt. %	NexSil™ 125K 0.5 wt. %	NexSil™ 85K 1 wt. %	NexSil™ 85K 1.5 wt. %
Oxidizing agent (B)	H ₂ O ₂ 2.5 wt. %	H ₂ O ₂ 2.5 wt. %	H ₂ O ₂ 2.5 wt. %	H ₂ O ₂ 2.5 wt. %
pH	3	3	3	3
Ge-MRR [Å/min]	0	1633	1935	2113
Ge-cSER [Å/min]	-	-	-	-
Ge-hSER [Å/min]	1109	1000	895	751
Ratio Ge-MRR to Ge-hSER	-	1.6	2.2	2.8
Oxide-MRR [Å/min]	0	98	223	334
Ratio Ge-MRR to Oxide-MRR	-	16.7	8.7	6.3

(Table 1: Continuation)

5

	Example 8
Particles (A)	NexSil™ 125K 5 wt. %
Oxidizing agent (B)	H ₂ O ₂ 2.5 wt. %
pH	3
Ge-MRR [Å/min]	2396
Ge-cSER [Å/min]	-
Ge-hSER [Å/min]	711
Ratio Ge-MRR to Ge-hSER	3.4
Oxide-MRR [Å/min]	617
Ratio Ge-MRR to Oxide-MRR	3.9

Comparative Example V6, Examples 3 and 4 are listed to show the impact of the addition of different amounts of H₂O₂ on the polishing performance at pH 3.

- 10 Comparative Example V7, Examples 5 to 8 are listed to show the impact of the addition of different amounts of colloidal silica particles on the polishing performance at pH 3.

The CMP processes of the invention using these examples of CMP compositions, especially the examples 1 and 2, show an improved polishing performance.

15

Claims:

1. A process for the manufacture of semiconductor devices comprising the chemical mechanical polishing of elemental germanium and/or $\text{Si}_{1-x}\text{Ge}_x$ material with $0.1 \leq x < 1$
5 in the presence of a chemical mechanical polishing (CMP) composition having a pH value in the range of from 3.0 to 5.5 and comprising:
(A) inorganic particles, organic particles, or a mixture or composite thereof,
(B) at least one type of an oxidizing agent, and
10 (C) an aqueous medium.
2. A process according to claim 1, wherein the total amount of further additives comprised in the CMP composition is not more than 1 wt.% based on the total weight of the CMP composition and
15 wherein said further additive is an additive other than particles (A), oxidizing agent (B), or aqueous medium (C) and is not an additive which is added to the CMP composition only for the purpose of adjusting its pH value.
3. A process according to claim 1, wherein the total amount of further additives comprised in the CMP composition is not more than 0.1 wt.% based on the total weight of the CMP composition and
20 wherein said further additive is an additive other than particles (A), oxidizing agent (B), or aqueous medium (C) and is not an additive which is added to the CMP composition only for the purpose of adjusting its pH value.
- 25 4. A process according to anyone of the claims 1 to 3 for the manufacture of semiconductor devices comprising the chemical mechanical polishing of elemental germanium.
- 30 5. A process according to anyone of the claims 1 to 4, wherein the elemental germanium has been filled or grown in trenches between silicon dioxide, silicon, or other isolating and semiconducting material used in the semiconductor industry.
- 35 6. A process according to anyone of the claims 1 to 5, wherein the elemental germanium has the shape of a layer and/or overgrowth and has a germanium content of more than 98% based on the total weight of the corresponding layer and/or overgrowth.
- 40 7. A process according to anyone of the claims 1 to 6, wherein the particles (A) are silica particles.

8. A process according to anyone of the claims 1 to 7, wherein the oxidizing agent (B) is hydrogen peroxide.
- 5 9. A process according to anyone of the claims 1 to 8, wherein the amount of particles (A) is in the range of from 0.01 to 5 wt.% based on the total weight of the CMP composition.
- 10 10. A process according to anyone of the claims 1 to 9, wherein the amount of the oxidizing agent (B) is in the range of from 0.4 to 5 wt.% based on the total weight of the CMP composition.
11. A process according to anyone of the claims 1 to 10, wherein the pH value of the CMP composition is in the range of from 3.7 to 4.3.
- 15 12. A process according to anyone of the claims 1 to 11, wherein the CMP composition has a pH value of 3.0 to 5.5 and comprises:
- (A) colloidal silica particles, in an amount of from 0.01 to 5 wt.% based on the total weight of the CMP composition,
- 20 (B) hydrogen peroxide, in an amount of from 0.4 to 5 wt.% based on the total weight of the CMP composition, and
- (C) water
- and wherein the total amount of further additives comprised in the CMP composition is not more than 1 wt.% based on the total weight of the CMP composition
- 25 and wherein said further additive is an additive other than particles (A), oxidizing agent (B), or aqueous medium (C) and is not an additive which is added to the CMP composition only for the purpose of adjusting its pH value.
- 30 13. A process according to anyone of the claims 1 to 12, wherein the selectivity of germanium to silicon dioxide is more than 4.5:1 with regard to the material removal rate.
- 35 14. Use of a CMP composition having a pH value in the range of from 3.5 to 4.5 and comprising
- (A) inorganic particles, organic particles, or a mixture or composite thereof,
- (B) at least one type of an oxidizing agent, and
- 40 (C) an aqueous medium
- for chemical-mechanical polishing of a substrate comprising an elemental germanium layer and/or overgrowth.

15. Use according to claim 14, wherein the particles (A) are colloidal silica particles,
the oxidizing agent (B) is hydrogen peroxide,
and wherein the total amount of further additives comprised in the CMP composi-
tion is not more than 1 wt.% based on the total weight of the CMP composition
5 and wherein said further additive is an additive other than particles (A), oxidizing
agent (B), or aqueous medium (C) and is not an additive which is added to the
CMP composition only for the purpose of adjusting its pH value.