

## SILICA PARTICLES, COMPOSITIONS COMPRISING SUCH PARTICLES, AND USES OF SUCH PARTICLES AND COMPOSITIONS

### 5      **Technical Field**

The present application relates to modified silica particles comprising a nitrogen- or phosphorus-containing group or compound, and to compositions comprising such particles as well as to uses of such modified silica particles and compositions comprising  
10      such silica particles.

### **Background**

Modern semiconductor devices, memory devices, integrated circuits, and the likes  
15      alternately comprise conductive layers, semiconductive layer, and dielectric (or insulating) layers, with the dielectric layers insulating conductive layers from each other. Connections between conductive layers may be established, for example, by metal vias. The production of such devices is a complex multi-step process, whereby conductive, semiconductive, and/or dielectric materials are consecutively deposited  
20      onto an underlying surface and may then be removed either in part or sometimes even completely again.

Over time semiconductor devices, memory devices, integrated circuits, and the likes have increased in performance, while simultaneously becoming smaller and smaller.  
25      To ensure such devices performing reliably and according to expectation, in spite of their ever increasing complexity, the requirements on the production process, for example, regarding precision, have increased as well. It is therefore necessary to have surfaces, onto which a subsequent layer is to be deposited, with a very high degree of planarity. As the required planarity cannot be achieved through deposition of the  
30      respective material, the wafer (respectively, the device to be produced) needs to be planarized by removing part or in some instances even all of such layer.

Chemical-mechanical polishing (CMP) is a widely used method for planarizing or removing part or all of a layer in the process of producing semiconductor devices and  
35      the likes. In the CMP process, an abrasive and/or corrosive chemical slurry, such as for example a slurry of silica particles, is used together with a polishing pad. Pad and substrate or surface, e.g. a wafer, are pressed together and generally rotated non-

concentrically, i.e. with different rotational axes, thereby abrading and removing material from the surface or substrate.

5 CMP may be used to polish a wide range of materials, such as metals or metal alloys (such as, for example, aluminum, copper or tungsten), metal oxides, silicon dioxide, or even polymeric materials. For each material, the polishing slurry needs to be specifically formulated so as to optimize its performance. For example, if a tungsten layer that has been deposited onto a silicon dioxide layer is to be polished, the polishing slurry preferably has a high removal rate for tungsten but a lower one for silicon dioxide  
10 so as to efficiently remove the tungsten but leave the silicon dioxide layer largely intact.

Further, because the polishing preferably is done by a combination of mechanical polishing and chemical corrosion, the silica particles need to fulfill certain requirements so as to be fully compatible with the respective formulation. For example, the  
15 composition of the silica particles needs to be modified depending upon whether the particles are to be anionic or cationic.

However, not only are the semiconductor and related industries subject to continuing cost pressures, in view of the rising pressure for increased sustainability there is also a  
20 need to reduce the amount of to be disposed-off wastes, such as CMP slurries after use. Furthermore, there is still a need in industry to provide silica particles with improved removal rates and/or allowing for good selectivity between conductive and/or semiconductive materials on the one hand, and dielectric materials on the other hand.

25 Thus, the present application aims at providing silica particles and compositions comprising such silica particles allowing for good selectivity between one or more conductive layer, which may comprise any one or more of metal, metal allow, polysilicon, and any other suitable material, and one of more dielectric layer, preferably  
30 at the same time allowing for a reduction of the silica concentration in the CMP slurry at the point of use.

### Summary

35 The present inventors have now surprisingly found that the above objects may be attained either individually or in any combination by the present modified silica particles, composition, and processes.

Thus, the present application provides for modified silica particles (i) comprising a nitrogen- or phosphorous-comprising group or compound, and (ii) having a zeta potential of at most +15 mV, determined at 25°C at 3 wt% of modified silica particles in deionized water.

The present application then also provides for a composition comprising water and such modified silica particles as defined herein, wherein the composition is acidic, preferably wherein the composition has a pH of at most 3.5.

Furthermore, the present application provides for a method of producing such modified silica particles as defined herein, said method comprising the step of

- (a) providing an aqueous dispersion of unmodified silica particles and a nitrogen- or phosphorous-comprising compound;
- (b) heating, preferably to boiling, the aqueous dispersion provided in step (a);
- (c) adding silicic acid, thereby depositing a shell of silica comprising the modifier onto the silica particles and yielding an alkaline aqueous dispersion of modified silica particles as defined herein;
- (d) passing the alkaline aqueous dispersion of modified silica particles obtained in step (c) through a cationic ion exchanger, thus yielding an acidic aqueous dispersion of modified silica particles.

Additionally the present application provides for a method for chemical mechanical polishing comprising the steps of

- (A) providing a substrate;
- (B) providing such composition as defined herein,
- (C) providing a chemical mechanical polishing pad with a polishing surface;
- (D) bringing the polishing surface of the chemical mechanical polishing pad and the composition provided in step (B) into contact with the substrate; and
- (E) polishing the substrate such that at least part of the substrate is removed.

#### Detailed description

Throughout this application, "Me" denotes a methyl group (CH<sub>3</sub>), and "Et" denotes an ethyl group (CH<sub>2</sub>-CH<sub>3</sub>).

As used herein, the term "water glass" is used to generally denote alkali salts (also referred to as "alkaline silicate" in this application), preferably sodium and potassium salts, of silicic acid  $\text{Si}(\text{OH})_4$ . The respective sodium and potassium salts may, for example, be represented by the formula  $\text{M}_{2x}\text{Si}_y\text{O}_{2y+x}$  or  $(\text{M}_2\text{O})_x \cdot (\text{SiO}_2)_y$ , with  $\text{M} = \text{Na}$  or  $\text{K}$  and, for example,  $x = 1$  and  $y$  being an integer of from 2 to 4.

As used herein, the term "water glass-based" is used to denote that the present silica particles are preferably produced from such alkali salts of silicic acid as starting material.

As used herein, the term "TMOS/TEOS-based" is used to generally denote silica particles that have been produced using  $\text{Si}(\text{OMe})_4$  ("TMOS") and/or  $\text{Si}(\text{OEt})_4$  ("TEOS") as starting material.

As used herein, the term "silicate" is used to generally denote salts and esters of silicic acid ( $\text{Si}(\text{OH})_4$ ), which throughout this application may also be referred to as "ortho-silicic acid", and its condensation products. It is also noted that a gel or a solution of silicic acid is understood to generally also comprise condensates of silicic acid.

As used herein, the term "colloidal" is used to denote particles dispersed in a medium having at least in one direction a dimension between 1 nm and 1  $\mu\text{m}$  (see also Compendium of Chemical Terminology, Gold Book, International Union of Pure and Applied Chemistry, Version 2.3.3, 2014-02-24, page 295).

In the present application, the term "point of use" denotes the chemical mechanical polishing (CMP) process. For example, the expression "composition at point of use" is used to denote the composition as used in the chemical mechanical polishing (CMP) process.

Unless otherwise specifically indicated, wt% are relative to the total weight of the respective solution or dispersion or composition.

Generally, silica particles may be obtained in a wet process in alkaline medium by polycondensation of silicic acid ( $\text{Si}(\text{OH})_4$ ) with an alkaline compound acting as catalyst. Such process is well known to the person skilled in the art and, for example, disclosed in R.K. Iler, "The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemistry of Silica", Wiley, 1979.

Starting from an alkaline silicate, such as sodium silicate and/or potassium silicate, the alkaline silicate is subjected to an ion exchange process, for example, by using a cationic ion exchanger or by adding a strong acid in sufficient amount, thereby forming silicic acid ( $\text{Si}(\text{OH})_4$ ), and following the addition of a base and rendering the solution basic, silicic acid will react (polycondensate) in presence of an alkaline catalyst to form the silica particles.

Alternatively to using an alkaline silicate as starting material, a tetraalkyl orthosilicate ( $\text{Si}(\text{OR})_4$  with R being an alkyl group, preferably methyl or ethyl) may be hydrolyzed to form silicic acid, which is subsequently polycondensated as described above to form silica particles.

For the purposes of the present application, the alkaline compound used as catalyst in the polycondensation of silicic acid is different from the modifier as defined herein. Preferably the alkaline compound used in the polycondensation of silicic acid is sodium hydroxide or potassium hydroxide, with potassium hydroxide being the more preferred one.

The production of silica particles in such a wet process may either be performed in a single step, i.e. starting from a solution/dispersion of silicic acid, or may be done using so-called seed particles, onto which then silica is further deposited to grow the silica particles to the desired size.

In general terms, the present application relates to particles comprising (i) a modifying group or compound, and (ii) a specific zeta potential (determined as described in the following).

The present modifying group or compound, which herein may also generally be referred to as “modifier”, is selected from the group consisting of nitrogen- and phosphorous-comprising groups or compounds.

Such nitrogen- and phosphorus-comprising groups or compounds may be selected from the group consisting of amines, ammonium compounds, phosphines, and phosphonium compounds, preferably organic amines, organic ammonium compounds, organic phosphines, and organic phosphonium compounds, which may be represented by the following chemical formulae (I-a) to (I-d)

|   |                   |       |
|---|-------------------|-------|
|   | $R^1R^2R^3N$      | (I-a) |
|   | $R^1R^2R^3R^4N^+$ | (I-b) |
|   | $R^1R^2R^3P$      | (I-c) |
| 5 | $R^1R^2R^3R^4P^+$ | (I-d) |

wherein  $R^1$ ,  $R^2$ ,  $R^3$ , and - if present -  $R^4$  may at each occurrence independently of each other be selected from the group consisting of hydrogen, alkyl comprising from 1 to 10 carbon atoms, arylalkyl having from 7 to 16 carbon atoms, and aryl having from 6 to 10 carbon atoms, provided that at least one of  $R^1$ ,  $R^2$ ,  $R^3$ , and - if present -  $R^4$  is not hydrogen.

Preferably  $R^1$ ,  $R^2$ ,  $R^3$ , and - if present -  $R^4$  are all alkyl comprising from 1 to 10 carbon atoms, preferably from 1 to 6 carbon atoms. Suitable alkyl may preferably be selected from the group consisting of methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl, and n-hexyl; with methyl and ethyl being more preferred, and ethyl being most preferred.

The present modifier is preferably a nitrogen-comprising group or compound, and more preferably an ammonium group or compound, and even more preferably a tetraalkyl ammonium group or compound.

Especially well suited nitrogen-comprising groups or compounds are tetramethyl ammonium ("TMA"), tetraethyl ammonium ("TEA"), tetramethyl ammonium hydroxide ("TMAH"), and tetraethyl ammonium hydroxide ("TEAH"). Tetraethyl ammonium hydroxide ("TEAH") is particularly preferred.

For the purposes of the present application the choice of (unmodified) silica particles as starting materials is not particularly limited. The silica particles used herein may, for example, be any type of colloidal silica particles. They may have been produced from any suitable starting material, and may, for example, be water glass-based or TMOS/TEOS-based as described above. Preferably, they are water glass-based colloidal silica particles or TEOS/TMOS-based colloidal silica particles, more preferably water glass-based colloidal silica particles.

Shape and dimensions of the silica particles used herein are not particularly limited, provided that such silica particles are suitable for use in CMP applications. Such silica

particles may, for example, be spherical, oval, curved, bent, elongated, branched, or cocoon-shaped.

5 For spherical silica particles, the average diameter is preferably at least 5 nm, more preferably at least 10 nm, and most preferably at least 15 nm. For spherical particles, the average diameter is preferably at most 200 nm, more preferably at most 150 nm or 100 nm, even more preferably at most 90 nm or 80 nm or 70 nm or 60 nm, still even more preferably at most 50 nm or 45 nm or 40 nm or 35 nm or 30 nm, and most preferably at most 25 nm. For example, particularly preferred silica particles have an  
10 average diameter of at least 15 nm and of at most 25 nm.

For elongated, curved, bent, branched, and oval silica particles their average diameter is preferably as described above for spherical colloidal silica particles. Preferably, such elongated or oval colloidal silica particles have an aspect ratio, i.e. the ratio of length  
15 to average diameter, of at least 1.1, more preferably of at least 1.2 or 1.3 or 1.4 or 1.5, even more preferably at least 1.6 or 1.7 or 1.8 or 1.9, and most preferably at least 2.0. Said aspect ratio is preferably at most 10, more preferably at most 9 or 8 or 7 or 6, and most preferably at most 5.

20 The present modified silica particles are produced by depositing a silica shell comprising the modifier onto unmodified silica particles.

Hence, the present modified silica particles may be produced by a production process comprising the step of

25 (a) providing an aqueous dispersion of (unmodified) silica particles as defined above and a modifier as defined above.

For the production of the present modified silica particles an aqueous dispersion of silica particles and modifier is heated, preferably to boiling, followed by the addition of  
30 silicic acid, preferably over time, thereby depositing a shell of silica comprising the modifier onto the silica particles, thus resulting in an alkaline aqueous dispersion of modified silica particles as defined herein. This step is performed with the modifier acting as alkaline catalyst, without further addition of an alkaline catalyst different from the modifier, such as sodium hydroxide or potassium hydroxide. Said alkaline aqueous  
35 dispersion of modified silica particles was then passed through a cationic ion exchanger, thereby rendering the dispersion acidic, to yield an acidic aqueous dispersion of modified silica particles as defined herein.

It is noted that when in alkaline (or basic) medium the silica particles are anionic, i.e. carry a negative charge, and when in acidic medium the silica particles are cationic, i.e. carry a positive charge.

5

The present process for producing modified silica particles therefore further comprises, preferably in sequence, the steps of

- (b) heating, preferably to boiling, the aqueous dispersion provided in step (a);
- (c) adding silicic acid, thereby depositing a shell of silica comprising the modifier  
10 onto the silica particles and yielding an alkaline aqueous dispersion of modified silica particles as defined herein;
- (d) passing the alkaline aqueous dispersion of modified silica particles obtained in step (c) through a cationic ion exchanger, thus yielding an acidic aqueous  
dispersion of modified silica particles.

15

The modifier is added in such an amount that the modified silica particles will have the specified zeta potential as defined herein. Such modifier amount to be added can easily be determined by the person skilled in the art.

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Preferably the amount of modifier to be added may be at least 1.0 wt%, more preferably at least 1.5 wt%, even more preferably at least 2.0 wt%, and most preferably at least 2.5 wt%, relative to the amount of SiO<sub>2</sub> added (see step (c) of the process above).

25

Preferably the amount of modifier to be added may at most be 4.5 wt%, more preferably at most 4.4 wt% or 4.3 wt%, even more preferably at most 4.2 wt%, still even more preferably at most 4.1 wt%, relative to the amount of SiO<sub>2</sub> added (see step (c) of the process above).

30

Without wishing to be bound by theory the present inventors have found that generally between about 40 % and about 60 %, for example about 50 %, of the modifier added will actually be incorporated into the shell of silica produced in the present process (see step (c) of the process above).

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It is noted that any modifier attached to the surface of the modified silica particle comprised in the alkaline aqueous dispersion produced in step (c) of the present

process will at least partly or in a major part or even completely be removed by the cationic ion exchanger in step (d) of the present process.

5 When in an acidic aqueous dispersion, i.e. in a composition comprising the modified silica particles as defined herein and water, the present modified silica particles are cationic, i.e. carry a permanent positive charge.

10 Preferably, the zeta potential of the present modified silica particles is at most +15 mV, preferably at most +10 mV, determined at 25°C at 3 wt% modified silica particles in deionized water as described below in detail.

15 Preferably, the zeta potential of the present modified silica particles is at least +2 mV, more preferably at least +3 mV, even more preferably at least +4 mV, and most preferably at least +5 mV, determined at 25°C at 3 wt% modified silica particles in deionized water as described below in detail.

20 The present modified silica particles may be used in a composition, the composition further comprising water. Thus, such composition comprises the present modified silica particles and water. The water is preferably deionized water.

The present composition comprising water and the above-described modified silica particles is acidic, i.e. is characterized by an acidic pH. The present composition preferably has a pH of at most 3.5 (for example, of at most 3.4, or of at most 3.3, or of at most 3.2, or of at most 3.1), and more preferably of at most 3.0.

25 Though the lower limit of the pH of the present composition is not really limited, it is preferred that such pH is at least 1.0, more preferably at least 1.5, even more preferably at least 2.0, and most preferably at least 2.5.

30 If supplied as a concentrate, which may then be diluted with water, preferably deionized water, prior to its use in a chemical mechanical polishing process, the present composition may comprise the modified silica particles in up to 20 wt%, preferably in up to 25 wt%, more preferably in up to 30 wt%, even more preferably in up to 35 wt%, still even more preferably in up to 40 wt% and most preferably in up to 50 wt%, with  
35 wt% relative to the total weight of the present composition.

Alternatively, at the point of use, i.e. when used in a chemical mechanical polishing process, the present composition preferably comprises the modified silica particles in at least 0.1 wt% (for example in at least 0.2 wt% or 0.3 wt% or 0.4 wt%), more preferably in at least 0.5 wt%, even more preferably in at least 1.0 wt%, still even more preferably in at least 1.5 wt%, and most preferably in at least 2.0 wt%, with wt% relative to the total weight of the present composition. In this case, the present composition preferably comprises the modified silica particles in at most 10 wt%, more preferably in at most 5.0 wt%, even more preferably in at most 4.0 wt%, still even more preferably in at most 3.5 wt%, and most preferably in at most 3.0 wt%, with wt% relative to the total weight of the present composition.

Optionally, the present composition further comprises any one or more of the group consisting of biocide, pH-adjusting agent, pH-buffering agent, oxidizing agent, chelating agent, corrosion inhibitor, and surfactant.

Such oxidizing agent may be any suitable oxidizing agent for the one or more metal or metal alloy of the substrate to be polished using the present composition. For example, the oxidizing agent may be selected from the group consisting of bromates, bromites, chlorates, chlorites, hydrogen peroxide, hypochlorites, iodates, monoperoxy sulfate, monoperoxy sulfite, monoperoxy phosphate, monoperoxy hypophosphate, monoperoxy pyrophosphate, organo-halo-oxy compounds, periodates, permanganate, peroxyacetic acid, ferric nitrates, and any blend of any of these. Such oxidizing agent may be added to the present composition in a suitable amount, for example, in at least 0.1 wt% and at most 6.0 wt%, with wt% relative to the total weight of the present composition at point of use.

Such corrosion inhibitor, which may, for example, be a film forming agent, may be any suitable corrosion inhibitor. For example, the corrosion inhibitor may be glycine, which may be added in an amount of at least 0.001 wt% to 3.0 wt%, with wt% relative to the total weight of the present composition at point of use.

Such chelating agent may be any suitable chelating or complexing agent for increasing the removal rate of the respective materials, preferably metal or metal alloy, to be removed, or alternatively or in combination for capturing trace metal contaminants that may unfavorably influence performance in the polishing process or in the finished device. For example, the chelating agent may be compounds comprising one or more functional groups comprising oxygen (such as carbonyl groups, carboxyl groups,

hydroxyl groups) or nitrogen (such as amine groups or nitrates). Examples of suitable chelating agents include, in a non-limiting way, acetylacetonates, acetates, aryl carboxylates, glycolates, lactates, gluconates, gallic acid, oxalates, phthalates, citrates, succinates, tartrates, malates, ethylenediaminetetraacetic acid and salts thereof, ethylene glycol, pyrogallol, phosphonates, ammonia, amino alcohols, di- and tri- amines, nitrates (e.g. ferric nitrates), and any blend of any of these.

Such biocide may be selected from any suitable biocide, for example, from isothiazolin derivative-comprising biocides. Such biocide is generally added in an amount of at least 1 ppm and of at most 100 ppm, with ppm relative to the total weight of the present composition at point of use. The amount of biocide added may be adapted depending, for example, upon the composition and planned storage period.

Such pH-adjusting agent may be selected from suitable acids, such as hydrochloric acid, nitric acid or sulfuric acid, with nitric acid or sulfuric acid being preferred, and with nitric acid being particularly preferred.

Such surfactant may be selected from any suitable surfactant, such as cationic, anionic and non-ionic surfactants. A particularly preferred example is an ethylenediamine polyoxyethylene surfactant. Generally, surfactants may be added in an amount of from 100 ppm to 1 wt%, with ppm and wt% relative to the total weight of the present composition at point of use.

Some of these compounds may exist in form of a salt, such as a metal salt, acid, or as a partial salt. Equally, some of these compounds may fulfill more than one function if comprised in a composition suitable for chemical mechanical polishing. For example, ferric nitrates, particularly  $\text{Fe}(\text{NO}_3)_3$ , may act as chelating agent and/or oxidizing agent and/or catalyst agent.

The present composition may be prepared by standard methods, well known to the person skilled in the art. Generally such preparation involves mixing and stirring phases. It can be performed either in continuous manner or batchwise.

The composition as described above may be used in a chemical mechanical polishing (CMP) process, wherein a substrate is polished. The substrate to be polished in the present CMP process comprises (i) at least one layer comprising, preferably essentially

consisting of, silicon oxide, and (ii) at least one layer comprising, preferably essentially consisting of one or more metal or metal alloy.

5 The present method for chemical mechanical polishing therefore comprises the following steps of

- (A) providing a substrate comprising (i) at least one layer comprising, preferably essentially consisting of, silicon oxide; and, preferably thereon, (ii) at least one layer comprising, preferably essentially consisting of, one or more metal or metal alloy; and
- 10 (B) providing the composition as defined herein.

As used herein, the term "thereon" is used to indicate that the metal or metal alloy-comprising layer is essentially placed / located on top of the silicon oxide-comprising layer. Expressed differently, and with respect to the chemical mechanical polishing, the layer on top is the layer that before starting to polish is in closer proximity to the polishing pad mounted on the CMP polisher.

As used herein, the term "essentially consisting of" is used to denote that such layer may comprise a minor amount of one or more different material, for example, in an amount of at most 5 wt% (for example in an amount of at most 4 wt% or 3 wt% or 2 wt% or 1 wt% or 0.5 wt% or 0.1 wt%), with wt% relative to the total weight of such layer.

Preferably, said silicon oxide comprised in the layer, which is in turn comprised in the substrate, may be selected from the group consisting of borophosphosilicate glass (BPSG), plasma-enhanced tetraethyl ortho silicate (PETEOS), thermal oxide, undoped silicate glass, high density plasma (HDP) oxide, and silane oxide.

In the CMP-process a polishing pad with a polishing surface is used for the actual polishing of the substrate. Such polishing pad may, for example, be a woven or non-woven polishing pad, and comprise or essentially consist of a suitable polymer. Exemplary polymers include polyvinylchloride, polyvinylfluoride, nylon, polypropylene, polyurethane, and any blend of these, to only name a few. Polishing pad and the to be polished substrate are generally mounted on a polishing apparatus, pressed together, and generally rotated non-concentrically, i.e. with different rotational axes, thereby - together with the compositions of the present application,

which is generally between the polishing pad and the substrate – abrading and removing material from the surface or substrate.

Thus, the present CMP process further comprises the steps of

- 5 (C) providing a chemical mechanical polishing pad with a polishing surface;
  - (D) bringing the polishing surface of the chemical mechanical polishing pad and the composition provided in step (B) above into contact with the substrate; and
  - (E) polishing the substrate such that at least a part of the substrate is removed.
- 10 The present CMP process may be applied in the production of flat panel displays, integrated circuits (ICs), memory or rigid disks, metals, interlayer dielectric devices (ILDs), semiconductors, micro-electro-mechanical systems, ferroelectrics, and magnetic heads. In other words, the substrate to be polished in the present CMP process may be selected from the group consisting of flat panel displays, integrated
- 15 circuits (ICs), memory or rigid disks, metals, interlayer dielectric devices (ILDs), semiconductors, micro-electro-mechanical systems, ferroelectrics, and magnetic heads.

### Examples

- 20 All of the materials used in the examples are commercially available. Water glass-based silica particles were obtained internally as aqueous dispersion, with SiO<sub>2</sub> content and average particle size as indicated in the following examples, from Merck KGaA, Darmstadt, Germany, and are commercially marketed under the Klebosol® tradename.
- 25 Silicic acid was obtained internally as an aqueous solution with an SiO<sub>2</sub> content as indicated in the respective examples. Tetraethyl ammonium hydroxide (denoted “TEAH”; 35 wt% in water; CAS-nr. 77-98-5) may, for example, be obtained from Sigma-Aldrich, a subsidiary of Merck KGaA, Darmstadt, Germany. Cation exchange resin used was AMBERJET™ 1200 H, supplied by DuPont de Nemours, Wilmington, Delaware, USA. Kathon ICP II biocide was obtained from DuPont de Nemours, Wilmington, Delaware, USA.
- 30

All water used was de-ionized.

- 35 Particle sizes, for which the z-average particle sizes are indicated, and zeta potential were determined by dynamic light scattering (DLS) and electrophoretic light scattering

(ELS), respectively, on a Zetasizer Nano ZSP, obtained from Malvern Instruments Limited, Worcestershire, UK.

5 For the determination of the zeta potential the instrument was first purged with ultrapure water (Type I water as defined in ASTM D 1193-06 having a resistivity of at least  $18.0 \text{ M}\Omega \cdot \text{cm}$  and a total organic carbon (TOC) content of at most 5 ppb), and then the aqueous dispersion of silica particles to be measured was injected into the instrument as is using a 10 ml syringe.

10 All wt% are relative to the total weight of the respective aqueous dispersion or solution, unless indicated otherwise.

#### Example 1

15 7840 g of an aqueous dispersion of silica particles (23.90 wt%  $\text{SiO}_2$ ; average particle size of 47.9 nm; specific surface area (SSA) of  $160.3 \text{ m}^2/\text{g}$ ) were diluted with de-ionized water to obtain 12089 g of aqueous dispersion with 15.5 wt%  $\text{SiO}_2$ , to which 17.85 g TEAH (35 wt% in water) were added at room temperature. The resulting reaction mixture was then heated to boiling. Then 4004 g of aqueous silicic acid solution (5.62 wt%  $\text{SiO}_2$ ) were added to the boiling reaction mixture, leading to about 2.78 wt% of TEAH relative to the amount of  $\text{SiO}_2$  added, under agitation over a period of about  $1\frac{3}{4}$  hours.

25 The resulting reaction mixture was kept agitated for a further 10 min at boiling temperature and subsequently allowed to cool to room temperature, all the while being agitated, yielding 11621 g of an intermediate aqueous dispersion with 18.06 wt%  $\text{SiO}_2$ .

30 The so-obtained intermediate aqueous dispersion was subsequently passed through a column of cation exchange resin, by addition of de-ionized water diluted to 13721 g of an aqueous dispersion comprising ca. 15 wt% of  $\text{SiO}_2$  and having a pH of 2.42, to which then 12.35 g of biocide Kathon ICP II were added, followed by subsequent filtration through filters having pore sizes of 5  $\mu\text{m}$ , 1.5  $\mu\text{m}$ , and 0.3  $\mu\text{m}$ , respectively. Properties of the resulting aqueous dispersion D-1 are given in Table 1 below.

35

Example 2

7840 g of an aqueous dispersion of silica particles (23.90 wt% SiO<sub>2</sub>; average particle size of 47.9 nm; specific surface area (SSA) of 160.3 m<sup>2</sup>/g) were diluted with de-ionized water to obtain 11711 g of aqueous dispersion with ca. 16 wt% SiO<sub>2</sub>, to which 21.41 g TEAH (35 wt% in water) were added at room temperature. The resulting reaction mixture was then heated to boiling. Then 4004 g of aqueous silicic acid solution (5.62 wt% SiO<sub>2</sub>) were added to the boiling reaction mixture, leading to about 3.33 wt% of TEAH relative to the amount of SiO<sub>2</sub> added, under agitation over a period of about 1¾ hours.

The resulting reaction mixture was kept agitated for a further 10 min at boiling temperature and subsequently allowed to cool to room temperature, all the while being agitated, yielding 11507 g of an intermediate aqueous dispersion with 18.24 wt% SiO<sub>2</sub>.

The so-obtained intermediate aqueous dispersion was subsequently passed through a column of cation exchange resin, by addition of de-ionized water diluted to 13642 g of an aqueous dispersion comprising ca. 15 wt% of SiO<sub>2</sub> and having a pH of 2.42, to which then 12.35 g of biocide Kathon ICP II were added, followed by subsequent filtration through filters having pore sizes of 5 µm, 1.5 µm, and 0.3 µm, respectively. Properties of the resulting aqueous dispersion D-2 are given in Table 1 below.

Example 3

7840 g of an aqueous dispersion of silica particles (23.90 wt% SiO<sub>2</sub>; average particle size of 47.9 nm; specific surface area (SSA) of 160.3 m<sup>2</sup>/g) were diluted with de-ionized water to obtain 11711 g of aqueous dispersion with ca. 16 wt% SiO<sub>2</sub>, to which 24.98 g TEAH (35 wt% in water) were added at room temperature. The resulting reaction mixture was then heated to boiling. Then 3828 g of the aqueous silicic acid solution (5.87 wt% SiO<sub>2</sub>) were added to the boiling reaction mixture, leading to about 3.89 wt% of TEAH relative to the amount of SiO<sub>2</sub> added, under agitation over a period of about 1¾ hours.

The resulting reaction mixture was kept agitated for a further 10 min at boiling temperature and subsequently allowed to cool to room temperature, all the while

being agitated, yielding 11593 g of an intermediate aqueous dispersion with 18.10 wt% SiO<sub>2</sub>.

The so-obtained intermediate aqueous dispersion was subsequently passed through a column of cation exchange resin, by addition of de-ionized water diluted to 13639 g of an aqueous dispersion comprising ca. 15 wt% of SiO<sub>2</sub> and having a pH of 2.46, to which then 12.28 g of biocide Kathon ICP II were added, followed by subsequent filtration through filters having pore sizes of 5 µm, 1.5 µm, and 0.3 µm, respectively. Properties of the resulting aqueous dispersion D-3 are given in Table 1 below.

**Table 1**  
Properties of aqueous dispersions D-1 to D-3

|                               |       | D-1   | D-2   | D-3   |
|-------------------------------|-------|-------|-------|-------|
| SiO <sub>2</sub> content      | [wt%] | 15.04 | 15.01 | 15.02 |
| Average particle size         | [nm]  | 50.3  | 45.2  | 44.2  |
| pH (at 20°C)                  |       | 2.57  | 2.61  | 2.67  |
| Zeta potential<br>(undiluted) | [mV]  | 4.8   | 7.1   | 8.1   |

Example 4

7810 g of an aqueous dispersion of silica particles (24.28 wt% SiO<sub>2</sub>; average particle size of 47.8 nm; specific surface area (SSA) of 155.9 m<sup>2</sup>/g) were diluted with 3300 g of de-ionized water, thereby obtaining 12642 g of aqueous dispersion with 15 wt% SiO<sub>2</sub>, to which 25.28 g TEAH (35 wt% in water) were added at room temperature. The resulting reaction mixture was then heated to boiling. Then 3753 g of the aqueous silicic acid solution (6.06 wt% SiO<sub>2</sub>) were added to the boiling reaction mixture, leading to about 3.89 wt% of TEAH relative to the amount of SiO<sub>2</sub> added, under agitation over a period of about 1.5 hours.

The resulting reaction mixture was kept agitated for a further 10 min at boiling temperature and subsequently allowed to cool to room temperature, all the while being agitated, yielding a first batch of 11056 g of an aqueous dispersion with 19.21 wt% SiO<sub>2</sub>.

In the same manner a further five batches were produced and then combined (or blended), yielding a total of 64174 g of an aqueous dispersion with 19.57 wt% SiO<sub>2</sub>. Respective weights and SiO<sub>2</sub> content of these batches as well as of the blend are indicated in the following Table 1.

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**Table 3**

|           | Weight<br>[g] | SiO <sub>2</sub> content<br>[wt%] |
|-----------|---------------|-----------------------------------|
| Batch 4-1 | 11056         | 19.21                             |
| Batch 4-2 | 10892         | 19.50                             |
| Batch 4-3 | 10698         | 19.85                             |
| Batch 4-4 | 10676         | 19.89                             |
| Batch 4-5 | 10464         | 19.40                             |
| Batch 4-6 | 10388         | 19.56                             |
| Blend 4   | 64174         | 19.57                             |

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The so-obtained Blend 4 was subsequently passed through a column of cation exchange resin, by addition of de-ionized water diluted to 83465 g of an aqueous dispersion (D-4) comprising ca. 15 wt% of SiO<sub>2</sub> having a pH of 2.46 were recovered, to which then 125.5 g of biocide Kathon ICP II were added. Properties of aqueous dispersion D-4 are given in Table 3 below.

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**Table 4**

Properties of aqueous dispersion D-4

|                            |                          |       |
|----------------------------|--------------------------|-------|
| SiO <sub>2</sub> content   | [wt%]                    | 14.82 |
| TEAH                       | [ppm]                    | 700   |
| Average particle size      | [nm]                     | 47.8  |
| pH (at 20°C)               |                          | 2.59  |
| Zeta potential (undiluted) | [mV]                     | 4.78  |
| Conductivity               | [mS • cm <sup>-1</sup> ] | 1.21  |

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Example 5

Chemical mechanical polishing was performed using an aqueous composition D-4' equivalent to D-4, diluted from about 15 wt% SiO<sub>2</sub> to 3 wt% SiO<sub>2</sub> using de-ionized water, and used without any further additives. Before use in chemical mechanical polishing the compositions may be filtered (0.3 μm pore size).

Polishing was then performed on a Bruker CP-4 (available from Bruker Corporation, Billerica, MA, USA) using an IC1000™ CMP polishing pad (available from DuPont de Nemours, Wilmington, Delaware, USA) on 4" TEOS (silicon oxide) wafers. Further polishing conditions were as indicated in the following Table 5.

Table 5

|                   |                       |
|-------------------|-----------------------|
| Flow rate         | 80 ml / min           |
| Polishing time    | 1 min                 |
| Dynamic force     | 3 psi as down force   |
| Platen speed (PS) | 115 rpm               |
| Head speed (HS)   | 90 rpm                |
| Pad conditioner   | A165-CIP1 (4.25", 3M) |

A comparative polishing test was performed under the same conditions using an aqueous particle composition D-5 comprising conventional silica particles, i.e. with 3 wt% SiO<sub>2</sub>.

Results of the chemical-mechanical polishing were as shown in Table 6 below, wherein example D-5 is comparative, with zeta potential determined at 25°C at 3 wt% of silica particles in deionized water.

Table 6

| Reference         | SiO <sub>2</sub><br>[wt%] | Zeta potential<br>[mV] | Removal rate<br>[A/min] |
|-------------------|---------------------------|------------------------|-------------------------|
| D-4'              | 3                         | +9.23                  | 2160                    |
| D-5 (comparative) | 3                         | -8.88                  | 117                     |

The data clearly shows that - counter to current standard knowledge - excellent removal rates, in the present case specifically for TEOS, may be obtained in acidic conditions at low zeta potentials.

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**Claims**

1. Modified silica particles (i) comprising a nitrogen- or phosphorous-comprising group or compound, and (ii) having a zeta potential of at most +15 mV, determined at 25°C at 3 wt% of modified silica particles in deionized water.  
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2. Modified silica particles according to claim 1, wherein the modified silica particles are core-shell particles, and the nitrogen- or phosphorus-comprising group or compound is comprised in the shell.  
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3. Modified silica particles according to claim 1 or claim 2, wherein the silica particles are colloidal silica particles.
4. Modified silica particles according to any of the preceding claims, wherein the silica particles are water glass-based or tetraalkoxy silane-based.  
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5. Modified silica particles according to any of the preceding claims, wherein the nitrogen comprising compound is an ammonium compound, preferably a tetraalkyl ammonium compound, more preferably a tetramethyl ammonium compound or a tetraethyl ammonium compound, even more preferably tetramethyl ammonium hydroxide or tetraethyl ammonium hydroxide, and most preferably tetraethyl ammonium hydroxide.  
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6. Composition comprising water and the modified silica particles of any one of claims 1 to 5, wherein the composition is acidic, preferably wherein the composition has a pH of at most 3.5.  
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7. Composition according to claim 6, wherein the composition has a pH of at least 1.0.  
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8. Composition according to claim 6 or claim 7, wherein the composition has a content of SiO<sub>2</sub> of at least 0.1 wt% and of at most 50 wt%, relative to the total weight of the composition.
9. Composition according to any one of claims 6 to 9, wherein the composition, has a zeta potential of at most +15 mV and preferably of at most +10 mV, determined at 25°C at 3 wt% of modified silica particles in deionized water.  
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10. Composition according to any one of claims 6 to 9, wherein the composition has a zeta potential of at least +2 mV, preferably of at least +3 mV, more preferably of at least +4 mV, and most preferably of at least +5 mV, determined at 25°C at 3 wt% of modified silica particles in deionized water.
11. Composition according to any one of the claims 7 to 10, wherein the composition comprises any one or more of the group consisting of biocide, pH-adjusting agent, pH-buffering agent, oxidizer, chelating agent, corrosion inhibitor, and surfactant.
12. Method of producing the modified silica particles of any one of claims claim 1 to 5, said method comprising the step of
- (a) providing an aqueous dispersion of unmodified silica particles and a nitrogen- or phosphorous-comprising compound;
  - (b) heating, preferably to boiling, the aqueous dispersion provided in step (a);
  - (c) adding silicic acid, thereby depositing a shell of silica comprising the modifier onto the silica particles and yielding an alkaline aqueous dispersion of modified silica particles as defined herein;
  - (d) passing the alkaline aqueous dispersion of modified silica particles obtained in step (c) through a cationic ion exchanger, thus yielding an acidic aqueous dispersion of modified silica particles.
13. Method for chemical mechanical polishing comprising the steps of
- (A) providing a substrate;
  - (B) providing the composition of any one of claims 6 to 11,
  - (C) providing a chemical mechanical polishing pad with a polishing surface;
  - (D) bringing the polishing surface of the chemical mechanical polishing pad and the composition provided in step (B) into contact with the substrate; and
  - (E) polishing the substrate such that at least part of the substrate is removed.
14. Method according to claim 13, wherein the substrate provided in step (A) comprises silicon oxide, preferably consists of silicon oxide.
15. Method according to claim 13 or claim 14, wherein the substrate is selected from the group consisting of flat panel displays, integrated circuits (ICs), memory or

rigid disks, interlayer dielectric devices (ILDs), semiconductors, micro-electro-mechanical systems, ferroelectrics, and magnetic heads.

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