

TITLE OF THE INVENTION:

SOFT POLYSILOXANE CORE-SHELL ABRASIVES
FOR CHEMICAL MECHANICAL PLANARIZATION

CROSS-REFERENCE OF RELATED APPLICATIONS

[0001] This application claims the benefit of priority to U.S. provisional application Serial No. 63/490,412, filed 03/15/2023, which is incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

[0002] This invention relates to soft polysiloxane core-shell abrasives or abrasive particles. More specifically, soft polysiloxane core-shell abrasives or abrasive particles are provided for the Chemical Mechanical Planarization (CMP) polishing with low defect rates.

[0003] In the semiconductor industry, Chemical Mechanical Planarization(CMP) is a well-known technology applied in fabricating advanced photonic, microelectromechanical, and micro-electronic materials and devices, such as semiconductor wafers. CMP polishing is an important step for recovering a selected material and/or planarizing the structure.

[0004] CMP utilizes the interplay of chemical and mechanical action to achieve the planarity of the to-be-polished surfaces. In CMP processes, chemicals and nanosized abrasives are used to planarize any irregularities which may have been generated during the deposition of the many different materials which make up a semiconductor chip.

[0005] CMP polishing composition typically comprises abrasive nanoparticles (usually colloidal particles) in aqueous solution. The nanoparticles are carefully classified in size, since too large particles may scratch the delicate structures which is a main cause for failure. However, there are many cases in which the standard nanoparticles which are known in the state of the art which are typically silica, ceria or alumina-based are still causing too many defects. The reasons for this are manifold.

[0006] It may be that the to-be-planarized structure is so delicate that even very few too big nanoparticles in a CMP polishing composition or slurry may cause damage, an irregular shape of the abrasives could cause defects, or the to-be-planarized materials are so mechanically weak or soft that even small and carefully classified nanoparticles cause unacceptable damage.

[0007] Typically, nanosized abrasives are often at least partially surface-modified with organic groups to carry charged moieties. This is done to tailor the zeta potential of the particles to be in a desired range. For example, silica may be modified with just enough aminosilanes so to exhibit a sufficiently high positive charge (positive zeta potential) at an acidic pH.

[0008] Without being bound by theory, it is believed that for achieving a stable colloidal abrasive particle dispersion, it is desirable to have the abrasive particles with a very high charge density and zeta potential. It is believed that the charge density on the abrasive particles can be a major contributor to composition performance in addition to providing repulsive forces to stabilize the colloidal abrasive particles.

[0009] Aminosilane has been used to modify the abrasive particles to have high charge density and zeta potential.

[0010] For example, US 9,028,572 B2 discloses a way to achieve abrasive particles with a charge density and zeta potential through the particle surface treatment with a compound selected from the group consisting of quaternary aminosilane compounds, dipodal aminosilane compounds, and combinations thereof.

[0011] The state of the art teaches that there are only tiny amounts of silanes necessary to significantly shift the zeta potential in a desired direction. Because the silanes are typically much more expensive than the unmodified abrasives, their concentration is kept very low, usually far below the theoretically possible amount which could bind to reactive groups on the available surfaces of the unmodified abrasives.

[0012] The known silane modification in the art does not form a separate material layer nor changes the mechanical properties of the nanoparticle in a substantial way. This is because the silane is usually bonded to the abrasives, but not to other silanes, at least not intentionally, thus, a separate layer formed by a combination of silane bonded to the surface and substantially bonded to each other is not formed. Some dimers or trimers of

silanes which may be formed by accident during surface modification are not enough to change the mechanical properties of the abrasives.

[0013] Hence, it should be readily apparent from the foregoing that there remains a need within the art for nanosized abrasives for CMP processes which cause significantly less defects, especially when used with delicate or soft materials like spin-on dielectrics (SoD) and spin-on carbon (SoC).

[0014] The present invention provides such nanosized abrasives for improved CMP polishing compositions, methods and systems. These and other advantages of the invention, as well as additional inventive features, will be apparent from the description of the invention provided herein.

SUMMARY OF THE INVENTION

[0015] The present invention provides nanosized soft polysiloxane core-shell abrasives. The CMP polishing compositions, methods, and systems using the soft polysiloxane core-shell abrasives are also provided.

[0016] In one aspect, there is provided nanosized soft polysiloxane core-shell abrasives wherein the core and the shell of the nanosized soft polysiloxane core-shell abrasives comprise different materials with different chemical and mechanical properties, the shell is preferably mechanically softer as having lower E-modulus than the core. The shell comprises crosslinked, entangled, or mixture of crosslinked and entangled polyorganosiloxane polymers. More specifically, the shell of the soft polysiloxane core-shell abrasives is polyorganosiloxane shell.

[0017] The core of nanosized soft polysiloxane core-shell abrasives comprises material having a reactive group including but being not limited to reactive OH- groups, preferably Si-OH groups around its surface to react with polyorganosiloxane shell and forming covalent bonds to bond the polyorganosiloxane shell to the surface of the core.

[0018] The core of nanosized soft polysiloxane core-shell abrasives includes but is not limited to oxides, nitrides or mixtures of at least one atom selected from the group consisting of: Si, Al, Ce, La, Zr, and Ti. Preferably, the core of nanosized soft polysiloxane core-shell abrasives is selected from the group consisting of colloidal silica, fumed silica, alumina, ceria, and combinations thereof.

[0019] The polyorganosiloxane polymer in the shell includes but is not limited to the polymers having organosiloxane moieties selected from the group consisting of silsesquioxane moieties $\text{RSiO}_{1.5}$, silicone moieties $\text{R}_1\text{R}_2\text{SiO}$, silicon moieties with 0 or 1 non-hydrolyzable group R: $\text{Si}(-\text{O}-)_4$ or $\text{SiR}(-\text{O}-)_3$; and mixtures of the moieties. Where, R can be linear or cyclic alkyl or aryl, combinations thereof and optionally can comprise heteroatoms such as O, S, N, and P; and R_1 and R_2 each independently can be aliphatic or aromatic group, combinations thereof; and optionally can comprise heteroatoms such as O, S, N, and P.

[0020] Preferably, the polyorganosiloxane shell contains > 50 molar %, >75 molar % , > 85 molar%, 90 molar %, or 95 molar % of a silicone-like structure $\text{O-Si}(\text{R}_1\text{R}_2)\text{-O}$ with each R independently being aliphatic and/or aromatic groups which may carry at least one heteroatom selected from the group consisting of S, N, O, and P.

[0021] Preferably, the polyorganosiloxane shell contains < 20 mol%, < 5mol%, < 2.5 % or 0% silicon moieties with 0 non-hydrolyzable group $\text{Si}(-\text{O}-)_4$ which function as crosslinkers.

[0022] The dominant crosslinking species or crosslinker in the polyorganosiloxane polymer are silsesquioxane moieties, silicon moieties with 0 non-hydrolyzable group: $\text{Si}(-\text{O}-)_4$, or combinations thereof. The crosslinker can either be present before or generated during the formation of the polyorganosiloxane shell.

[0023] The polyorganosiloxane shell comprises non-ionic hydrophilic groups and optionally organic C-OH groups or other hydrophilic groups. Non-ionic hydrophilic groups can also be a single component of polyorganosiloxane shell.

[0024] The polyorganosiloxane shell may also contain other groups including but not being limited to $\text{NR}_1\text{R}_2\text{R}_3$ groups and/or $\text{NR}_1\text{R}_2\text{R}_3\text{R}_4$ groups with each R independently being H, organic aliphatic and/or aromatic groups.

[0025] Polyorganosiloxane shell contains charge carriers and other hydrophilic moieties for enhancing good water or water-comprising solvents compatibility and good colloidal stability of the nanosized soft polysiloxane core-shell abrasives particles.

[0026] The polyorganosiloxane polymers can be partially crosslinked which might leave dangling ends of polymer with end groups, such as polymer- $\text{O-SiR}_1\text{R}_2\text{-OH}$ or polymer- $\text{O-SiR}(\text{OH})_2$.

[0027] The polyorganosiloxane polymers can be completely uncrosslinked with dangling ends only physically entangled with each other.

[0028] The polyorganosiloxane polymers can be additionally or solely crosslinked by organic crosslinkers. These organic crosslinkers can be short- or long-chain alkyl or aryl groups as defined above and are covalently connected to at least 2 silicon moieties

[0029] The shell can comprise crosslinked, entangled, or mixtures thereof of inorganic-organic hybrid polyorganosiloxane polymers where the crosslinkers are both inorganic polysiloxane crosslinkers using polysiloxane bonds and organic crosslinkers which are from the shell-forming precursor having more than one crosslinker moieties.

[0030] The shell is a non-ionic or anionic modified polyorganosiloxane shell.

[0031] The shell is hydrophilic, optionally comprising charge carriers being either cationic, anionic or zwitterionic at a given pH.

[0032] The shell has a thickness of >0.2 nm and <20 nm, >0.2 nm and <10 nm, >0.2 and <5 nm, or >0.2 nm and <2 nm.

[0033] The shell is mainly bonded to the core by covalent bonds via silicone moieties and silicon moieties, either $\text{Core-O-SiR}_1\text{R}_2\text{-O-}$ or Core-O-SiR(-O-)_2 or Core-O-Si(-O-)_3 with $\text{Core-O-SiR}_1\text{R}_2\text{-O-}$ or Core-O-SiR(-O-)_2 being preferred. The core surface need to contain OH- or Si-OH groups which react with silicon moieties to form covalent bonds, as an example Si-OH groups react with silicon moieties to form covalent Si-O-Si bonds.

[0034] The shell may also but is not preferred to be bonded to the core by physisorption of the polyorganosiloxane without a covalent chemical bond.

[0035] In another aspect, there is provided a method of making nanosized soft polysiloxane core-shell abrasives, comprising the steps of:

- a. providing a dispersion of core abrasives having reactive groups on their surfaces;
- b. providing a shell-forming precursor;
- c. adding the shell-forming precursor to the dispersion of core abrasives to form polyorganosiloxane shells on surfaces of the core abrasives;
- d. forming the nanosized soft polysiloxane core-shell abrasives by covalently bonding the polyorganosiloxane shells around the surfaces of the core abrasives.

[0036] The core of nanosized soft polysiloxane core-shell abrasives includes but is not limited to oxides, nitrides or mixtures of at least one atom selected from the group consisting of: Si, Al, Ce, La, Zr, and Ti. Preferably, the core of nanosized soft polysiloxane core-shell abrasives is selected from the group consisting of colloidal silica, fumed silica, alumina, ceria, and combinations thereof.

[0037] The shell-forming precursor comprises organosilane, organosiloxane, or mixtures thereof. It includes but is not limited to chlorosilanes, organoalkoxysilanes, oximatosilanes, silanols (e.g. diphenylsilandiol), siloxane oligomers with hydrolysable groups or Si-OH groups like C₅ (dimethylsiloxane with 5 repetitive units and Si-OH end groups), and combinations thereof; wherein the shell-forming precursor contains or/and generates Si-OH groups during formation of the shell.

[0038] The organoalkoxysilanes includes but is not limited to hydrolysable organoalkoxysilanes, preferably organoalkoxysilanes with at least 1, or at least 2 non-hydrolyzable groups, leading to a silicone-like, silsesquioxane-like, or mixture thereof of polyorganosiloxane; wherein the non-hydrolyzable groups can be aliphatic, aromatic, or mixtures, and may have one or more heteroatoms such as O, S, N, and P attached or included in their structure.

[0039] Additionally, the non-hydrolyzable group of the organoalkoxysilane can be covalently bonded to more than one to non-limiting number of organoalkoxysilane moiety; such as <10, <6, or <4 organoalkoxysilane moieties.

[0040] When such shell-forming precursor are used in the formation of the polyorganosiloxane shell, the polyorganosiloxane shell comprises polyorganosiloxane polymer being additionally or dominantly crosslinked by non-hydrolyzable groups so that the polyorganosiloxane shell comprises inorganic-organic hybrid polymer being crosslinked by both inorganic polysiloxane crosslinker using polysiloxane bonds and organic crosslinkers which are from the shell-forming precursor having more than one crosslinker moieties.

[0041] The organoalkoxysilane includes but is not limited to 3-(dimethoxymethylsilyl)propylamine, N-[3-(trimethoxysilyl)propyl]aniline, 3-glycidoxypropyltrimethoxysilane, (3-glycidoxypropyl)methyldiethoxysilane, (3-triethoxysilyl)propylsuccinic anhydride, 1,2-bis(triethoxysilyl)ethane, bis-(3-trimethoxysilylpropyl)amine, N,N'-bis(3-trimethoxysilylpropyl)urea, 2-(3,4-epoxycyclohexyl)ethyltriethoxysilane.

[0042] Furthermore, a reactant which is different from the shell-forming precursor can also be provided in the method, wherein non-silane reactant includes but is not limited to organic monomers, oligomers or polymers; preferably the non-silane reactant reacts with at least part of the polyorganosiloxane and is covalently incorporated in the shell structure during shell formation. Example includes but is not limited to glycidol, 1,2-diaminoethan, 1,4-diaminobutan, ethyleneglycol-1,2 diglycidylether, or poly(ethylene glycol)diglycidyl ether.

[0043] Catalysts and the process conditions of the inventive method are preferably chosen to foster hydrolysis and condensation of the organoalkoxysilane, so that the formation of the polyorganosiloxane can take place effectively.

[0044] Thus, the method of making nanosized soft polysiloxane core-shell abrasives can further comprises a step after step a, b or c: adding a catalyst to the dispersion of core abrasives.

[0045] The catalysts can be acids, bases, or metal ions; such as polymeric catalysts like ion exchangers.

[0046] The bases include but are not limited to NH_3 , amines, amino alcohols, quaternary ammonium compounds. Preferably the base is NH_3 .

[0047] The acids are mineral or organic acids. Preferably, the used acids are acids which are also used in CMP processes like nitric acid.

[0048] The metal ions are the ones used and/or at least tolerated in CMP processes, like Ce, Al, Ti, Zr, W, Cu.

[0049] The method of making nanosized soft polysiloxane core-shell abrasives can further have a process condition of: pH is from 2 to 5 or from 8 to 11.

[0050] In yet another aspect, there is provided a CMP polishing composition comprising:

nanosized soft polysiloxane core-shell abrasives disclosed above; and
a solvent selected from the group consisting of water, water-soluble solvent,
and combinations thereof;
wherein
the composition has a pH of 2 to 10, 2 to 6, 2 to 5, 2 to 4, or 2 to 3.

[0051] The water includes but is not limited to deionized (DI) water, distilled water, and the water-soluble solvent t is not limited to alcoholic organic solvents.

[0052] The CMP polishing composition can optionally comprise at least one of:
organic and inorganic salt as colloidal stabilizer;
acid/base buffer agent;
biocide;
oxidizer;
catalyst;
corrosion inhibitor;
organic polymers as erosion, dishing and corrosion reducer; wherein example polymers include but are not limited to hydrophilic polymers, polymers with organic functional groups like -OH, -NH, CN, ester, amide, halogen, ether, inorganic polymers for like mono-metal- or mixed-metal polymetalhydroxide clusters, polyanions, polycations, especially those containing Al, Ce, Zr, Fe as metal ions;
surface-active molecules/oligomers/polymers like cationic-, anionic- or nonionic surfactants and polymers which attach by either physical adsorption, ionic or covalent bonding.

[0053] In another aspect, there is provided a method of CMP polishing a substrate having at least one surface comprising at least one material selected from the group consisting of a metal includes but is not limited to tungsten, copper, ruthenium, cobalt, aluminum, and combinations thereof; metal alloys; a dielectric material includes but is not limited to silicon dioxide and/or silicon nitride; spin-on dielectrics (SoD); and spin-on carbon(SoC); using the CMP polishing composition described above.

[0054] The silicon dioxide polished silicon oxide films can be Chemical vapor deposition (CVD), Plasma Enhance CVD (PECVD), High Density Deposition CVD(HDP), or spin on silicon oxide films.

DETAILED DESCRIPTION OF THE INVENTION

[0055] This invention relates to soft polysiloxane core-shell abrasives, more specifically, the Chemical Mechanical Planarization (CMP) polishing composition (also known as slurry or formulation), methods, and systems using soft polysiloxane core-shell abrasives with amino-functional polyorganosiloxane shell.

[0056] The CMP polishing compositions, method and system using soft polysiloxane core-shell abrasives are specifically suitable for low defects CMP applications for polishing a substrate having at least one surface comprising at least one material selected from the group consisting of a metal includes but is not limited to tungsten, copper, ruthenium, cobalt, aluminum, and combinations thereof; metal alloys; dielectric material includes but is not limited to silicon dioxide and/or silicon nitride; spin-on dielectrics (SoD); and spin-on carbon (SoC) using the CMP polishing composition described above.

[0057] The soft polysiloxane core-shell abrasive has a core containing standard abrasive materials or particles such as silica or ceria; and a covalently bonded shell consisting of a chemical and mechanical different material from the core. The shell is softer by exhibiting a lower Young's modulus or E-modulus and showing plastic and/or viscoelastic properties unlike the core. Preferably, the shell consists of polyorganosiloxane(s).

[0058] The shell showing either cationic, anionic, non-ionic or zwitterionic charge depending on the pH or independent of the pH by carrying so called permanent charge carriers like tetraalkylammonium ions.

[0059] The soft polysiloxane core-shell abrasive particles have a zeta potential of ≥ 20 mV or ≤ -20 mV at a given pH in water; having a zeta potential near zero is possible without affecting the colloidal stability when the polymer is hydrophilic enough and comprises enough hydrophilic non-ionic moieties to ensure a steric stabilization.

[0060] The shell is thick enough with different mechanical properties compared to the core, so that the consequences of an impact of the abrasive on the to-be-planarized surfaces are effectively mitigated. On the other hand, the shell is not too thick so to degrade the desired high removal rate.

[0061] The shell has a thickness of >0.2 nm and <20 nm, >0.2 nm and <10 nm, >0.2 nm and <5 nm, or >0.2 nm and <2 nm.

[0062] Without wanting to be bound by any theory, it is believed that the shell with silicone- or silsesquioxane-like moieties changes the micro-tribological behavior of the abrasives so that defects, especially scratch generation is mitigated. The thickness of the shell is significantly larger than a monolayer of silanes which is known by the state of the art.

[0063] Surprisingly and unexpectedly, the removal rates of the soft polysiloxane core-shell abrasives increased or at least did not decrease compared to the original unmodified or state of the art modified (silanized) abrasive. This is counterintuitive and could not reasonably be expected, since a soft surface modification of a hard abrasive is meant to also decrease the abrasiveness of the particles in the CMP process.

[0064] The present invention provides the core-shell abrasives for CMP process making it possible to combine both highest removal rates and exceptionally low defectivity for the needs of the microelectronic fabrication of today's and future nodes.

[0065] The invention can even be demonstrated by using fumed silica as cores for the soft polysiloxane core-shell abrasives. The fumed silica abrasives are well known in the art for causing an undesirably high defect level in the CMP process. The defect level for soft polysiloxane core-shell abrasives using fumed silica as the cores can be shown to be even below the level of colloidal silica which is known to have low defect level in the art.

[0066] Typically, silicone- and silsesquioxane-like structures are hydrophobic and tend to destabilize in water-borne colloidal dispersions. The present invention overcomes the problem by using hydrophilic and/or charge-carrying silicone moieties to make the soft polysiloxane core-shell abrasives or abrasive particles stable against precipitation or flocculation.

[0067] In one aspect, there is provided nanosized soft polysiloxane core-shell abrasives wherein the core and the shell of the nanosized soft polysiloxane core-shell abrasives comprise different materials with different chemical and mechanical properties preferably the shell is mechanically softer such as having lower E-modulus; and the shell comprises crosslinked, entangled, or mixture of crosslinked and entangled polyorganosiloxane polymers.

Cores Of The Inventive Abrasives

[0068] The cores of the inventive soft polysiloxane core-shell abrasives can be inorganic or inorganic/organic hybrids. The cores may have a surface modification according to the state of the art like silanes attached to their surface. The cores can have any shape includes but is not limited to round, egg shape, elongated or branched

shapes. The surface of the core can be any quality or condition, includes but is not limited to smooth, rough, with or without protrusions.

[0069] The cores can be of any composition with reactive groups around its surface which are capable of reacting with the polyorganosiloxane shell and forming covalent bonds. For example, the cores can exhibit reactive OH-groups on their surface which can covalently bound to OH-groups of the polyorganosiloxane shell. Examples of the composition includes but is not limited to oxides and/or nitrides comprising at least one of the following atoms: Si, Al, Ce, La, Zr, and Ti.

[0070] Preferably the core consists of SiO₂ with Si-OH groups around the surface. The core can be either made by wet processes (e.g. Stöber process) or thermal processes (flame synthesis, gas phase synthesis).

[0071] The cores have a mean particle size(MPS) measured by Dynamic Light Scattering (DLS) < 500 nm, < 400 nm, < 300 nm, or < 200 nm; and > 2 nm, > 10 nm, >15 nm, or > 25 nm.

Raw Materials as Shell-Forming Precursor For Making The Shell

[0072] All raw materials as shell-forming precursors comprise organosilane, organosiloxane, or mixtures of the two. The shell-forming precursors form the shell and covalently bond the shell around the surfaces of the cores upon reacting with the reactive groups around the surfaces of the cores.

[0073] Examples of shell-forming precursors include but are not limited to: chlorosilanes, organoalkoxysilanes, oximatosilanes, silanols (e.g. diphenylsilandiol), or siloxane oligomers with hydrolysable groups or Si-OH groups like C5 (dimethylsiloxane with 5 repetitive units and Si-OH end groups): generally all precursors contain or/and can generate Si-OH groups under the conditions of the shell formation.

[0074] The organoalkoxysilanes include but are not limited to hydrolysable organoalkoxysilanes. Preferably, the hydrolysable organoalkoxysilanes have at least 1, preferably 2 non-hydrolyzable groups, leading to a silicone-like, silsesquioxane-like, or mixtures thereof; wherein the non-hydrolyzable groups can be aliphatic, aromatic, or mixtures, and may have one or more heteroatoms such as O, S, N, and P attached or included in their structure.

[0075] Additionally, the non-hydrolyzable group of the organoalkoxysilanes can be covalently bonded to more than one and non-limiting number of organoalkoxysilane moiety; such as <10, <6, and preferably <4 organoalkoxysilane moieties.

[0076] An example is the reaction product of 3-glycidoxypropyltrimethoxysilane with 3-aminopropylmethyldimethoxysilane. The epoxy group and the amino group react to form an organic crosslinker which connects 2 silane moieties with hydrolysable alkoxy groups. Another example is the reaction product of hexamethyldiisocyanate with 3-aminopropyltrimethoxysilane. Both reactions yield a silane in which 2 organoalkoxysilane moieties are covalently linked by one non-hydrolyzable group. Another example is the reaction product of 3-aminopropylmethyldimethoxysilane with (3-triethoxysilyl)propylsuccinic anhydride. Also, commercially available bipodal silanes like e.g. 1,2-bis(triethoxysilyl)ethane, bis-(3-trimethoxysilylpropyl)amine or N,N'-bis(3-trimethoxysilylpropyl)urea can be used.

[0077] When such organoalkoxysilanes are used in the formation of the polyorganosiloxane shell, the polyorganosiloxane shell comprises both inorganic polysiloxane crosslinker using polysiloxane bonds and organic crosslinkers yielding an inorganic-organic hybrid polymer.

[0078] Preferably, at least >25 molar %, > 50 molar %, preferably > 75 molar % of the hydrolysable organoalkoxysilanes have hydrophilic- and/or charge carrying groups.

[0079] If especially soft materials are to be planarized, it is preferred if at least a part of the non-hydrolyzable groups comprise aromatic structure moieties. More preferably, these aromatic moieties are bonded to the Si-atom via an aliphatic spacer which may comprise one or more heteroatoms such as O, S, N, and P.

Shells Of The Inventive Abrasives

[0080] The shells of the inventive soft polysiloxane core-shell abrasives comprise inorganic-organic polymer or organic polymer; preferably inorganic-organic polymer, most preferably polyorganosiloxane polymer.

[0081] Importantly, in contrast to the state-of-the-art simple silane surface modification in which silanes are linked to the surface of the cores but are essentially not crosslinked or polymerized with each other, polymer such as polyorganosiloxane polymer

modification involves crosslinking, entangling, or polymerizing among the polymers as well in the present invention.

[0082] The mechanical properties of the shell are different from the core. Preferably, the shell is softer than the core such as having lower E-modulus and having viscoelastic or plastic deformability under the conditions of the CMP process unlike the core.

[0083] The polyorganosiloxane polymer in the shell includes but is not limited to the polymers having organosiloxane moieties selected from the group consisting of silsesquioxane moieties $\text{RSiO}_{1.5}$, silicone moieties $\text{R}_1\text{R}_2\text{SiO}$, silicon moieties with 0 or 1 non-hydrolyzable group R: $\text{Si}(-\text{O}-)_4$ or $\text{SiR}(-\text{O}-)_3$; and combinations of the moieties. Where R can be linear or cyclic alkyl or aryl, combinations thereof and optionally can comprise heteroatoms such as O, S, N, and P; and R_1 and R_2 each independently can be aliphatic or aromatic group, combinations thereof and optionally can comprise heteroatoms such as O, S, N, and P.

[0084] Preferably, the polyorganosiloxane shell contains > 50 molar %, >75 molar %, > 85 molar%, 90 molar %, or 95 molar % of a silicone-like structure $\text{O-Si}(\text{R}_1\text{R}_2)\text{-O}$ with each R independently being aliphatic and/or aromatic groups which may carry at least one heteroatom selected from the group consisting of S, N, O, and P.

[0085] Preferably, the polyorganosiloxane shell contains < 20 mol%, < 5mol%, < 2.5 % or 0% silicon moieties with 0 non-hydrolyzable group $\text{Si}(-\text{O}-)_4$ which function as crosslinkers.

[0086] The dominant crosslinking species or crosslinker in the polyorganosiloxane polymer are silsesquioxane-moieties, silicon moieties with 0 non-hydrolyzable group: $\text{Si}(-\text{O}-)_4$, or combinations thereof. The crosslinker can either be present before or generated during the formation of the polyorganosiloxane shell

[0087] The polyorganosiloxane shell comprises polyorganosiloxane polymer being crosslinked, entangled with each other, or the mixtures of both. The polyorganosiloxane shell can have loose ends or can be completely bonded to the core surface.

[0088] The polyorganosiloxane shell is preferably covalently bonded to the core surface by Si-O- linkers.

[0089] The polyorganosiloxane shell comprises crosslinked, entangled, or mixtures thereof of polyorganosiloxane polymers where the crosslinker is inorganic polysiloxane crosslinkers using polysiloxane bonds. The polyorganosiloxane polymers can be partially

crosslinked which might leave dangling ends of polymer with end groups, such as polymer-O-SiR₁R₂-OH or polymer-O-SiR(OH)₂. The polyorganosiloxane polymers can be completely uncrosslinked with dangling ends only physically entangled with each other.

[0090] The polyorganosiloxane polymers can be additionally or solely crosslinked by organic crosslinkers. These organic crosslinkers can be short- or long-chain alkyl or aryl groups as defined above and are covalently connected to at least 2 silicon moieties

[0091] Furthermore, the polyorganosiloxane shell comprises polyorganosiloxane polymer being additionally or dominantly crosslinked by non-hydrolyzable groups so that the polyorganosiloxane shell comprises inorganic-organic hybrid polymer being crosslinked by both inorganic polysiloxane crosslinker using polysiloxane bonds and organic crosslinkers.

[0092] Optionally, polyorganosiloxane shell comprises non-ionic hydrophilic groups as part of or single component of the polyorganosiloxane shell, and/or organic C-OH groups or other hydrophilic groups.

[0093] Polyorganosiloxane shell may also contains NR₁R₂R₃ groups and/or NR₁R₂R₃R₄ groups with each R independently being H, organic aliphatic and/or aromatic groups.

[0094] Polyorganosiloxane shell contains charge carriers and other hydrophilic moieties for enhancing good water or water-comprising solvents compatibility and good colloidal stability of the nanosized soft polysiloxane core-shell abrasives particles.

[0095] The shell has mechanical properties which are different from the core by at least > 10% different, preferably > 20% and most preferably > 50% different, such as measured by Atomic Force Microscopy (AFM) nanoindentation or other method.

[0096] The soft polysiloxane core-shell abrasives have amino-functional polyorganosiloxane shell with a thickness of <20 nm, <10 nm, <5 nm, or <2 nm; and >0.2 nm.

[0097] The shell is mainly bonded to the core by covalent bonds via silicon moiety, either Core-O-SiR₁R₂-O- or Core-O-SiR(-O-)₂ or Core-O-Si(-O-)₃ with Core-O-SiR₁R₂-O- or Core-O-SiR(-O-)₂ being preferred. The core surface must contain OH- or Si-OH groups which react with silicon moieties to form covalent bonds, as an example Si-OH groups react with silicon moieties to form covalent Si-O-Si bonds.

[0098] The shell may also but is not preferred to be bonded to the core by physisorption of the polyorganosiloxane without a covalent chemical bond.

Soft polysiloxane core-shell Abrasives

[0099] The soft polysiloxane core-shell abrasives are hydrophilic, optionally comprising charge carriers. Charge carriers are either cationic, anionic or zwitterionic at a given pH.

[00100] The soft polysiloxane core-shell abrasives are colloidally stable upon dispersion in water or water-comprising solvents either by charge carriers or other hydrophilic groups (e.g. -OH, ether). Preferably, the soft polysiloxane core-shell abrasives are colloidally stable up to a solid content of 40 wt. %

[00101] The inventive soft polysiloxane core-shell abrasives can have narrow or broad, monomodal or polymodal size distributions. The shape of the soft polysiloxane core-shell abrasives can be any shape; includes but is not limited to round, egg, elongated, irregular or branched, or combinations thereof. The surface of the soft polysiloxane core-shell abrasives can be smooth, rough, with or without protrusions.

[00102] The inventive soft polysiloxane core-shell abrasives are also compatible with typical CMP additives like oxidizers, catalysts, surfactants, inhibitors, topo additives and the like, also in concentrated CMP slurries, and are hydrophilic and good-wetting of to-be-planarized surfaces

[00103] The soft polysiloxane core-shell abrasives usually have a MPS measured by Dynamic Light Scattering (DLS) ranging from 5 to 500 nm, 10 to 400 nm, 15 to 300nm, 20 to 200 nm, or 30 to 150 nm.

Process To Make Inventive Soft polysiloxane core-shell Abrasives

[00104] The process to make soft polysiloxane core-shell abrasives can start with a dispersion of core abrasives in a solvent optionally comprising water.

[00105] The shell-forming precursor(s) are added to the dispersion of core abrasives at a given pH under agitation (acid and alkaline processes are possible).

[00106] Preferably, the shell-forming precursors are monomers, but can also comprise dimers, trimers, oligomers or polymers which have been pre-formed by a separate

process step which may comprise adding water and optionally a catalyst to the precursors.

[00107] The reaction medium contains optional additional catalysts and reactants to foster shell formation. The pH is adjusted so that the shell forms and the polymer reacts with the surface reactive groups of the core. Preferably, the pH is either kept < 5 or > 8 ; such as a pH from 2 to 5 or a pH from 8-11.

[00108] The downstream processing involves at least one purification step to remove soluble and/or insoluble byproducts of the reaction. Preferably, after the reaction the volatile organic reactants and byproducts are removed from the dispersion and the solvent is replaced by water.

[00109] The preferred process to make soft polysiloxane core-shell abrasives is to provide a dispersion of a nanoparticle dispersion in a solvent which comprises water at a pH of either 2-3 or 10-11 and add the shell-forming precursors slowly dropwise under intensive agitation and pH control. Then, after an additional reaction time of 1-4 hours, the volatile byproducts are removed by distillation and replaced by water while the pH is kept constant. Then the pH may be adjusted by adding acid or base or exposing the dispersion to an ion-exchanger resin. The dispersion may be further purified by centrifugation/redispersion or membrane filtration.

[00110] The catalysts can be acids, bases, or metal ions; such as polymeric catalysts like ion exchangers.

[00111] The bases include but are not limited to NH_3 , amines, amino alcohols, quaternary ammonium compounds. Preferably the base is NH_3 .

[00112] The acids are mineral or organic acids. Preferably, the used acids are acids which are also used in CMP processes like nitric acid.

[00113] The metal ions are the ones used and/or at least tolerated in CMP processes, like Ce, Al, Ti, Zr, W, Cu.

[00114] Solvents include but are not limited to water, alcohols (preferred), methanol, ethanol, propanol; and other common polar protic and aprotic solvents like ketones, esters, ethers, acetamides. xxx

[00115] Preferably solvents which are at least partially miscible with water, and which do not react with amino groups or other chemical groups of the polyorganosiloxane.

[00116] In another aspect, there is provided a method of making nanosized soft polysiloxane core-shell abrasives, comprising the steps of:

- a. providing a dispersion of core abrasives wherein the core abrasives have reactive groups around its surface;
- b. providing a shell-forming precursor;
- c. adding the shell-forming precursor to the dispersion of core abrasives to form polyorganosiloxane shells on surfaces of the core abrasives;
- d. forming the nanosized soft polysiloxane core-shell abrasives by covalently bonding the polyorganosiloxane shells around the surfaces of the core abrasives.

[00117] The shell-forming precursor comprises organosilane, organosiloxane, or mixtures. The shell-forming precursor includes but is not limited to of chlorosilanes, alkoxy silanes, oximatosilanes, silanols (e.g. diphenylsilandiol), siloxane oligomers with hydrolysable groups or Si-OH groups like C₅ (dimethylsiloxane with 5 repetitive units and Si-OH end groups), and combinations thereof; wherein the shell-forming precursor contains or generates Si-OH groups during formation of the shell.

[00118] The organosiloxane includes but is not limited to hydrolysable organoalkoxy silanes, preferably organoalkoxy silanes with at least 1, preferably 2 non-hydrolyzable groups, leading to a silicone-like, silsesquioxane-like, or mixture thereof of polyorganosiloxane; wherein the non-hydrolyzable groups can be aliphatic, aromatic, or mixtures thereof, and may have one or more heteroatoms such as O, S, N, and P attached or included in their structure.

[00119] Additionally, the non-hydrolyzable group of the organoalkoxy silanes can be covalently bonded to more than one and non-limiting number of organoalkoxy silane moiety; such as <10, <6, and preferably <4 organoalkoxy silane moieties.

[00120] An example is the reaction product of 3-lycidoxypropyltrimethoxysilane with 3-aminopropylmethyldimethoxysilane. The epoxy group and the amino group react to form an organic crosslinker which connects 2 silane moieties with hydrolysable alkoxy groups. Another example is the reaction product of hexamethyldiisocyanate with 2 moles of 3-aminopropyltrimethoxysilane. Both reactions yield a silane in which 2 organoalkoxy silane moieties are covalently linked by one non-hydrolyzable group. Another example is the reaction product of 3-aminopropylmethyldimethoxysilane with (3-

triethoxysilyl)propylsuccinic anhydride. Also, commercially available bipodal silanes like e.g. 1,2-bis(triethoxysilyl)ethane, bis-(3-trimethoxysilylpropyl)amine or N,N'-bis(3-trimethoxysilylpropyl)urea can be used.

[00121] When such organosiloxane s are used in the formation of the polyorganosiloxane shell, the polyorganosiloxane shell will be crosslinked by both polysiloxane bonds and organic crosslinkers at the same time yielding an inorganic-organic hybrid polymer.

[00122] The organosiloxane includes but is not limited to 3-(dimethoxymethylsilyl)propylamine, N-[3-(trimethoxysilyl)propyl]aniline, 3-glycidoxypropyltrimethoxysilane, (3-glycidoxypropyl)methyldiethoxysilane, (3-triethoxysilyl)propylsuccinic anhydride, 1,2-bis(triethoxysilyl)ethane, bis-(3-trimethoxysilylpropyl)amine, N,N'-bis(3-trimethoxysilylpropyl)urea, 2-(3,4-epoxycyclohexyl)ethyltriethoxysilane,

[00123] Furthermore, a non- organosiloxane reactant can also be provided in the method, wherein non-silane reactant includes but is not limited to organic monomers, oligomers or polymers; preferably the non-silane reactant reacts with at least part of the polyorganosiloxane and is covalently incorporated in the shell structure during shell formation.

[00124] Example of the reactant includes but is not limited to glycidol, 1,2-diaminoethan, 1,4-diaminobutan, ethyleneglycol-1,2 diglycidylether or poly(ethylene glycol)diglycidyl ether.

[00125] The process conditions of the inventive method are preferably chosen to foster hydrolysis and condensation of the silane, so that the formation of the polyorganosiloxane can take place effectively. This can be done by any method known in the art, preferably by choosing a suitable pH or by introducing catalysts. It is preferred to have a pH either from 2 to 5 or from 8-11 to avoid further catalysts.

[00126] In yet another aspect, there is provided a CMP polishing composition comprises:

nanosized soft polysiloxane core-shell abrasives disclosed above; and
a solvent selected from the group consisting of water, water-soluble solvent, and combinations thereof;

wherein

the composition has a pH of 2 to 10, 2 to 8, 2 to 6, 2 to 5, 2 to 4, or 2 to 3.

[00127] The water includes but is not limited to deionized (DI) water, distilled water, and the water-soluble solvent t is not limited to alcoholic organic solvents.

[00128] The CMP polishing composition can optionally comprise at least one of:
organic and inorganic salt as colloidal stabilizer;
acid/base buffer agent;
biocide;
oxidizer;
catalyst;
corrosion inhibitor;
organic polymers as erosion, dishing and corrosion reducer; wherein example polymers include but are not limited to hydrophilic polymers, polymers with organic functional groups like -OH, -NH, -CN, ester, amide, halogen, ether, inorganic polymers for like mono-metal- or mixed-metal polymetalhydroxide clusters, polyanions, polycations, especially those containing AL, Ce, Zr, Fe as metal ions;
surface-active molecules/oligomers/polymers like cationic-, anionic- or nonionic surfactants and polymers which attach by either physical adsorption, ionic or covalent bonding.

[00129] In another aspect, there is provided a method of chemical mechanical polishing (CMP) a substrate having at least one surface comprising at least one material selected from the group consisting of a metal includes but is not limited to tungsten, copper, ruthenium, cobalt, aluminum, and combinations thereof; metal alloys; a dielectric material includes but is not limited to silicon dioxide and/or silicon nitride; spin-on dielectrics (SoD); and spin-on carbon(SoC); using the CMP polishing composition described above.

[00130] The silicon dioxide films can be Chemical vapor deposition (CVD), Plasma Enhance CVD (PECVD), High Density Deposition CVD(HDP), or spin on silicon oxide films.

CMP Methodology

[00131] In the examples presented below, CMP experiments were running using the procedures and experimental conditions given below.

GLOSSARY

PARAMETERS

General

- [00132] Å or A: angstrom(s) – a unit of length
- [00133] BP: back pressure, in psi units
- [00134] CMP: chemical mechanical planarization = chemical mechanical polishing
- [00135] CS: carrier speed
- [00136] DF: Down force: pressure applied during CMP, units: psi
- [00137] min: minute(s)
- [00138] ml: milliliter(s)
- [00139] mV: millivolt(s)
- [00140] psi: pounds per square inch
- [00141] PS: platen rotational speed of polishing tool, in rpm (revolution(s) per minute)
- [00142] SF: composition flow, ml/min
- [00143] wt. %: weight percentage (of a listed component)
- [00144] TEOS: tetraethyl orthosilicate
- [00145] SOC: spin-on-carbon
- [00146] SoD: spin-on-dielectric
- [00147] W: TEOS Selectivity: (removal rate of W)/ (removal rate of TEOS)
- [00148] HDP: high density plasma deposited TEOS
- [00149] TEOS or HDP Removal Rates: Measured TEOS or HDP removal rate at a given down pressure.

Synthesis Of Soft Polysiloxane Core-Shell Abrasives

1. Synthesis of Soft Polysiloxane Core-Shell Structure Abrasives Using Fumed Silica As Core Particles

Example 1

[00150] In a 1000 ml 4-neck flask equipped with a condenser and KPG stirrer, 397 g of a fumed silica powder dispersion in water (806.3 mmol SiO₂; Brunauer-Emmett-Teller (BET) surface area of approx. 300 m²/g; tradename Aerosil® 300 from Evonik AG) were adjusted under vigorous stirring to pH 2 with nitric acid.

[00151] In a 250 ml round flask, concentrated nitric acid (65 w%; 4.87 ml; 69.88 mmol) was added to methanol (120.42 ml; 2,968.92 mmol) under magnetic stirring. Then, 3-(dimethoxymethylsilyl)propylamine (3.80 g; 23.29 mmol) was added and the mixture was quickly added to the fumed silica dispersion under vigorous stirring.

[00152] The temperature of the fumed silica dispersion which was at room temperature raised to 30°C after the addition and was allowed to cool down naturally. After 1 hour, the temperature was raised to 70°C and kept for 2 hours under continuous stirring.

[00153] The reaction mixture was transferred to a round flask and the volatile organic solvents were removed and replaced by deionized water so that a solid content of soft core-shell silica of approximately 20 wt. % was achieved.

[00154] Yield: 293.3 g; solid content 18.0%wt; pH: 1.15; MPS (determined by DLS): 66.6 nm; polydispersity index (PDI): 0.157; Zetapotential: 31.1 mV

Example 2

[00155] In a 1000 ml 4-neck flask equipped with a condenser and KPG stirrer, 318,6 g of a fumed silica powder dispersion in water (915,4 mmol SiO₂; BET surface area of approx. 50 m²/g; tradename Aerosil® OX50 from Evonik AG) were adjusted under vigorous stirring to pH 2 with nitric acid.

[00156] In a 250 ml round flask, concentrated nitric acid (65 w%; 5.45 ml; 79.20 mmol) was added to methanol (102.57 ml; 2,529,03 mmol) under magnetic stirring. Then, 3-

(dimethoxymethylsilyl)propylamine (4.54 ml; 26.40 mmol) was added and the mixture was quickly added to the fumed silica dispersion under vigorous stirring.

[00157] The temperature of the fumed silica dispersion which was at room temperature raised to 30°C after the addition and was allowed to cool down naturally. After 1 hour, the temperature was raised to 70°C and kept for 2 hours under continuous stirring.

[00158] The reaction mixture was transferred to a round flask and the volatile organic solvents were removed and replaced by deionized water so that a solid content of soft core-shell silica of approximately 20 wt.% was achieved.

[00159] Yield: 269.6g; solid content: 21.9%; MPS (determined by DLS): 237.7nm; PDI: 0.142; zetapotential: 49.2mV

Example 3

[00160] In a 2000 ml 4-neck flask equipped with a condenser and KPG stirrer, 1,150.00 g of a fumed silica dispersion (offered as predispersed product Aerodisp® W7622 from company Evonik AG; 3.827,97 mmol SiO₂; ion-exchanged until the pH was < 4.5) was adjusted to pH 3 with nitric acid.

[00161] In a 250 ml round flask, concentrated nitric acid (65 w%; 15.41 ml; 224.06 mmol) was added to methanol (170.28 ml; 4,198.29 mmol) under magnetic stirring. Then, 3-(dimethoxymethylsilyl)propylamine (11.9 ml; 69.19 mmol) was added and the mixture was quickly added to the fumed silica dispersion under vigorous stirring.

[00162] The temperature of the silica dispersion which was at room temperature raised to 27°C after the addition and was allowed to cool down naturally. After 1 hour, the temperature was raised to 70°C and kept for 2 hours under continuous stirring.

[00163] The reaction mixture was transferred to a round flask and the volatile organic solvents were removed and replaced by deionized water so that a solid content of soft core-shell silica of approximately 20 wt.% was achieved. The product was pressure-filtered over a 2 µm filter

[00164] Yield: 1132.6 g; solid content: 21.6 wt.%; MPS (determined by DLS): 117.0 nm; PDI: 0.169; Zetapotential: 32.0mV.

2. Comparative Example Synthesis Of Abrasives Using Fumed Silica As Core Particles But Having No Soft Polysiloxane Core-Shell Structure

Comparative Example 1

[00165] In a 1000 ml 4-neck flask equipped with a condenser and KPG stirrer, 399 g of a fumed silica powder dispersion in water (806.3 mmol SiO₂; BET surface area of approx. 300 m²/g, tradename Aerosil® 300 from Evonik AG) were adjusted under vigorous stirring to pH 2 with nitric acid.

[00166] In a 250 ml round flask, concentrated nitric acid (65 w%; 0.304 ml; 4.36 mmol) was added to methanol (30.1ml; 742.23 mmol) under magnetic stirring. Then, 3-(dimethoxymethylsilyl)propylamine (0.237 g; 1.455 mmol) was added and the mixture was quickly added to the fumed silica dispersion under vigorous stirring.

[00167] The temperature of the fumed silica dispersion which was at room temperature raised to 22°C after the addition and was allowed to cool down naturally. After 1 hour, the temperature was raised to 70°C and kept for 2 hours under continuous stirring.

[00168] The reaction mixture was transferred to a round flask and the volatile organic solvents were removed and replaced by deionized water so that a solid content of core-shell silica of approximately 20 wt.% was achieved.

[00169] Yield: 282.1 g; Solid content: 18.5 wt.%; pH: 1.9; MPS (determined by DLS): 158.3 nm; PDI: 0.147; Zetapotential: 27.3 mV

Comparative Example 2

[00170] In a 1000 ml 4-neck flask equipped with a condenser and KPG stirrer, 321.9 g of a fumed silica powder dispersion in water (921.1 mmol SiO₂; BET surface area of approx. 50 m²/g; tradename Aerosil® OX50 from Evonik AG) were adjusted under vigorous stirring to pH 2 with nitric acid.

[00171] In a 250 ml round flask, concentrated nitric acid (65 w%; 0.059 ml; 0.856 mmol) was added to methanol (24.42 ml; 602.15 mmol) under magnetic stirring. Then, 3-(dimethoxymethylsilyl)propylamine (4.54 ml; 0.2855 mmol) was added and the mixture was quickly added to the fumed silica dispersion under vigorous stirring.

[00172] The temperature of the fumed silica dispersion which was at room temperature raised to 21°C after the addition and was allowed to cool down naturally. After 1 hour, the temperature was raised to 70°C and kept for 2 hours under continuous stirring.

[00173] The reaction mixture was transferred to a round flask and the volatile organic solvents were removed and replaced by deionized water so that a solid content of core-shell silica of approximately 20 wt.% was achieved.

[00174] Yield: 260.8 g; Solid content 21.2 wt.%; pH: 1.9; MPS (determined by DLS): 231.2nm; PDI: 0.148; Zetapotential: 31.4 mV

Comparative Example 3

[00175] In a 2000 ml 4-neck flask equipped with a condenser and KPG stirrer, 1,150.00 g of a fumed silica dispersion (offered as predispersed product Aerodisp® W7622 by Evonik; 3.827,97 mmol SiO₂; ion-exchanged until the pH was < 4) was adjusted to pH 3 with nitric acid.

[00176] In a 250 ml round flask, concentrated nitric acid (65 w%; 1.54 ml; 22.41 mmol) was added to methanol (17.03 ml; 419.83 mmol) under magnetic stirring. Then, 3-(dimethoxymethylsilyl)propylamine (1.19 ml; 6.92 mmol) was added and the mixture was quickly added to the fumed silica dispersion under vigorous stirring.

[00177] The temperature of the silica dispersion which was at room temperature raised to 20°C after the addition and was allowed to cool down naturally. After 1 hour, the temperature was raised to 70°C and kept for 2 hour under continuous stirring.

[00178] The reaction mixture was transferred to a round flask and the volatile organic solvents were removed and replaced by deionized water so that a solid content of core-shell silica of approximately 20 wt.% was achieved.

[00179] The product was pressure-filtered over a 2 µm filter

[00180] Yield: 1139.1 g; Solid content: 20.9 wt.%; MPS (measured by DLS): 108.0 nm; PDI: 0.159; Zetapotential: 23.3 mV

3. Synthesis Of Soft Polysiloxane Core-Shell Structure Abrasives Using Elongated-Shaped Silica Nanoparticles As The Core Particles

[00181] The synthesis of elongated-shaped silica nanoparticles particles has been disclosed in WO 2022/226471 A1. The disclosure of which is incorporated herein by reference.

Example 4 Synthesis of abrasives with aminofunctional soft polysiloxane core-shell structure

[00182] In a 4-neck 1000 ml round shaped flask equipped with magnetic stirrer, a dispersion of elongated-shaped nanoparticles was given (384.60 g; 0.42 mol SiO_2) which had been ion exchanged with Amberlite IRN-150 before (Particle size: 90.29 (DLS) a PDI of 0.044 and a pH of 4.0.).

[00183] In a 100 ml round flask, nitric acid 65% (2.52 ml; 36.09 mmol) and methanol (41.37 ml; 1.02 mol) were mixed. 3-[dimethoxy(methyl)silyl]propylamine (2.07 ml; 12.03 mmol) was added and the mixture was shaken by hand for 5 seconds and then added quickly to the intensively stirred dispersion of SiO_2 particles. Stirring was continued for 1 hour at room temperature and 2 h at 70°C.

[00184] 200 ml deionized water were added to the reaction mixture and the resulting dispersion was concentrated on a rotary evaporator until the solid content reached about 20 weight%.

[00185] Yield: 107.8g; solid content: 20.3%; pH= 1.03; Mean particle size: 87.9nm (by DLS); PDI: 0.045; zeta potential: 46.7 mV.

Example 5 Synthesis Of Abrasives With A Soft Polysiloxane Shell Comprising An Aromatic Amine

[00186] A dispersion of ion-exchanged, elongated silica nanoparticles 87 nm MPS, measured by DLS; pH 4.1; 232.98 g/665.78 mmol SiO_2) was transferred to a 500 ml 4-neck flask, equipped with condenser and KPG stirrer. The dispersion was heated to 70°C while being stirred.

[00187] Via 2 pumps equipped with tubes, 2 solutions were added simultaneously within 1 hour while the dispersion was stirred intensively. The 2 reactant streams were mixed by connecting the tubes with a Y-connector directly before adding them to the dispersion.

[00188] Solution A was made by mixing N-[3-(trimethoxysilyl)propyl]aniline (3.69 ml; 14.40 mmol) with methanol (29.50 ml; 727.40 mmol).

[00189] Solution B was made by mixing nitric acid (65wt.%, 1.09 ml; 15.84 mmol) with methanol (32.10 ml; 791.57 mmol).

[00190] After the reactant solutions were added, the dispersion was stirred for additional 2 hours at 70°C and let cool down to room temperature naturally.

[00191] 200 ml of deionized water was added, and the dispersion was concentrated with a rotary evaporator until a solid content of about 20wt.% was reached. The dispersion was filtered with a 5 µm- and subsequently with a 1 µm syringe filter.

[00192] Yield: 197.19 g dispersion, Solid content: 21.50 wt.%, pH= 1.81, MPS (by DLS): 89.6 nm, PDI: 0.026.

Example 6 Synthesis Of Abrasives With Soft Polysiloxane Non-Ionic Core-Shell Structure

[00193] In a 4-neck 1000 ml round shaped flask equipped with magnetic stirrer, a dispersion of elongated-shaped SiO₂ nanoparticles in water was given (83,217 mmol; 60.02 g; SiO₂ content: 8.3 wt.%; mean particle size 48.3 nm measured by DLS) which had been ion exchanged with Amberlite IRN-150 before and subsequently adjusted to a pH of 3 with HNO₃.

[00194] In a 100 ml round flask, nitric acid 65% (2.18 mmol; 0.21 g; 0.149 ml) and methanol (1.900 mmol; 0,023 eq.; 3.740 g; 0.077 ml) were mixed. 3-glycidoxypropyltrimethoxysilane (1.80 mmol; 0.425 g; 0.448 ml) was added and the mixture was shaken by hand for 5 seconds and then added quickly to the intensively stirred dispersion of SiO₂ particles. Stirring was continued for 1 hour at room temperature and 2 hours at 70°C.

[00195] 500 ml deionized water were added to the reaction mixture and the resulting dispersion was concentrated on a rotary evaporator until the solid content reached about 20 weight%.

[00196] Yield: 25.8 g, solid content: 19.8 %, pH: 2.73, Mean Particle size: 49.5nm (by DLS), PDI: 0.039.

Example 7 Synthesis Of Abrasives With Soft Polysiloxane Non-Ionic Core-Shell Structure

[00197] In a 4-neck 1000 ml round shaped flask equipped with magnetic stirrer, a dispersion of elongated-shaped SiO₂ nanoparticles in water was given (166.426 mmol; 57.14 g; SiO₂ content: 17.5 wt.%; mean particle size 79.5 nm measured by DLS; pH 9.6).

[00198] Deionized water was added while stirring to adjust the concentration of SiO₂ nanoparticles to 10 wt.%. Under continuous stirring, the dispersion was heated to 70 °C.

[00199] Within 12 hours, a solution of 3-glycidoxypolytrimethoxysilane (2.40 mmol; 0.568 g; 0.60 ml) in ethanol (0.11 mol; 5.112 g; 6.47 ml) was added dropwise while the reaction mixture was continuously stirred. During the reaction, the pH was controlled and kept above pH 9 by adding aqueous NH₃ if necessary.

[00200] 500 ml 0.05 mol/l aqueous NH₃ was added in 2 portions to the reaction mixture and the resulting dispersion was each time concentrated with the help of a rotary evaporator until the solid content reached about 20 wt.%.

[00201] Yield: 51.3 g, solid content: 19.4 %, pH: 8.9, Mean Particle size: 82.2 nm (by DLS), PDI: 0.065.

Example 8 Synthesis Of Abrasives With Soft Polysiloxane Non-Ionic Core-Shell Structure

[00202] In a 4-neck 1000 ml round shaped flask equipped with magnetic stirrer, a dispersion of elongated-shaped SiO₂ nanoparticles in water was given (166.426 mmol; 57.14 g; SiO₂ content: 17.5 wt.%; mean particle size 79.5 nm measured by DLS; pH 9.6).

[00203] Deionized water was added while stirring to adjust the concentration of SiO₂ nanoparticles to 10 wt.%. Under continuous stirring, the dispersion was heated to 70 °C.

[00204] Within 12 hours, a solution of 3-glycidoxypropylmethyldimethoxysilane (2.40 mmol; 0.529 g) in ethanol (0.11 mol; 5.112 g; 6.47 ml) was added dropwise while the reaction mixture was continuously stirred. During the reaction, the pH was controlled and kept above pH 9 by adding aqueous NH_3 if necessary.

[00205] 500 ml 0.05 mol/l aqueous NH_3 was added in 2 portions to the reaction mixture and the resulting dispersion was each time concentrated with the help of a rotary evaporator until the solid content reached about 20 wt.%.

[00206] Yield: 50.8 g, solid content: 19.7 %, pH: 9.0, Mean Particle size: 80.7 nm (by DLS), PDI: 0.061.

Example 9 Abrasives With Soft Polysiloxane Anionic Carboxy-Functional Core-Shell Structure

[00207] In a 4-neck 1000 ml round shaped flask equipped with magnetic stirrer, a dispersion of elongated-shaped SiO_2 nanoparticles in water was given (166.426 mmol; 57.14 g; SiO_2 content: 17.5 wt.%; mean particle size 79.5 nm measured by DLS; pH 9.6).

[00208] Deionized water was added while stirring to adjust the concentration of SiO_2 nanoparticles to 10 wt.%. Under continuous stirring, the dispersion was heated to 70 °C.

[00209] Within 12 h, a solution of (3-triethoxysilyl)propylsuccinic anhydride (2.40 mmol; 0.731 g) in ethanol (0.11 mol; 5.112 g; 6.47 ml) was added dropwise while the reaction mixture was continuously stirred. During the reaction, the pH was controlled and kept above pH 9 by adding aqueous NH_3 .

[00210] 500 ml 0.05 mol/l aqueous NH_3 was added in 2 portions to the reaction mixture and the resulting dispersion was each time concentrated with the help of a rotary evaporator until the solid content reached about 20 wt.%.

[00211] Yield: 50.9 g, solid content: 19.9 %, pH: 9.1, Mean Particle size: 81.9 nm (by DLS), PDI: 0.071.

4. Comparative Example: Synthesis of Abrasives Using Elongated-Shaped Nanoparticles As Core With Aminosilane Surface Modification

Comparative Example 4

[00212] In a 4-neck 1000 ml round shaped flask equipped with magnetic stirrer, a dispersion of elongated-shaped nanoparticles was given (374.20 g; 0.409 mol SiO₂) which had been ion exchanged with Amberlite IRN-150 before (Particle size: 90.29 nm (by DLS) a PDI of 0.044 and a pH of 4.1.).

[00213] In a 100 ml round flask, nitric acid 65% (0.0265 ml; 0.38 mmol) and methanol (4.14 ml; 0.1 mol) were mixed.

3-[dimethoxy(methyl)silyl]propylamine (0.127 ml; 0.7365 mmol) was added and the mixture was shaken by hand for 5 seconds and then added quickly to the intensively stirred dispersion of SiO₂ particles. Stirring was continued for 1 hour at room temperature and 2 hours at 70°C.

[00214] 200 ml deionized water were added to the reaction mixture and the resulting dispersion was concentrated on a rotary evaporator until the solid content reached about 20 weight%.

[00215] Yield: 121.9 g, solid content: 20.1%, pH= 1.73, Mean Particle size: 84.7nm (by DLS), PDI: 0.048, zetapotential: 31.1 mV.

Comparative Example 5

In a 4-neck 1000 ml round shaped flask equipped with magnetic stirrer, a dispersion of elongated-shaped nanoparticles was given (357.80 g; 0.409 mol SiO₂) which had been ion exchanged with Amberlite IRN-150 before (Particle size: 45.29 nm (by DLS) a PDI of 0.034 and a pH of 4.3).

[00216] In a 100 ml round flask, nitric acid 65% (0.0265 ml; 0.38 mmol) and methanol (4.14 ml; 0.1 mol) were mixed. 3-[dimethoxy(methyl)silyl]propylamine (0.127 ml; 0.7365 mmol) was added and the mixture was shaken by hand for 5 seconds and then added quickly to the intensively stirred dispersion of SiO₂ particles. Stirring was continued for 1 hour at room temperature and 2 hours at 70°C.

[00217] 200 ml deionized water were added to the reaction mixture and the resulting dispersion was concentrated on a rotary evaporator until the solid content reached about 20 weight%.

[00218] Yield: 120.8 g, solid content: 19.9%, pH= 1.84, Mean Particle size: 47.9nm (by DLS), PDI: 0.038, zetapotential: 29.8 mV.

CMP Polishing Experiments

CMP Tool

[00219] The polishing results were obtained by polishing 300 mm diameter wafers having the appropriate layers using a Reflexeon LK-300mm CMP tool, IC-1000 polishing pad (Dow Chemicals) and AK45 conditioner (Seasol) at a downforce of 3 psi and a slurry flow rate of 200 ml/min. Removal rates for W, TEOS, and SOC spin-on-carbon films were measured using 4-point probe (RS-100, KLA Tencor) and Ellipsometry (Spectra FX100, KLA Tencor). Defect counts were obtained using SP2 surfscan tool (KLA Tencor).

Wafers

[00220] Polishing experiments were conducted using W, and PECVD TEOS wafers. These blanket wafers were purchased from Silicon Valley Microelectronics, 2985 Kifer Rd., Santa Clara, CA 95051.

[00221] The CMP slurries were disclosed in US Patent US 11,111,435 B2, which is entirely incorporated herein by reference.

Example 10 CMP using Soft Polysiloxane Core-Shell Structure Abrasives Having Fumed Silica As Core

[00222] The polishing rates or removal rate and defect count of Tungsten (W) and TEOS layers from the CMP polishing compositions containing different abrasives using fumed silica as core particles were evaluated in this example.

[00223] Each of the CMP polishing compositions included 0.1 wt.% abrasive particles as shown in Table 1. The CMP polishing compositions were filtered prior to polish tests (Pall CMP StarKleen Capsule 0.3 μ m filter size).

[00224] The abrasive, removal rate (RR) and defect count were shown in Table 1.

Table 1

Abrasive	Description	W RR Å/min	TEOS RR Å /min	RR Selectivity W/TEOS	Defect Count
Example 1	Fumed silica powder + inventive shell. Fumed silica with 300 m ² /g	782	8	97,8	165
Example 2	Fumed silica powder + inventive shell. Fumed silica with 50 m ² /g	908	12	75,7	353
Example 3	Predispersed fumed silica powder + inventive shell	1002	12	83,5	83
Comparative example 1	Fumed silica powder + aminosilane zeta-potential modification. Fumed silica with 300 m ² /g	262	8	32,7	450
Comparative example 2	Fumed silica powder + aminosilane zeta-potential modification. Fumed silica with 50 m ² /g	298	19	15,7	1201
Comparative example 3	Predispersed fumed silica powder + aminosilane zeta-potential modification	453	17	26,6	323

[00225] It is evident that the CMP performance of the tested abrasives follows a clear trend regarding removal rates and defectivity. Abrasives with the inventive soft core-shell structure show favorably higher removal rates of W and lower removal rates of TEOS resulting in a better selectivity; and importantly a significant reduction in defectivity.

Example 11 CMP Using Abrasives Having Elongated-Shaped Nanoparticles As Core Particles

[00226] The polishing rates and defectivity of Tungsten and TEOS layers were evaluated in this example for compositions containing different abrasives. Each of the polishing compositions included 0.1wt% abrasive particles.

[00227] Composition 1A contained the aminosilane-modified abrasives from Comparative Example 4; Composition 1B contained abrasives with aminofunctional soft polysiloxane core-shell structure from Example 4; and Composition 1C contained the aminosilane-modified abrasives from Comparative Example 5. All compositions were filtered prior to polish tests (Pall CMP Starkleen Capsule 0.3 µm filter size).

[00228] The results were shown in Table 2.

Table 2

Polish composition (abrasives)	Polish rate – W (Å /min)	Polish rate – TEOS (Å /min)	Defect count (>45nm)
1A (comparative example 4)	1180	8	231,000
1B (Example 4)	1240	12	2,300
1C (comparative example 5)	1110	14	189,000

[00229] It is evident that composition 1B using aminofunctional soft polysiloxane core-shell structure made in Example 4, despite having a silicone-like shell, surprisingly not only shows a significant reduction in defect counts, but also slightly higher removal rates than the aminosilane-modified abrasives which do not have a silicone-like shell.

[00230] The embodiments of this invention listed above, including the working example, are exemplary of numerous embodiments that may be made of this invention. It is contemplated that numerous other configurations of the process may be used, and the materials used in the process may be elected from numerous materials other than those specifically disclosed.

Claims

1. Nanosized soft polysiloxane core-shell abrasive comprising a core and a shell;
wherein
the core and the shell comprise different materials having different chemical and mechanical properties, preferably the shell has lower E-modulus and is mechanically softer than the core;
the core comprises reactive groups around its surface ; and
the shell comprises crosslinked, entangled, or combinations of crosslinked and entangled polyorganosiloxane polymers.
2. The nanosized soft polysiloxane core-shell abrasive according to Claim 1 ,
wherein the reactive groups are selected from the groups consisting of OH-groups, Si-OH groups, and combinations thereof; preferably Si-OH groups.
3. The nanosized soft polysiloxane core-shell abrasive according to any one of Claims 1 - 2, wherein the core comprises at least one oxide, nitride or combinations thereof, of an atom selected from the group consisting of Si, Al, Ce, La, Zr, and Ti.
4. The nanosized soft polysiloxane core-shell abrasive according to any one of Claims 1 - 3, wherein the core is selected from the group consisting of colloidal silica, fumed silica, alumina, ceria, and combinations thereof.
5. The nanosized soft polysiloxane core-shell abrasive according to any one of Claims 1 - 4, wherein the core comprises SiO₂ having Si-OH groups around its surface.
6. The nanosized soft polysiloxane core-shell abrasive according to any one of Claims 1 - 5, wherein the core is colloidal silica or fumed silica having Si-OH groups around its surface.
7. The nanosized soft polysiloxane core-shell abrasive according to any one of Claims 1 - 6, wherein the core has a mean particle size(MPS) measured by

Dynamic Light Scattering (DLS) from 5 to 500 nm, 10 to 400 nm, 15 to 300nm, 20 to 200 nm, or 30 to 150 nm.

8. The nanosized soft polysiloxane core-shell abrasive according to any one of Claims 1 - 7, wherein
the polyorganosiloxane polymer comprises organosiloxane moieties selected from the group consisting of silsesquioxane moieties $\text{RSiO}_{1.5}$, silicone moieties $\text{R}_1\text{R}_2\text{SiO}$ moieties, silicon moieties with 0 or 1 non-hydrolyzable group R: $\text{Si}(-\text{O})_4$ or $\text{SiR}(-\text{O})_3$; and combinations thereof; wherein
R is selected from the group consisting of linear or cyclic alkyl, linear or cyclic aryl, and combinations thereof; and optionally comprise at least one heteroatom selected from the group consisting of O, S, N, and P; and
 R_1 and R_2 each independently is selected from the group consisting of aliphatic group, aromatic group, and combinations thereof; and optionally comprise at least one heteroatom selected from the group consisting of O, S, N, and P.
9. The nanosized soft polysiloxane core-shell abrasive according to any one of Claims 1 - 8, wherein the polyorganosiloxane polymers comprise crosslinkers selected from the group consisting of silsesquioxane moieties, silicon moieties with 0 non-hydrolyzable group $\text{Si}(-\text{O})_4$, and combinations thereof to crosslink the polyorganosiloxane polymers; wherein the crosslinker can either be present before or generated during formation of the polyorganosiloxane shell.
10. The nanosized soft polysiloxane core-shell abrasive according to any one of Claims 1 - 9, wherein the polyorganosiloxane polymers are inorganic-organic hybrid polymers.
11. The nanosized soft polysiloxane core-shell abrasive according to any one of Claims 1 - 10, wherein the polyorganosiloxane polymer has chains with their end-groups only bonded around surface of the core, and the polyorganosiloxane polymers are entangled with each other.

12. The nanosized soft polysiloxane core-shell abrasive according to any one of Claims 1 - 11, wherein the shell comprises non-ionic hydrophilic groups; and optionally comprises organic C-OH groups or other hydrophilic groups.
13. The nanosized soft polysiloxane core-shell abrasive according to any one of Claims 1 – 12, wherein the shell further comprises $\text{NR}_1\text{R}_2\text{R}_3$ groups, $\text{NR}_1\text{R}_2\text{R}_3\text{R}_4$ groups, or mixtures thereof with each R independently selected from the group consisting of H, organic aliphatic, aromatic group, and combination thereof.
14. The nanosized soft polysiloxane core-shell abrasive of according to any one of Claims 1 - 13, wherein the shell comprises > 50 molar %, > 85 molar %, >90 molar %, or >95 molar % of silicone structure $\text{O-Si(R}_1\text{R}_2\text{)-O}$ with each R independently being aliphatic or aromatic group and optionally carrying at least one heteroatom selected from the group consisting of O, S, N, and P; and <20 molar %, <10 molar %, <5 molar %, <2.5 molar %, or 0 molar % of silicon moieties with 0 non-hydrolyzable groups Si(-O-)_4 .
15. The nanosized soft polysiloxane core-shell abrasive according to any one of Claims 1 - 14, wherein the shell is a non-ionic or anionic modified polyorganosiloxane shell.
16. The nanosized soft polysiloxane core-shell abrasive according to any one of Claims 1 - 15, wherein the shell is hydrophilic, optionally comprises charge carrier selected from the group consisting of cationic, anionic, and zwitterionic at a given pH.
17. The nanosized soft polysiloxane core-shell abrasive according to any one of Claims 1 - 16, wherein the shell has a thickness of > 0.2 nm and <20 nm, < 10 nm, <5 nm, or <2 nm.
18. The nanosized soft polysiloxane core-shell abrasive according to any one of Claims 1 - 17, wherein the core has a surface modification by an organosilane.

19. The nanosized soft polysiloxane core-shell abrasive according to any one of Claims 1 - 18, wherein the silicone moieties and silicon moieties in the shell react with the reactive groups on the surface of the core to form covalent bonds to bond the shell to the core.
20. A method of making nanosized soft polysiloxane core-shell abrasive comprising:
- providing a dispersion of core, wherein the core has reactive groups around its surface;
 - providing a shell-forming precursor;
 - adding the shell-forming precursor to the dispersion of core to form shell; and
 - forming the nanosized soft polysiloxane core-shell abrasive; wherein
the shell-forming precursor is selected from the group consisting of organosilane, organosiloxane, and combinations thereof;
the shell comprises crosslinked, entangled, or combinations of crosslinked and entangled polyorganosiloxane polymers; and
the shell is covalently bonded around surface of the core.
21. The method of making nanosized soft polysiloxane core-shell abrasive according to Claim 20, wherein the reactive groups around the surface of the core are -OH groups, preferably Si-OH groups.
22. The method of making nanosized soft polysiloxane core-shell abrasive according to any one of Claims 20 - 21, wherein the core is selected from the group consisting of colloidal silica, fumed silica, alumina, ceria, and combinations thereof.
23. The method of making nanosized soft polysiloxane core-shell abrasive according to any one of Claims 20 - 22, wherein the core is selected from the group consisting of colloidal silica, fumed silica, and the combinations thereof; and the reactive groups around the surface of the core are Si-OH groups.

24. The method of making nanosized soft polysiloxane core-shell abrasive according to any one of Claims 20 - 23, wherein the shell comprises organosiloxane moieties selected from the group consisting of silsesquioxane moieties $\text{RSiO}_{1.5}$, silicone moieties $\text{R}_1\text{R}_2\text{SiO}$ moieties, silicon moieties with 0 or 1 non-hydrolyzable group $\text{R Si}(-\text{O}-)_4$ or $\text{SiR}(-\text{O}-)_3$, and combinations thereof; wherein R is selected from the group consisting of linear or cyclic alkyl, linear or cyclic aryl, and combinations thereof; and optionally comprise at least one heteroatom selected from the group consisting of O, S, N, and P; and R_1 and R_2 each independently is selected from the group consisting of aliphatic group, aromatic group, and combinations thereof; and optionally comprise at least one heteroatom selected from the group consisting of O, S, N, and P.
25. The method of making nanosized soft polysiloxane core-shell abrasive according to any one of Claims 20 - 24, wherein the shell-forming precursor is selected from the group consisting of chlorosilane, alkoxysilane, oximatosilane, silanol preferably diphenylsilandiol, siloxane oligomer with hydrolysable groups or Si-OH groups preferably dimethylsiloxane with 5 repetitive units and Si-OH end groups, and combinations thereof; wherein the shell-forming precursor contains or generates Si-OH groups during formation of the shell.
26. The method of making nanosized soft polysiloxane core-shell abrasive according to any one of Claims 20 - 25, wherein the shell-forming precursor is hydrolysable organoalkoxysilanes, preferably organoalkoxysilanes with at least 1 or at least 2 non-hydrolyzable groups, forming a silicone-like, silsesquioxane-like, or mixtures thereof of polyorganosiloxane polymers.
27. The method of making nanosized soft polysiloxane core-shell abrasive according to Claim 26, wherein the non-hydrolyzable group is selected from the group consisting of aliphatic group, aromatic group, and combinations thereof, and optionally have at least one heteroatom selected from the group consisting of O, S, N, and P attached or included in structure.
28. The method of making nanosized soft polysiloxane core-shell abrasive according to any one of Claims 20 - 27, wherein the shell-forming precursor comprises at least two organoalkoxysilane moieties which share same non-hydrolyzable group;

and the polyorganosiloxane polymers comprise both polysiloxane crosslinkers using polysiloxane bonds and non-hydrolyzable organic groups; and the polyorganosiloxane polymers are inorganic-organic hybrid polymers.

29. The method of making nanosized soft polysiloxane core-shell abrasive according to any one of Claims 20 - 28, wherein the shell-forming precursor is selected from the group consisting of 3-(dimethoxymethylsilyl)propylamine, N-[3-(trimethoxysilyl)propyl]aniline, 3-glycidoxypropyltrimethoxysilane, (3-glycidoxypropyl)methyldiethoxysilane, (3-triethoxysilyl)propylsuccinic anhydride, 1,2-bis(triethoxysilyl)ethane, bis-(3-trimethoxysilylpropyl)amine, N,N'-bis(3-trimethoxysilylpropyl)urea, 2-(3,4-epoxycyclohexyl)ethyltriethoxysilane, and combinations thereof.
30. The method of making nanosized soft polysiloxane core-shell abrasive according to any one of Claims 20 - 29, wherein at least >25 molar %, > 50 molar %, or > 75 molar % part of the shell-forming precursor has hydrophilic group, charge carrying group, or combinations thereof.
31. The method of making nanosized soft polysiloxane core-shell abrasive according to any one of Claims 20 - 30, wherein the core is selected from the group consisting of colloidal silica, fumed silica, and the combinations thereof; and the shell-forming precursor is selected from the group consisting of 3-(dimethoxymethylsilyl)propylamine, N-[3-(trimethoxysilyl)propyl]aniline, 3-glycidoxypropyltrimethoxysilane, (3-triethoxysilyl)propylsuccinic anhydride, and combinations thereof.
32. The method of making nanosized soft polysiloxane core-shell abrasive according to any one of Claims 20 - 31, further comprising a step after step a, b or c: providing a reactant selected from the group consisting of organic monomers, oligomers or polymers; preferably the non-silane reactant reacts with at least part of the polyorganosiloxane and is covalently incorporated in the shell structure during shell formation; wherein the reactant is not a shell-forming precursor and

the reactant makes up < 75 molar %, < 50 molar % , or < 25 molar % of mass of the shell.

33. The method of making nanosized soft polysiloxane core-shell abrasive according to Claim 32, wherein the reactant is selected from the group consisting of glycidol, 1,2-diaminoethan, 1,4-diaminobutan, ethyleneglycol-1,2 diglycidylether, poly(ethylene glycol)diglycidyl ether, and combinations thereof.
34. The method of making nanosized soft polysiloxane core-shell abrasive according to any one of Claims 20 - 33, wherein the method further comprises a step after step a, b or c: providing a catalyst; wherein the catalyst is selected from the group consisting of mineral or organic acid, base selected from the group consisting of NH_3 , amine, amino alcohol, and quaternary ammonium compound; metal ion selected from the group consisting of Ce, Al, Ti, Zr, W, Cu, and combinations thereof.
35. The method of making nanosized soft polysiloxane core-shell abrasive according to any one of Claims 20 - 34, wherein method is conducted at a pH from 2 to 5 or a pH from 8-11.
36. The method of making nanosized soft polysiloxane core-shell abrasive according to any one of Claims 20 - 35, wherein the reactive groups around the surface of the core react with the silicone moieties and silicon moieties in the shell and form covalent bonds to bond the shell around surface of the core.
37. A chemical mechanical polishing(CMP) composition comprises:
the nanosized soft polysiloxane core-shell abrasives of any one of claims 1 to 19;
and
a solvent selected from the group consisting of water, water-soluble solvent, and combinations thereof;
wherein the CMP polishing composition has a pH of 2 to 10, 2 to 8, 2 to 6, 2 to 5, 2 to 4, or 2 to 3.

38. A chemical mechanical polishing (CMP) method comprises:
providing a substrate;
providing a chemical mechanical polishing (CMP) composition comprises:
the nanosized soft polysiloxane core-shell abrasive of any one of claims 1 to 19; and
a solvent selected from the group consisting of water, water-soluble solvent, and combinations thereof;
wherein the CMP polishing composition has a pH of 2 to 10, 2 to 8, 2 to 6, 2 to 5, 2 to 4, or 2 to 3;
contacting the surface of the semiconductor substrate with the polishing pad and the chemical mechanical polishing composition; and
polishing the surface; wherein
the substrate has at least one surface comprising at least one material selected from the group consisting of a metal selected from the group consisting of tungsten, copper, ruthenium, cobalt, aluminum, and combinations thereof; metal alloys; a dielectric material selected from the group consisting of silicon dioxide and/or silicon nitride; spin-on dielectrics (SoD); and spin-on carbon (SoC);.
39. The chemical mechanical polishing (CMP) method of claim 38, wherein the surface of the semiconductor substrate comprises W and silicon dioxide film; and removal selectivity of W: SiO₂ is greater than 30, 50, 80, 100, 120, or 140.
40. A chemical mechanical polishing (CMP) system comprises:
a polishing pad;
a substrate;
a chemical mechanical polishing (CMP) composition comprises:
the nanosized soft polysiloxane core-shell abrasives of any one of claims 1 to 19; and
a solvent selected from the group consisting of water, water-soluble solvent and combinations thereof;
wherein the CMP polishing composition has a pH of 2 to 10, 2 to 8, 2 to 6, 2 to 5, 2 to 4, or 2 to 3;
wherein the substrate has a surface comprising at least one material selected from the group consisting of a metal selected from the group consisting of

tungsten, copper, ruthenium, cobalt, aluminum, and combinations thereof; metal alloys; a dielectric material selected from the group consisting of silicon dioxide and/or silicon nitride; spin-on dielectrics (SoD); and spin-on carbon(SoC); and the surface of the semiconductor substrate is in contact with the polishing pad and the chemical mechanical polishing composition so the surface can be polished.

41. The chemical mechanical polishing (CMP) system of claim 40, wherein the surface of the semiconductor substrate comprises W and silicon dioxide film; and removal selectivity of W: SiO₂ is greater than 30, 50, 80, 100, 120, or 140.