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, and the shell has lower E-modulus and is mechanically softer than the core;

   wherein

   the core comprises at least one selected from the group consisting of Si, Al, Ce, La, Zr, and Ti; and reactive groups around surface of the core selected from the groups consisting of OH- groups, Si-OH groups, and combinations thereof;

   the shell comprises crosslinked, entangled, or combinations of crosslinked and entangled polyorganosiloxane polymers having chains with their end-groups only covalently bonded the shell around the surface of the core;

   the core has a mean particle size (MPS) measured by Dynamic Light Scattering (DLS) from 10 to 400nm, or 30 to 150 nm;

   the shell has a thickness of > 0.2 nm and <20 nm, or > 0.2 nm and <2 nm; and

   the shell is covalently bonded around the surface of the core.

2. The nanosized soft polysiloxane core-shell abrasive of Claim 1, wherein the core is selected from the group consisting of colloidal silica, fumed silica, alumina, ceria, and combinations thereof; and the polyorganosiloxane polymers comprises organosiloxane moieties selected from the group consisting of silsesquioxane moieties $RSiO_{1.5}$, silicone moieties R_1R_2SiO moieties, silicon moieties with 0 or 1 non-hydrolyzable group R: $Si(-O-)_4$ or $SiR(-O-)_3$, and combinations thereof; wherein

   R is selected from the group consisting of linear or cyclic alkyl, linear or cyclic aryl, and combinations thereof; or R is selected from the group consisting of linear or cyclic alkyl, linear or cyclic aryl, and combinations thereof; and 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; or R_1 and R_2 each independently is selected from the group consisting of aliphatic

group, aromatic group, and combinations thereof; and at least one heteroatom selected from the group consisting of O, S, N, and P.

3. The nanosized soft polysiloxane core-shell abrasive of Claim 1 or 2, wherein the polyorganosiloxane polymers comprise crosslinkers selected from the group consisting of silsesquioxane moieties, silicon moieties with 0 non-hydrolyzable group $Si(-O-)_4$, and combinations thereof to crosslink the polyorganosiloxane polymers; wherein the crosslinker can either be present before or generated during formation of the polyorganosiloxane shell.

4. The nanosized soft polysiloxane core-shell abrasive according to any one of Claims 1 - 3, wherein the polyorganosiloxane polymers are inorganic-organic hybrid polymers.

5. The nanosized soft polysiloxane core-shell abrasive according to any one of Claims 1 - 4, wherein the shell comprises non-ionic hydrophilic groups; or non-ionic hydrophilic groups and organic C-OH groups.

6. The nanosized soft polysiloxane core-shell abrasive according to any one of Claims 1 – 5, wherein the shell further comprises $NR_1R_2R_3$ groups, $NR_1R_2R_3R_4$ groups, or mixtures thereof with each R independently selected from the group consisting of H, organic aliphatic, aromatic group, and combinations thereof.

7. The nanosized soft polysiloxane core-shell abrasive of according to any one of Claims 1 - 6, wherein the shell comprises > 85 molar %, or >95 molar % of silicone structure $O-Si(R_1R_2)-O$ with each R independently being aliphatic or aromatic group; and <10 molar %, or <2.5 molar % of silicon moieties with 0 non-hydrolyzable groups $Si(-O-)_4$, 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.

8. The nanosized soft polysiloxane core-shell abrasive according to any one of Claims 1 -74, having at least one of (1) the shell is a non-ionic or anionic modified polyorganosiloxane shell; and (2) the core has a surface modification by an organosilane.

9. A method of making nanosized soft polysiloxane core-shell abrasive comprising:
    a. providing a dispersion of core, wherein the core comprises at least one selected from the group consisting of Si, Al, Ce, La, Zr, and Ti and has reactive –OH groups or Si-OH groups around surface of the core;
    b. providing a shell-forming precursor selected from the group consisting of organosilane, organosiloxane, and combinations thereof;
    c. adding the shell-forming precursor to the dispersion of core to form shell wherein the shell comprises crosslinked, entangled, or combinations of crosslinked and entangled polyorganosiloxane polymers; and
    d. forming the nanosized soft polysiloxane core-shell abrasive wherein the shell is covalently bonded around surface of the core;
    wherein
    the method is conducted at a pH from 2 to 5 or a pH from 8-11.

10. The method of making nanosized soft polysiloxane core-shell abrasive of Claim 9, 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.

11. The method of making nanosized soft polysiloxane core-shell abrasive of Claim 9 or 10, wherein the shell comprises organosiloxane moieties selected from the group consisting of silsesquioxane moieties $RSiO_{1.5}$, silicone moieties R_1R_2SiO moieties, silicon moieties with 0 or 1 non-hydrolyzable group R $Si(-O-)_4$ or $SiR(-O-)_3$, 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;
    the core is selected from the group consisting of colloidal silica, fumed silica, alumina, ceria, and combinations thereof; and
    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.

12. The method of making nanosized soft polysiloxane core-shell abrasive according to any one of Claims 9 - 11, wherein the shell-forming precursor is selected from the group consisting of chlorosilane, alkoxysilane, oximatosilane, silanol, siloxane oligomer with hydrolysable groups or Si-OH groups hydrolysable organoalkoxysilanes with at least 1 or at least 2 non-hydrolyzable groups selected from the group consisting of aliphatic group, aromatic group, and combinations thereof; or selected from the group consisting of aliphatic group, aromatic group, at least one heteroatom selected from the group consisting of O, S, N, and P attached or included in structure of the shell-forming precursor; and combinations thereof; wherein the shell-forming precursor contains or generates Si-OH groups during formation of the shell.

13. The method of making nanosized soft polysiloxane core-shell abrasive according to any one of Claims 9 - 12, 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.

14. The method of making nanosized soft polysiloxane core-shell abrasive according to any one of Claims 9 - 13, wherein the shell-forming precursor is selected from the group consisting of diphenylsilandiol, dimethylsiloxane with 5 repetitive units and Si-OH end groups, 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; and the core is selected from the group consisting of colloidal silica, fumed silica, and the combinations thereof.

15. The method of making nanosized soft polysiloxane core-shell abrasive according to any one of Claims 9 - 14, 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.

16. The method of making nanosized soft polysiloxane core-shell abrasive according to any one of Claims 9 - 15, 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.

17. The method of making nanosized soft polysiloxane core-shell abrasive according to any one of Claims 9 - 16, wherein step c further comprising at least one step of: (1) adding a reactant 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; wherein the 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 %, or < 25 molar % of mass of the shell; and (2) adding a catalyst 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; wherein the catalyst fosters hydrolysis and condensation of the organoalkoxysilane.

18. A chemical mechanical polishing (CMP) composition comprises:
the nanosized soft polysiloxane core-shell abrasives of any one of Claims 1 to 8; 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 8, or 2 to 4.

19. 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 8; 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 8, or 2 to 4;

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); and

removal selectivity of W: SiO_2 is greater than 80 or 140.

20. 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 8; 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; and

removal selectivity of W: SiO_2 is greater than 80 or 140.