

about 25 ppm, at least about 50 ppm, at least about 75 ppm, or at least about 100 ppm) to at most about 1000 ppm (e.g., at most about 900 ppm, at most about 800 ppm, at most about 700 ppm, at most about 600 ppm, at most about 500 ppm, or at most about 250 ppm) based on the total weight of the composition.

5 In one or more embodiments, the nitride removal rate reducing agent has a hydrophobic portion containing a hydrocarbon group that includes at least 12 carbon atoms (C_{12}) (e.g., at least 14 carbon atoms (C_{14}), at least 16 carbon atoms (C_{16}), at least 18 carbon atoms (C_{18}), at least 20 carbon atoms (C_{20}), or at least 22 carbon atoms (C_{22})) and/or at most 40 carbon atoms (C_{40}) (e.g., at most 38 carbon atoms (C_{38}), at most 36 carbon atoms (C_{36}), at most 10 34 carbon atoms (C_{34}), at most 32 carbon atoms (C_{32}), at most 30 carbon atoms (C_{30}), at most 28 carbon atoms (C_{28}), at most 26 carbon atoms (C_{26}), at most 24 carbon atoms (C_{24}), or at most 22 carbon atoms (C_{22})). The hydrocarbon groups mentioned herein refer to groups that contain only carbon and hydrogen atoms and can include both saturated groups (e.g., linear, branched, or cyclic alkyl groups) and unsaturated groups (e.g., linear, branched, or cyclic alkenyl groups; 15 linear, branched, or cyclic alkynyl groups; or aromatic groups (e.g., phenyl or naphthyl)). In one or more embodiments, the hydrophilic portion of the nitride removal rate reducing agent contains at least one group selected from a phosphate group and a phosphonate group. It is to be noted that the term "phosphonate group" is expressly intended to include phosphonic acid groups.

20 In one or more embodiments, the nitride removal rate reducing agent is selected from the group consisting of naphthalenesulfonic acid-formalin condensate, lauryl phosphate, myristyl phosphate, stearyl phosphate, octadecylphosphonic acid, oleyl phosphate, behenyl phosphate, octadecyl sulfate, lacceryl phosphate, oleth-3-phosphate, and oleth-10-phosphate.

25 In one or more embodiments, the polishing compositions described herein optionally further include at least one (e.g., two or three) dish cleaning reducing agent (e.g., anionic dish cleaning reducing agent). In one or more embodiments, the at least one dish cleaning reducing agent is a compound including at least one group selected from the group consisting of hydroxy, sulfate, phosphonate, phosphate, sulfonate, amine, nitrate, nitrite, carboxylate, and carbonate groups. In one or more embodiments, the at least one dish cleaning reducing agent is at least one selected

50 ppm, at most about 10 ppm, or at most about 1 ppm) of one or more of the above ingredients that are substantially free from the polishing compositions. In some embodiments, the polishing compositions described can be completely free of one or more the above ingredients.

5 In one or more embodiments, the polishing compositions described herein have a ratio of a removal rate for silicon oxide (e.g., TEOS) to a removal rate for silicon nitride (i.e., a removal rate selectivity) of at least about 3:1, or at least about 4:1, or at least about 5:1, or at least about 10:1, or at least about 25:1, or at least about 50:1, or at least about 60:1, or at least about 75:1, or at least about 100:1, or at least about 150:1, or at least about 200:1, or at least
10 about 250:1, or at least about 300:1, or at least about 500:1, or at least about 750:1, or at most about 1000:1, or at most about 5000:1. In one or more embodiments, the ratios described above can be applicable when measuring removal rates for polishing either blanket wafers or patterned wafers (i.e., wafers including at least silicon nitride patterns, in which the silicon nitride patterns are overlayed with at least silicon oxide (and optionally with other materials
15 such as metals and dielectrics)).

 In one or more embodiments, at most about 1000 angstroms, or at most about 500 angstroms, or at most about 375 angstroms, or at most about 250 angstroms, or at most about 200 angstroms, or at most about 100 angstroms, or at most about 50 angstroms, and/or at least about 0 angstrom of silicon oxide (e.g., TEOS) dishing occurs when polishing a patterned
20 wafer (which can include at least silicon nitride patterns overlayed with at least silicon oxide) with the polishing composition (e.g., until the polishing exposes the silicon nitride patterns on the patterned wafer). In one or more embodiments, at most about 500 angstroms, or at most about 400 angstroms, or at most about 300 angstroms, or at most about 250 angstroms, at most about 200 angstroms, at most about 100 angstroms, or at most about 75 angstroms, or at
25 most about 65 angstroms, or at most about 50 angstroms, or at most about 32 angstroms and/or at least about 0 angstrom of silicon nitride erosion occurs when polishing a patterned wafer (which can include at least silicon nitride patterns overlayed with at least silicon oxide) with the polishing composition (e.g., until the polishing exposes the silicon nitride patterns on the patterned wafer).

In one or more embodiments, the planarization efficiency (i.e., the change in silicon oxide step height divided by the amount of silicon oxide removed during the polish, multiplied by 100) is at least about 14% (e.g., at least about 20%, at least about 30%, at least about 38%, at least about 40%, at least about 46%, at least about 50%, at least about 60%, at least about 70%, or at least about 74%) and at most about 100% (e.g., at most about 99.9%, at most about 99%, at most about 95%, at most about 90%, at most about 80%, at most about 70%, or at most about 60%) when polishing a patterned wafer using a polishing composition according to the present disclosure. In one or more embodiments, the total defect count on a patterned wafer having a diameter of 12 inches (i.e., about 300 mm) is at most 175 (e.g., at most 170, at most 160, at most 150, at most 125, at most 100, at most 75, at most 50, at most 25, at most 10, or at most 5) when polishing the patterned wafer using a polishing composition according to the present disclosure (e.g., a composition including a silica abrasive and the nitride removal rate reducing agent). As described herein, the defects counted are those at least about 90 nm in size.

In one or more embodiments, this disclosure features a method of polishing that can include applying a polishing composition according to the present disclosure to a substrate (e.g., a wafer) having at least silicon nitride and silicon oxide on a surface of the substrate; and bringing a pad into contact with the surface of the substrate and moving the pad in relation to the substrate. In some embodiments, when the substrate includes at least silicon nitride patterns overlaid with at least silicon oxide (e.g., silicon oxide in the presence of other materials such as silicon based dielectrics (e.g., silicon carbide, etc.), metals, metal oxides and nitrides, etc.), the above method can remove at least a portion of the silicon oxide (e.g., the silicon oxide on active, non-trench areas) to expose silicon nitride. It is to be noted that the terms “silicon nitride” and “silicon oxide” described herein are expressly intended to include both un-doped and doped versions of silicon nitride and/or silicon oxide. For example, in one or more embodiments, the silicon nitride and silicon oxide can, independently, be doped with at least one dopant selected from carbon, nitrogen (for silicon oxide), oxygen, hydrogen, or any other known dopants for silicon nitride or silicon oxide. Some examples of silicon oxide film types include TEOS (Tetra-ethyl orthosilicate), SiOC, SiOCN, SiOCH, SiOH and SiON, to name a

dynamic light scatter technique. Slurries were stored in an oven set to 60°C and measured every 7 days. As per the Arrhenius relationship for accelerated aging tests, the full test run of 21 days corresponds to roughly one year of room temperature aging. In other words, if the slurry is kept at 60°C for 21 days and the MPS of the silica does not grow appreciably, it can be certified that the slurry has a real time shelf-life/expiration date of one year.

Table 7. Accelerated aging (60°C) of slurry concentrates

Sample	Type	pH	MPS [nm] Day 0	MPS [nm] Day 7	MPS [nm] Day 14	MPS [nm] Day 21
7A	2x single pot	2.2	68	69	69	69
7B	2x single pot	3.0	65	65	66	66
7C	5x two-part	9.5	72	73	73	74

As shown in Table 7, all formulations are stable through the full test run. Stability in the acidic region for neutral silica is typically difficult to achieve. The single pot solutions were stable from pH of about 2 to about 6.5 at a 2x concentration (select data shown in Table 7) and at other concentration levels (e.g., 3x, 4x, and up to 10x concentrations) (not shown). In the two-part solution (7C), all components, with the exception of the acid, could be concentrated to a much greater degree and remained stable (up to 10x also remains stable). At point of use, the acid and water would be added to reconstitute the slurry before running it on a polishing tool.

Example 8: Demonstration of patterned wafer removal rate selectivity

In this example, polishing compositions used in samples 8A, 8B, and 8C, which contained a colloidal silica abrasive and a nitride removal rate reducing agent shown in Tables 1, 3 and 5, were used to polish 200 mm STI patterned wafers wherein patterned silicon nitride is filled with high density silicon oxide as shown in Figure 2. The pattern in the silicon nitride was such that a wide array of line space, square, checker, and mesh arrays of varying pitch and densities were arranged across the entire wafer face.

Polishing occurred on an Applied Materials 200 mm Mirra polishing tool, which was equipped with a Dow VP6000 pad, 3M A165 CIP1 conditioning disk, and employing a 2

CLAIMS

1. A polishing composition comprising:
 - at least one abrasive;
 - at least one nitride removal rate reducing agent comprising:
 - a hydrophobic portion comprising a C₁₂ to C₄₀ hydrocarbon group; and
 - a hydrophilic portion comprising at least one group selected from the group consisting of a sulfinite group, a sulfate group, a sulfonate group, a carboxylate group, a phosphate group, and a phosphonate group; and
 - wherein the hydrophobic portion and the hydrophilic portion are separated by zero to ten alkylene oxide groups;
 - an acid or a base; and
 - water;
 - wherein the polishing composition has a pH of about 2 to about 6.5.
2. The polishing composition of claim 1, further comprising:
 - at least one dishing reducing agent;
 - wherein the at least one dishing reducing agent is a compound comprising at least one group selected from the group consisting of hydroxyl, sulfate, phosphonate, phosphate, sulfonate, amine, nitrate, nitrite, carboxylate, and carbonate groups.
3. The polishing composition of claim 2, wherein the at least one dishing reducing agent is at least one selected from the group consisting of a polysaccharide and a substituted polysaccharide.
4. The polishing composition of claim 2, wherein the at least one dishing reducing agent comprises carrageenan, xanthan gum, hydroxypropyl cellulose, methyl cellulose, ethyl cellulose, hydroxypropyl methylcellulose, or carboxymethylcellulose.

5. The polishing composition of claim 1, wherein the hydrophobic portion comprises a C₁₂ to C₃₂ hydrocarbon group.

6. The polishing composition of claim 1, wherein the hydrophobic portion comprises a C₁₆ to C₂₂ hydrocarbon group.

7. The polishing composition of claim 1, wherein the hydrophilic portion comprises a phosphate group or a phosphonate group.

8. The polishing composition of claim 1, wherein the at least one nitride removal rate reducing agent is selected from the group consisting of naphthalenesulfonic acid-formalin condensate, lauryl phosphate, myristyl phosphate, stearyl phosphate, octadecylphosphonic acid, oleyl phosphate, behenyl phosphate, octadecyl sulfate, lacceryl phosphate, oleth-3-phosphate, and oleth-10-phosphate.

9. The polishing composition of claim 1, wherein the at least one nitride removal rate reducing agent has zero alkylene oxide group separating the hydrophobic portion and the hydrophilic portion.

10. The polishing composition of claim 2, wherein the at least one nitride removal rate reducing agent and the at least one dishing reducing agent are chemically distinct from each other.

11. The polishing composition of claim 1, wherein the polishing composition has a ratio of a removal rate for a silicon oxide to a removal rate for a silicon nitride of at least about 3:1.

12. The polishing composition of claim 1, wherein the polishing composition has a ratio of a removal rate for a silicon oxide to a removal rate for a silicon nitride of at least about 100:1.

13. The polishing composition of claim 1, wherein the at least one abrasive is selected from the group consisting of cationic abrasives, substantially neutral abrasives, and anionic abrasives.

14. The polishing composition of claim 1, wherein the at least one abrasive is selected from the group consisting of alumina, silica, titania, ceria, zirconia, co-formed products thereof, coated abrasives, surface modified abrasives, and mixtures thereof.

15. The polishing composition of claim 1, wherein the acid is selected from the group consisting of formic acid, acetic acid, malonic acid, citric acid, propionic acid, malic acid, adipic acid, succinic acid, lactic acid, oxalic acid, hydroxyethylidene diphosphonic acid, 2-phosphono-1,2,4-butane tricarboxylic acid, aminotrimethylene phosphonic acid, hexamethylenediamine tetra(methylenephosphonic acid), bis(hexamethylene)triamine phosphonic acid, amino acetic acid, peracetic acid, potassium acetate, phenoxyacetic acid, glycine, bicine, diglycolic acid, glyceric acid, tricine, alanine, histidine, valine, phenylalanine, proline, glutamine, aspartic acid, glutamic acid, arginine, lysine, tyrosine, benzoic acid, nitric acid, sulfuric acid, sulfurous acid, phosphoric acid, phosphonic acid, hydrochloric acid, periodic acid, and mixtures thereof.

16. The polishing composition of claim 1, wherein the base is selected from the group consisting of potassium hydroxide, sodium hydroxide, cesium hydroxide, ammonium hydroxide, triethanolamine, diethanolamine, monoethanolamine, tetrabutylammonium hydroxide, tetramethylammonium hydroxide, lithium hydroxide, imidazole, triazole, aminotriazole, tetrazole, benzotriazole, tolytriazole, pyrazole, isothiazole, and mixtures thereof.

17. A method, comprising:

applying the polishing composition of claim 1 to a substrate having at least a silicon nitride and at least a silicon oxide on a surface of the substrate; and

bringing a pad into contact with the surface of the substrate and moving the pad in relation to the substrate.

18. The method of claim 17, wherein at least one of the silicon nitride and silicon oxide is doped with at least one dopant selected from the group consisting of carbon, nitrogen, oxygen, and hydrogen.

19. The method of claim 17, further comprising forming a semiconductor device from the substrate.

20. The method of claim 18, further comprising forming a semiconductor device from the substrate.