slurries also frequently suffer from dishing-erosion, defectivity, and surface topography problems.

[0007] Another metal of interest in semiconductor applications is silver, which shares many properties and characteristics in common with copper *vis-à-vis* CMP, such as corrosion properties and passivating properties. For example, both silver and copper effectively form films with and are passivated by benzotriazole. In addition, Cu and Ag both readily dissolve in acidic pH with a formation of metal ions (for Cu, Cu^{+1} and Cu^{+2} and for silver Ag^{+1}) and passivate at higher pHs with a formation of oxides.

[0008] There is an ongoing need to develop new CMP compositions and methods utilizing relatively low-solids CMP slurries with a reduced level of dishing-erosion and defectivity, relatively high copper and/or silver removal rates, as well as superior corrosion protection and surface inhibition compared to conventional CMP slurries. 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

[0009] The present ~~invention~~disclosure provides chemical-mechanical polishing (CMP) compositions and methods for polishing substrates comprising copper and/or silver. The disclosed methods ~~of the present invention~~ entail abrading a surface of the substrate with a CMP composition ~~of the invention~~as disclosed herein, preferably in the presence of an oxidizing agent (e.g., hydrogen peroxide). The compositions and methods of the ~~invention~~disclosure can provide relatively high copper and/or silver removal rates with good passivation, compared to conventional CMP slurries.

[0010] The CMP compositions of the ~~invention~~disclosure comprise a particulate abrasive, a primary film-forming metal-complexing agent, a secondary film-forming metal-passivating agent, and an aqueous carrier. Preferred primary film-forming metal-complexing agents include compounds of general formula (I): A−X−Y−OH, salts thereof, and partially neutralized forms thereof (e.g., a combination of acid form and a salt form), in which A is $-N(R^1)-C(=O)-R^2$ or $-C(=O)-NH-OH$; and either X is $-C(R^3)(R^4)-$ and Y is $-C(=O)-$, or X and Y together form an aryl group in which the A and OH groups in formula (I) are positioned in a 1,2 or "ortho" relationship to one another. In formula (I), R^1 is H, substituted C_1-C_4 alkyl, or unsubstituted C_1-C_4 alkyl; R^2 is substituted C_8-C_{20} alkyl or unsubstituted C_8-C_{20} alkyl; and R^3 and R^4 are

each independently H, substituted C_1–C_4 alkyl, or unsubstituted C_1–C_4 alkyl. Compounds of formula (I) include N-acyl glycine compounds (e.g., N-lauroyl glycine and N-lauroyl sarcosine), *o*-hydroxyaryl hydroxamic acid compounds (e.g., salicylhydroxamic acid), *o*-hydroxy-N-acyl aniline compounds, and malonomonohydroxamic acid. Preferred compounds of formula (I) are *o*-hydroxyaryl hydroxamic acids, such as salicylhydroxamic acid (SHA), and N-acyl sarcosine compounds, such as N-lauroyl sarcosine, as well as the salts and partially neutralized forms thereof. Preferred salt forms of the metal-complexing agents are alkali metal salts (e.g., lithium, sodium, and potassium salts). A preferred composition of the ~~invention~~disclosure comprises 0.01 to 10 percent by weight (wt %) of a particulate abrasive, 0.001 to 1 wt % of the primary film-forming metal-complexing agent, and 0.005 to 0.5 wt % of the secondary film-forming metal-passivating agent, dissolved and/or suspended in an aqueous carrier.

[0011] The primary film-forming metal-complexing agent is believed to act as an anchor molecule for produce a thin film directly on the copper surface. The secondary film-forming passivating agent has a strong affinity (e.g., by ionic and/or covalent bonding) for binding to the film formed by the complexing agent. The initial anchor film and the passivating film formed thereon together provide a passivating film that affords a desirably lower static etch rate (SER) and lower friction development over time compared to the use of either the complexing agent or the secondary film-forming passivating agent alone. The two components thus surprising act in a synergistic manner.

[0012] Preferred secondary film-forming metal-passivating agents are compounds having the general formula (II): $Z–X^2(Y^2R^5)(Y^3R^6)$, as well as salts thereof, and partially neutralized forms thereof. In formula (I), Z is NH_2 or OH; X^2 is P=O or C; Y^2 and Y^3 are each independently N, NH, or O; and R^5 and R^6 can each independently comprise $R^7–(OCH_2CH_2)_n–$, wherein R^7 can be H, C_1–C_{20}-alkyl, phenyl, C_1–C_{20}-alkyl-substituted phenyl; and wherein "n" has an average value in the range of 2 to 1000, or when Y^2 and Y^3 each independently are N or NH, R^5 and R^6 each independently can be N, NH, or CH, and together form a five-membered ring heterocycle with X^2, Y^2 and Y^3. Thus, in some embodiments, R^5 and Y^6 each independently are selected from alkyl or polyethylene glycol (PEG) groups such as poly(oxyethylene), aryl-terminated poly(oxyethylene), alkyl-terminated poly(oxyethylene), and alkylaryl-terminated poly(oxyethylene). Non-limiting examples of compounds of formula (II)

include amino-substituted heterocycles such as 5-aminotetrazole, and phosphate esters such as bis-pegylated phosphate esters), particularly phosphates esterified with PEG chains at two oxygens of the phosphate group, wherein the PEG chains are terminated by an aryl ether group (e.g., a phenyl ether), an alkylphenyl ether group (e.g., a C_1–C_{20}-alkyl-substituted phenyl, such as nonylphenyl), or a C_1–C_{20}-alkyl ether group (e.g., bis-(nonylphenylpoly(oxyethylene) phosphate diester). Preferred salt forms of the metal-passivating agents are alkali metal salts (e.g., sodium and potassium salts) in the case of acidic materials and mineral acid addition salts in the case of basic materials.

[0013] Optionally, the compositions ~~of the present invention~~as disclosed herein can include one or more auxiliary metal (e.g., cooper and/or silver)-chelating agents (e.g., 0.01 to 20 wt % of the auxiliary metal-chelating agent) such as compounds having an acidic OH group and an additional oxygen-bearing or nitrogen-bearing substituent. Non-limiting examples of such auxiliary metal-chelating agents include oxalic acid, amino-substituted carboxylic acids (e.g., alpha-amino acids such as glycine, or amino polycarboxylic acids, such as iminodiacetic acid, and the like), and hydroxyl-substituted carboxylic acids (e.g., citric acid, and the like), as well as salts of the chelating agents (e.g., alkali metal salts).

[0013a] In one aspect, there is provided a chemical-mechanical polishing (CMP) composition suitable for polishing a substrate comprising copper and/or silver, the composition comprising:

(a) 0.01 to 10 percent by weight of a particulate abrasive;

(b) 0.001 to 1 percent by weight of a primary film-forming metal-complexing agent that comprises an *o*-hydroxyaryl hydroxamic acid, a salt thereof, or a partially neutralized form thereof;

(c) 0.005 to 0.5 percent by weight of a secondary film-forming metal-passivating agent comprising a compound of formula (II): $Z–X^2(Y^2R^5)(Y^3R^6)$, a salt thereof, or a partially neutralized form thereof; wherein Z is NH_2 or OH; X^2 is P=O or C; Y^2 and Y^3 are each independently N, NH, or O; and R^5 and R^6 can each independently can be $R^7–(OCH_2CH_2)_n–$, or when Y^2 and Y^3 each independently are N or NH, then R^5 and R^6 each independently can be N, NH, or CH, and together Y^2 and Y^3 form a five-membered ring heterocycle with X^2, Y^2 and Y^3; each R^7 independently is H, C_1–C_{20}-alkyl, phenyl, or C_1–C_{20}-alkyl-substituted phenyl; and "n" has an average value in the range of about 2 to about 1000; and

(d) an aqueous carrier therefor.

[0013b] In another aspect, there is provided a chemical-mechanical polishing (CMP) composition suitable for polishing a substrate comprising copper and/or silver, the composition comprising:

(a) 0.01 to 10 percent by weight of a particulate abrasive;

(b) 0.001 to 1 percent by weight of salicylhydroxamic acid, a salt thereof or a partially neutralized form thereof;

(c) 0.005 to 0.5 percent by weight of at least one secondary film-forming metal-passivating agent selected from the group consisting of an amine-substituted nitrogen heteroaromatic compound and a bis-(poly(oxyethylene)) phosphate ester; and

(d) an aqueous carrier therefor.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] FIG. 1 shows the chemical structures of selected primary film-forming metal-complexing agents useful in the compositions and methods of the invention.

[0015] FIG. 2 provides two schematic representations of possible mechanisms by which the primary and secondary film-formers passivate a metal surface and reduce polishing drag force.

[0016] FIG. 3 shows plots of copper removal rate (Cu RR) versus down force (DF) obtained by polishing copper wafers utilizing a composition comprising a primary film-forming metal-complexing agent and an auxiliary chelating agent, compared to results obtained with a control composition.

[0017] FIG. 4 provides a contour plot of static etch rate (SER) as a function of the level of the primary film-forming metal-complexing agent (anchor molecule) and the secondary film-forming metal-passivating agent for CMP compositions containing salicylhydroxamic acid (SHA) and 5-aminotetrazole (ATA).