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(71) Applicant: CABOT MICROELECTRONICS CORPORATION [US/US]; 870 N. Commons Drive, Aurora, IL 60504 (US).

(72) Inventors: WANG, Shumin; 1006 Dakota Circle, Naperville, IL 60563 (US). KAUFMAN, Vlasta, Brusic; 721 Easton Avenue, Geneva, IL 60134 (US). GRUMBINE, Steven, K.; 2523 Crestview Drive, Aurora, IL 60504 (US). ZHOU, Renjie; 2181 Walcott Road, #102, Aurora, IL 60504 (US). CHERIAN, Isaac, K.; 1036 Lakestone Lane, Aurora, IL 60504 (US).

(74) Agents: LANDO, Michelle, B.; Cabot Corporation, 157 Concord Road, P.O. Box 7001, Billerica, MA 01821-7001 et al. (US).

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(54) Title: POLISHING SYSTEM AND METHOD OF ITS USE

(57) Abstract: The invention provides a system for polishing one or more layers of a multi-layer substrate that includes a first metal layer and a second layer comprising (i) a liquid carrier, (ii) at least one oxidizing agent, (iii) at least one polishing additive that increases the rate at which the system polishes at least one layer of the substrate, wherein the polishing additive is selected from the group consisting of pyrophosphates, condensed phosphates, phosphonic acids and salts thereof, amines, amino alcohols, amides, imines, imino acids, nitriles, nitros, thiols, thioesters, thioethers, carbothiolic acids, carbothionic acids, thiocarboxylic acids, thiosalicylic acids, and mixtures thereof, and (iv) a polishing pad and/or an abrasive. The invention also provides a method of polishing a substrate comprising contacting a surface of a substrate with the system and polishing at least a portion of the substrate therewith. Moreover, the invention provides a method for polishing one or more layers of a multi-layer substrate that includes a first metal layer and a second layer comprising (a) contacting the first metal layer with the system, and (b) polishing the first metal layer with the system until at least a portion of the first metal layer is removed from the substrate.

POLISHING SYSTEM AND METHOD OF ITS USE

TECHNICAL FIELD OF THE INVENTION

This invention pertains to a polishing system and a method of polishing a substrate, particularly a multi-layer substrate that includes a first metal layer and a second layer.

BACKGROUND OF THE INVENTION

Integrated circuits are made up of millions of active devices formed in or on a substrate, such as a silicon wafer. The active devices are chemically and physically connected into a substrate and are interconnected through the use of multilevel interconnects to form functional circuits. Typical multilevel interconnects comprise a first metal layer, an interlevel dielectric layer, and sometimes a third and subsequent metal layer. Interlevel dielectrics, such as doped and undoped silicon dioxide (SiO_2) and/or low-κ dielectrics, are used to electrically isolate the different metal layers.

The electrical connections between different interconnection levels are made through the use of metal vias. U.S. Patent 5,741,626, for example, describes a method for preparing dielectric TaN layers. Moreover, U.S. Patent 4,789,648 describes a method for preparing multiple metallized layers and metallized vias in insulator films. In a similar manner, metal contacts are used to form electrical connections between interconnection levels and devices formed in a well. The metal vias and contacts may be filled with various metals and alloys, such as, for example, titanium (Ti), titanium nitride (TiN), aluminum copper (Al-Cu), aluminum silicon (Al-Si), copper (Cu), tungsten (W), and combinations thereof (hereinafter referred to as "via metals").

The via metals generally employ an adhesion layer (i.e., a barrier film), such as a titanium (Ti), titanium nitride (TiN), tantalum (Ta), tantalum nitride (TaN), tungsten (W), or tungsten nitride (WN) barrier film, to adhere the via metals to the SiO_2 substrate. At the contact level, the barrier film acts as a diffusion barrier to prevent the via metals from reacting with SiO_2.

In one semiconductor manufacturing process, metal vias and/or contacts are formed by a blanket metal deposition followed by a chemical-mechanical polishing (CMP) step. In a typical process, via holes are etched through an interlevel dielectric (ILD) to interconnection lines or to a semiconductor substrate. Next, a barrier film is formed over the ILD and is directed into the etched via hole. Then, a via metal is blanket-deposited over the barrier film and into the via hole. Deposition is continued until the via hole is filled with the blanket-deposited metal. Finally, the excess metal is removed by chemical-mechanical polishing (CMP) to form metal vias. Processes for manufacturing and/or CMP of vias are disclosed in U.S. Patents 4,671,851, 4,910,155, and 4,944,836.

Typical metal CMP systems contain an abrasive material, such as silica or alumina, suspended in an oxidizing, aqueous medium. U.S. Patent 5,244,534, for example, discloses a system containing alumina, hydrogen peroxide, and either potassium or ammonium hydroxide, which is useful in removing tungsten with little removal of the underlying insulating layer. U.S. Patent 5,209,816 discloses a system useful for polishing aluminum that comprises perchloric acid, hydrogen peroxide, and a solid abrasive material in an aqueous medium. U.S. Patent 5,340,370 discloses a tungsten polishing system comprising potassium ferricyanide, potassium acetate, acetic acid, and silica. U.S. Patent 5,391,258 and U.S. Patent 5,476,606 disclose systems for polishing a composite of metal and silica which includes an aqueous medium, abrasive particles and an anion which controls the rate of silica removal. U.S. Patent 5,770,095 discloses polishing systems comprising an oxidizing agent, a chemical agent, and an etching agent selected from aminoacetic acid and amidosulfuric acid. Other polishing systems for use in CMP applications are described in U.S. Patents 4,956,313, 5,137,544, 5,157,876, 5,354,490, and 5,527,423.

Barrier films of titanium, titanium nitride, and like metals, such as tungsten, are chemically active in general. Thus, such barrier films are similar in chemical nature to via metals. Consequently, a single system can be used effectively to polish both Ti/TiN barrier films and via metals at similar rates. Ta and TaN barrier films, however, are significantly different from Ti, TiN, and like barrier films. Ta and TaN are relatively inert in chemical nature as compared to Ti and TiN. Accordingly, the aforementioned systems are significantly less effective at polishing tantalum layers than they are at polishing titanium layers (e.g., the tantalum removal rate is significantly lower than the titanium removal rate). While via metals and barrier metals are conventionally polished with a single system due to their similarly high removal rates, joint polishing of via metals and tantalum and similar materials using conventional polishing systems results in undesirable effects, such as oxide erosion and via metal dishing.

Consequently, there remains a need for a system and/or method of polishing a substrate comprising a first metal layer and a second layer in a manner such that planarization efficiency, uniformity, and removal rate are maximized and undesirable effects, such as surface imperfections and damage to underlying topography, are minimized. The invention provides such a system and method. These and other characteristics and advantages of the present invention will be apparent from the description of the invention provided herein.

BRIEF SUMMARY OF THE INVENTION

The present invention provides a system for polishing one or more layers of a multi-layer substrate that includes a first metal layer and a second layer comprising (i) a liquid carrier, (ii) at least one oxidizing agent, (iii) at least one polishing additive that increases the rate at which the system polishes at least one layer of the substrate, wherein the polishing additive is selected from the group consisting of pyrophosphates, condensed phosphates, diphosphoic acids, triphosphonic acids, polyphosphonic acids, phosphonoacetic acids and salts thereof, aminoethylethanolamine, polyethyleneimine, amino alcohols, amides, imines, imino acids, nitriles, nitros, thiols, thioesters, thioethers, carbothiolic acids, carbothionic acids, thiocarboxylic acids, thiosalicylic acids, and mixtures thereof, (iv) at least one passivation film-forming agent, and (v) a polishing pad and/or an abrasive.

The present invention also provides a method of polishing a substrate comprising contacting a surface of the substrate with a polishing system comprising a liquid carrier, at least one oxidizing agent, at least one polishing additive that increases the rate at which the system polishes at least one layer of the substrate, wherein the polishing additive is selected from the group consisting of pyrophosphates, condensed phosphates, phosphonic acids and salts thereof, amines, amino alcohols, amides, imines, imino acids, mitriles, nitros, thiols, thioesters, thioethers, carbothiollic acids, carbothionic acids, thiocarboxylic acids, thiosalicylic acids, and mixtures thereof, and a polishing pad and/or an abrasive, and polishing at least a portion of the substrate therewith.

The present invention further provides a method of polishing one or more layers of a multi-layer substrate that includes a first noble metal layer and a second layer comprising contacting the substrate with a chemical-mechanical polishing system comprising a liquid carrier, at least one oxidizing agent, at least one polishing additive that increases the rate at which the system polishes the noble metal layer of the substrate, wherein the polishing additive is selected from the group consisting of carboxylates and acids thereof, hydroxylates and acids thereof, carbonylates and acids thereof, pyrophosphates, condensed phosphates, phosphonic acids and salts thereof, amines, amino alcohols, amides, imines, imino acids and salts thereof, nitriles, nitros, thiols, thioesters, thioethers, carbothiolic acids and salts thereof, carbothionic acids and salts thereof, thiocarboxylic acids and salts thereof, sulfonic acids and salts thereof, thiosalicylic acids and salts thereof, and mixtures thereof, and a polishing pad and/or an abrasive, and abrading at least a portion of the substrate to polish the substrate.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a system and method for polishing one or more layers of a multi-layer substrate that includes a first metal layer and a second layer. The system for polishing one or more layers of a multi-layer substrate that includes a first

metal layer and a second layer comprising (i) a liquid carrier, (ii) at least one oxidizing agent, (iii) at least one polishing additive that increases the rate at which the system polishes at least one layer of the substrate, wherein the polishing additive is selected from the group consisting of pyrophosphates, condensed phosphates, phosphonic acids and salts thereof, amines, amino alcohols, amides, imines, imino acids, nitriles, nitros, thiols, thioesters thioethers, carbothiolic acids, carbothionic acids, thiocarboxylic acids, thiosalicylic acids, and mixtures thereof, and (iv) a polishing pad and/or an abrasive. Components (i), (ii), and (iii) of the system of the present invention are collectively referred to hereinafter as "the liquid portion of the system." The abrasive forms part of the liquid portion of the system when present and suspended in the liquid carrier.

The system of the present invention can be used to polish any suitable substrate, especially one or more layers of a multi-layer substrate. Preferably, the system of the present invention is used to polish a multi-layer substrate that includes a first metal layer, a second layer, and optionally one or more additional layers. Suitable first metal layers include, for example, copper (Cu), aluminum (Al), aluminum copper (Al-Cu), aluminum

silicon (Al-Si), titanium (Ti), titanium nitride (TiN), tungsten (W), tungsten nitride (WN), noble metals (e.g., iridium (Ir), ruthenium (Ru), gold (Au), silver(Ag), and platinum (Pt)), and combinations thereof. Suitable second layers include, for example, titanium (Ti), titanium nitride (TiN), tantalum (Ta), tantalum nitride (TaN), tungsten (W), tungsten nitride (WN), oxides (e.g., silicon dioxide), low-κ materials and dielectrics (e.g., porous silica, fluorine-doped glass, carbon-doped glass, and organic polymers), and combinations thereof. The system of the present invention is particularly well suited for polishing a substrate comprising a first metal layer of copper or a copper alloy (i.e., a combination of copper and one or more metals), an adhesive layer of Ta or TaN, and one or more oxide layers.

The liquid carrier can be any suitable carrier (e.g., solvent). Suitable liquid carriers include, for example, aqueous carriers (e.g., water) and non-aqueous carriers. Preferably, the liquid carrier is water.

The oxidizing agent can be any suitable oxidizing agent. Suitable oxidizing agents include, for example, one or more per-compounds, which comprise at least one peroxy group (-O-O-). Suitable per-compounds include, for example, peroxides, persulfates (e.g., monopersulfates and dipersulfates), percarbonates, and acids thereof, and salts thereof, and mixtures thereof. Other suitable oxidizing agents include, for example, oxidized halides (e.g., chlorates, bromates, iodates, perchlorates, perbromates, periodates, and acids thereof, and mixtures thereof, and the like), perboric acid, perborates, percarbonates, peroxyacids (e.g., peracetic acid, perbenzoic acid, m-chloroperbenzoic acid, salts thereof, mixtures thereof, and the like), permanganates, chromates, cerium compounds, ferricyanides (e.g., potassium ferricyanide), mixtures thereof, and the like. Preferred oxidizing agents include, for example, hydrogen peroxide, urea-hydrogen peroxide, sodium peroxide, benzyl peroxide, di-t-butyl peroxide, peracetic acid, monopersulfuric acid, dipersulfuric acid, iodic acid, and salts thereof, and mixtures thereof.

Any suitable amount of the oxidizing agent can be present in the system of the present invention. Preferably, the oxidizing agent is present in the liquid portion of the system in an amount of about 0.1-30 wt.%. More preferably, the oxidizing agent is present in the liquid portion of the system in an amount of about 0.3-17 wt.%. Most preferably, the oxidizing agent is present in the liquid portion of the system in an amount of about 0.5-10 wt.%.

The polishing additive can be any suitable compound that increases the rate at which the system polishes at least one layer of the substrate. Suitable polishing additives include, for example, compounds that bind to copper. Preferably, at least one polishing additive is an organic polishing additive. It is also preferable for the polishing additive to be at least one compound selected from the group consisting of a phosphorous-containing

compound, a nitrogen-containing compound, a sulfur-containing compound, an oxygen-containing compound, and mixtures thereof The polishing additive can be any suitable phosphorous-containing compound.

The polishing additive can be any suitable phosphourous-containing compound. Suitable phosphorous-containing compounds include, for example, phosphates (e.g., pyrophosphates, tri-phosphates, condensed phosphates), phosphonic acids (e.g., mono-phosphonic acids, di-phosphonic acids, tri-phosphonic acids, poly-phosphonic acids), and salts of phosphonic acids. Preferred phosphorous-containing compounds include, for example, pyrophosphates, phosphonoacetic acid, ethylene diphosphonic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, and mixtures thereof. Preferred phosphorous-containing compounds also include, for example, $M_n^{+l}H_{3-n}PO_4$ and $M_m^{+l}H_{4-m}P_2O_7$, wherein M^{+1} is a cationic species (e.g., Na, K, Cs, Rb, NH_4^+), n = 0-3, and m = 0-4. Moreover, a preferred phosphorous-containing compound is R-O-PO_3, wherein R is an organic moiety selected from the group consisting of alkyl, aryl, cyclic, and aromatic groups having from 1- 18 carbon atoms.

The polishing additive also can be any suitable nitrogen-containing compound. Suitable nitrogen-containing compounds comprise, for example, one or more groups selected from amines, amides, amino acids, imines, imides, imino acids, nitriles, nitros (R-NO^2), and mixtures thereof. Accordingly, suitable nitrogen-containing compounds can comprise, for example, one or more groups selected from primary amines, secondary amines, tertiary amines, amino alcohols, hydroxylated amines, and mixtures thereof.

Preferably, at least one polishing additive comprises the structure XY-$NCR^1R^2CR^3R^4N$-X'Y', wherein X, Y, X', Y', R^1, R^2, R^3, and R^4 are selected from the group consisting of hydrogen (H) atoms, heteroatom-containing functional groups, alkyl groups, heteroatom-containing alkyl groups, cyclic groups, heteroatom-containing cyclic groups, aromatic groups, heteroatom-containing aromatic groups, and combinations thereof. More preferably, at least one polishing additive comprises the structure XY-$NCR^1R^2CR^3R^4N$-X'Y', wherein X and X' are H atoms, and wherein Y, Y', R^1, R^2, R^3, and R^4 are selected from the group consisting of hydrogen (H) atoms, heteroatom-containing functional groups, alkyl groups, heteroatom-containing alkyl groups, cyclic groups, heteroatom-containing cyclic groups, aromatic groups, heteroatom-containing aromatic groups, and combinations thereof. Even more preferably, at least one polishing additive comprises the structure XY- $NCR^1R^2CR^3R^4N$-X'Y', wherein X, Y, X', and Y' are H atoms, and wherein R^1, R^2, R^3, and R^4 are selected from the group consisting of hydrogen (H) atoms, heteroatom-containing functional groups, alkyl groups, heteroatom-containing alkyl groups, cyclic groups, heteroatom-containing cyclic groups, aromatic groups, heteroatom-containing aromatic groups, and combinations thereof. In this regard, nitrogen-containing compounds that consist of primary amine groups are preferred over

nitrogen-containing compounds that comprise secondary amine groups and/or tertiary amine groups, alone or in combination with primary amine groups. Moreover, it is suitable for at least one polishing additive to comprise the structure as described above, wherein the structure is in the form of a polymer comprising about four or more (e.g., about 10 or more, about 15 or more, about 20 or more, about 30 or more, about 40 or more, or even about 50 or more) dissimilar, similar, or even identical adjoined structures. Most preferably, the nitrogen-containing compound is selected from the group consisting of polyethylenimine, 1,3-diamino-2-propanol, imino-diacetic acid, 2-amino-l-butanol, ethylenediamine, aminoethylethanolamine, 2,2'-aminoethoxyethanol, and mixtures thereof.

"Heteroatom" is defined herein as any atom other than carbon and hydrogen atoms. Suitable heteroatorn-containing functional groups include, for example, hydroxyl groups, carboxylic acid groups, ester groups, ketone groups, amino groups (e.g., primary, secondary, and tertiary amino groups), amido groups, imido groups, thiol ester groups, thioether groups, nitrile groups, nitros groups, halogen groups, and combinations thereof. "Alkyl groups" are defined herein as any suitable alkyl group (e.g., a C_1-C_{30} alkyl group, a C_1-C_{24} alkyl group, a C_1-C_{18} alkyl group, a C_1-C_{12} alkyl group, or even a C_1-C_6 alkyl group) such as, for example, linear, branched, cyclic, saturated or unsaturated, aromatic or heteroarornatic alkyl groups. "Cyclic groups" are defined herein as any suitable cyclic group (e.g., a cyclic group having 4-20 members, such as a C_4-C_{20} Cyclic group).

The polishing additive can be any suitable sulfur-containing compound. Suitable sulfur-containing compounds include, for example, thiols, thioesters, thioethers, (R'C)(O)(SR") carbothiolic acids, (RC)(O)(SH) carbothionic acids, (RCS)(OH) thiocarboxylic acids, sulfonic acids, thiosalicylic acids, salts thereof and mixtures thereof, wherein R, R' and R" are selected from the group consisting of alkyl, aryl, cyclic, and aromatic groups having from 1- 18 carbon atoms. Preferred sulfur-containing compounds include, for example, thiodiacetic acid, thiosalicylic acids, and a mixture thereof.

The polishing additive can be any suitable oxygen-containing compound. Suitable oxygen-containing compounds include, for example, hydroxylates, carbonylates, carboxylates, and acids thereof. Suitable carboxylic acids include, for example, di-carboxylic acids, tri-carboxylic acids, and poly-carboxylic acids. Preferred oxygen-containing compounds include, for example, malonic acid, oxalic acid, citric acid, tartaric acid, succinic acid, malic acid, adipic acid, salts thereof, and mixtures thereof.

Suitable polishing additives also include one or more compounds selected from the group consisting of (i) compounds that are both phosphorous-containing compounds and nitrogen-containing compounds, (ii) compounds that are both phosphorous-containing compounds and sulfur-containing compounds, (iii) compounds that are both nitrogen-containing compounds and sulfur-containing compounds, and (iv) compounds that are

phosphorous-containing compounds, nitrogen containing compounds, and sulfur-containing compounds. Preferred polishing additives include, for example, compounds selected from the group consisting of 2-aminoethylphosphonic acid, amino(trimethylenephosphonic acid), diethylenetriaminepenta(methylenephosphonic acid), hexamethylenediamine-tetra(methylenephosphonic acid), and mixtures thereof. Moreover, preferred polishing additives include, for example, phosphonic compounds containing primary, secondary and/or tertiary amines, such as, for example, N-(phosphonomethyl)iminodiacetic acid, 2-aminoethyl dihydrogen phosphate, 2-aminoethylphosphonic acid, 2-aminoethylphosphonic acid, aminotri(methylenephosphonic acid) (i.e., Dequest® 2000 product), 1-hydroxyethylidene-1, 1-diphosphonic acid (i.e., Dequest® 2010 product), and diethylenetriaminepenta(methylenephosphonic acid) (i.e., Dequest® 2060 product).

The polishing additive can be present in the system of the present invention in any suitable concentration. Preferably, the polishing additive is present in the liquid portion of the system in an amount ranging from about 0.05-10 wt.%. More, preferably, the polishing additive is present in the liquid portion of the system in an amount ranging from about 0.3-5 wt.%.

The system of the present invention also can comprise any suitable stopping compound. Suitable stopping compounds include, for example, any suitable compound that inhibits the ability of the system to polish at least a portion of one or more layers of a multi-layer substrate. Suitable stopping compounds interact with (e.g., adhere to) the first metal layer, the second layer, and/or the one or more additional layers of a multi-layer substrate as described above and at least partially inhibit the removal of the layer(s) by the system of the present invention. Preferably, the stopping compound interacts with (e.g., adheres to) a second layer of a multi-layer substrate as described above and at least partially inhibits the removal of the second layer by the system. The term "at least partially inhibits" as used herein means that the system has a polishing selectivity of the first metal layer:second layer (e.g., Cu:Ta/TaN) of at least about 10:1, preferably at least about 30:1, more preferably at least about 50:1, and most preferably at least about 100:1.

The stopping compound can be any suitable cationically charged nitrogen-containing compound selected from the group of compounds comprising amines, imines, amides, imides, polymers thereof, and mixtures thereof. The term "cationically charged" as used herein means that a portion (e.g., about 5% or more, about 10% or more, about 15% or more, or about 20% or more) of the stopping compound in the liquid portion of the system is in cationic form at the operating pH of the system of the present invention. Preferably, the stopping compound has a pKa value that is 1 or more units greater than the operating pH of the liquid portion of the system. For example, in a system with a pH of 6.5, prefer-red stopping compounds would have a pKa value of about 7.5 or more.

Preferred stopping compounds also are oppositely charged from the surface charge of the second layer of the substrate layer. Suitable stopping compounds include, for example, compounds comprising primary amines, secondary amines, tertiary amines, quaternary amines (i.e., quaternary ammonium salts), etheramines, oligomeric amines, oligomeric imines, oligomeric amides, oligomeric imides, polymeric amines, polymeric imines, polymeric amides, polymeric imides, or mixtures thereof. Moreover, suitable stopping compounds include, for example, amino acids, amino alcohols, amino ether alcohols, or mixtures thereof. Preferred stopping compounds also include, for example, polyetheramines, polyethylenimines, N_4-amino(N,N'-bis-[3-aminopropyl]ethylenediamine), 4,7,10-trioxatridecane-1,13-diamine, 3,3-dimethyl-4,4-diaminodicyclohexylmethane, 2-phenylethylamine, N,N-dimethyldipropylenetriamine, 3-[2-methoxyethoxy]propylamine, dimethylaminopropylamine, 1,4-bis(3-aminopropyl)piperazine, and mixtures thereof. In addition, preferred stopping compounds include, for example, isophorone diamine, hexamethylenediamine, cyclohexyl-1,3-propanediamine, thiomicamine, (aminopropyl)-1,3-propanediamine, tetraethylenepentamine, tetramethylbutanediamine, propylamine, diaminopropanol, aminobutanol, (2-aminoethoxy)ethanol, or mixtures thereof.

The stopping compound can be present in the system of the present invention in any suitable concentration. It is suitable, for example, for the stopping compound to be present in the liquid portion of the system in a concentration of about 5 wt.% or less (e.g., about 0.001-5 wt.%). Preferably, the stopping compound is present in the liquid portion of the system in a concentration of about 3 wt.% or less (e.g., about 0.05 to about 3 wt.%).

The system of the present invention can comprise any suitable combination of at least one polishing additive and at least one stopping compound. For example, the system can comprise polyethylenimine and at least one polishing additive selected from the group consisting of a carboxylic acid (preferably, a di-, tri-, or poly-carboxylic acid), a phosphate (preferably, a pyrophosphate, a tri-phosphate, or a condensed phosphate), an acid thereof, and a phosphonic acid (preferably, a di-, tri-, or poly-phosphonic acid). The system also can comprise at least one polishing additive selected from the group consisting of a carboxylic acid (preferably, a di-, tri-, or poly-carboxylic acid), a phosphate (preferably, a pyrophosphate, a tri-phosphate, or a condensed phosphate), an acid thereof, and a phosphonic acid (preferably, a di-, tri-, or poly-phosphonic acid) and at least one stopping compound comprising two or more, three or more, four or more, five or more, or even six or more nitrogen atoms (e.g., at least one stopping compound comprising two or more primary amine groups, at least one stopping compound comprising two or more amino groups and 4 or more carbon atoms, or at least one stopping compound comprising two or more primary amine groups containing 3 or more carbon atoms). Moreover, the system can comprise at least one polishing additive selected from the group consisting of a

carboxylic acid (preferably, a di-, tri-, or poly-carboxylic acid), a phosphate (preferably, a pyrophosphate, a tri-phosphate, or a condensed phosphate), an acid thereof, and a phosphonic acid (preferably, a di-, tri-, or poly-phosphonic acid) and a quaternary ammonium salt comprising the structure $NR^1R^2R^3R^4$, wherein R^1, and R^2 are methyl groups and R^3 and R^4 are selected from the group consisting of of hydrogen (H) atoms, heteroatom-containing functional groups, alkyl groups, heteroatom-containing alkyl groups, cyclic groups, heteroatom-containing cyclic groups, aromatic groups, heteroatom-containing aromatic groups, and combinations thereof. In addition, the system can comprise at least one polishing additive selected from the group consisting of a carboxylic acid (preferably, a di-, tri-, or poly-carboxylic acid), a phosphate (preferably, a pyrophosphate, a tri-phosphate, or a condensed phosphate), an acid thereof, and a phosphonic acid (preferably, a di-, tri-, or poly-phosphonic acid) and at least one stopping compound comprising an amino propyl group and/or at least one stopping compound having a molecular weight (MW) of about 80 or more (e.g.. a MW of about 100 or more, a MW of about 250 or more). Furthermore, the system can comprise a peroxide, aminotri(methylenephosphonic acid), and 1,4-bis(3-aminopropyl)piperazine, and optionally, at least one passivation film forming agent comprising one or more 5-6 member heterocyclic nitrogen-containing rings. The system also can comprise a peroxide, tartaric acid, and a polyethylenimine, and, optionally, at least one passivation film forming agent comprising one or more 5-6 member heterocyclic nitrogen-containing rings.

The system of the present invention can comprise any suitable polishing pad and/or abrasive. It is suitable, for example, for the system of the present invention to comprise a polishing pad (e.g., an abrasive pad or a non-abrasive pad) and/or an abrasive that is suspended in the liquid carrier (e.g., water) of the system, thereby being a part of the liquid portion of the system. Moreover, it is suitable for the system of the present invention to comprise a polishing pad (e.g., an abrasive pad or a non-abrasive pad), wherein no abrasive is suspended in the liquid carrier of the system.

The polishing pad can be any suitable abrasive or non-abrasive pad. Suitable polishing pads are described, for example, in U.S. Patents 5,849,051 and 5,849,052.

Suitable polishing pads also include, for example, woven and non-woven polishing pads. Moreover, suitable polishing pads can comprise any suitable polymer of varying density, hardness, thickness, compressibility, ability to rebound upon compression, and compression modulus. Suitable polymers include, for example, polyvinylchloride, polyvinylfluoride, nylon, fluorocarbon, polycarbonate, polyster, polyacrylate, polyether, polyethylene,

polyamide, polyurethane, polystyrene, polypropylene, and coformed products thereof, and mixtures thereof. When an abrasive is fixed (e.g., embedded), in whole or in part, in or on the polishing pad of the system, such fixation on the polishing pad can be accomplished in any suitable manner.

Suitable abrasives include, for example, metal oxide abrasives, such as, for example, alumina, silica, titania, zirconia, germania, ceria, and co-formed products thereof, and mixtures thereof. The abrasives can be fumed products. Preferably, the abrasive of the system is alumina (e.g., fumed alumina) and/or silica (e.g., fumed silica).

The abrasive, as described above, can be fixed, in whole or in part, in or on the polishing pad of the system. Moreover, the abrasive can be present in the liquid portion of the system in any suitable amount. Preferably, the abrasive is present in the liquid portion of the system in an amount of about 0.1-30.0 wt.%. More preferably, the abrasive is present in the liquid portion of the system in an amount of about 0.5-6.0 wt.%.

The system of the present invention further may comprise one or more additional additives that improve or enhance the performance of the system. Suitable additional additives include, for example, passivation film-forming additives, polymeric compounds that reduce the polishing rate of at least one layer of the substrate, dispersants, surfactants, stabilizers, pH adjusters, regulators, buffers, and/or other additives that promote and/or control the polishing of metals and oxides. Such additional additives are known to those of skill in the art.

Suitable passivation film-forming agents include, for example any compound, or mixture of compounds, that facilitates the formation of a passivation layer (i.e., a dissolution-inhibiting layer) on a metal layer and/or a metal oxide layer. Suitable passivation film-forming agents include, for example, nitrogen-containing heterocyclic compounds. Preferably, the passivation film-forming agent comprises one or more 5-6 member heterocyclic nitrogen-containing rings. More preferably, the passivation film-forming agent is selected from the group consisting of 1,2,3-triazole, 1,2,4-triazole, benzotriazole, benzimidazole, benzothiazole, and derivatives thereof, such as, for example, hydroxy-, amino-, imino-, carboxy-, mercapto-, nitro-, urea-, thiourea-, or alkyl-substituted derivatives thereof. Most preferably, the passivation film-forming agent is selected from the group consisting of benzotriazole (BTA), 1,2,3-triazole, 1,2,4-triazole, and mixtures thereof.

The passivation film-forming agent can be present in the system of the present invention in any suitable concentration. Preferably, the passivation film-forming agent is present in the liquid portion of the system in an amount of about 0.005-1 wt.%. Preferably, the passivation film-forming agent is present in the liquid portion of the system in an amount of about 0.01-0.2 wt.%.

The system of the present invention further can comprise a source of ammonia (e.g., ammonia or an ammonium salt). Ammonia and/or ammonium salts enhance the removal rate and/or removal selectivity (e.g., Cu:Ta removal selectivity) of the system, by interacting with one or more components of the system (e.g., the polishing additive). Preferably, the system of the present invention comprises ammonia and/or ammonium salts and one or more polishing additives. Preferably, the system comprises a source of ammonia and at least one polishing additive selected from the group consisting of a carboxylic acid (preferably, a di-, tri-, or poly-carboxylic acid), a phosphate (preferably, a pyrophosphate, a tri-phosphate, or a condensed phosphate), an acid thereof, and a phosphonic acid (preferably, a di-, tri-, or poly-phosphonic acid). For example, the system can comprise aminotri(methylenephosphonic acid) and a source of ammonia (e.g., ammonia and/or an ammonium salt).

Suitable polymeric compounds include, for example, any suitable polymeric compound that reduces the polishing rate of at least one layer associated with the substrate. Preferably, the system comprises at least one polymeric compound comprising a polyvinylalcohol, a polyethylene oxide, a polypropylene oxide, a sulfonic acid polymer, a sulfonate polymer, or a mixture thereof.

Suitable surfactants include, for example, cationic surfactants, anionic surfactants, nonionic surfactants, amphoteric surfactants, fluorinated surfactants, mixtures thereof, and the like. Suitable pH adjusters, regulators, or buffers include, for example, sodium hydroxide, sodium carbonate, sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid, citric acid, potassium phosphate, mixtures thereof, and the like.

The present invention also provides a method of polishing a substrate with a system as described herein. Moreover, the present invention provides a method of polishing a multi-layer substrate as described above with the system. The system of the present invention is capable of polishing a substrate (e.g., a multi-layer substrate) at a relatively high rate, e.g., removing the first metal layer, the second layer, and/or the one or more additional layers of the substrate at a relatively high rate.

A substrate can be treated with the system of the present invention by any suitable technique that involves the use of a polishing pad. Preferably, the system is applied to the surface of a substrate and polished, such that at least a portion of one or more layers of the substrate is removed. More preferably, the system is applied to the first metal layer of a multi-layer substrate that includes a first metal layer and a second layer, and the first metal layer is polished with the system until at least a portion of the first metal layer is removed from the substrate. A second polishing system, composition, and/or slurry can be used in a subsequent polishing step to remove at least a portion of a second layer, dielectric layer, and/or one or more additional layers of a multi-layer substrate. Preferably, the second

polishing system has a greater polishing selectivity for the second layer (e.g., Ta or TaN) of the multi-layer substrate than for the first metal layer (e.g., Cu) of the substrate. Moreover, cleaning compositions can be used after some or all successive polishing steps, in order to remove remnants of the polished substrate and/or remnants of the polishing system, composition, and/or slurry.

It is suitable for the liquid portion of the system to be formulated prior to delivery to the polishing pad or to the surface of the substrate, e.g., in a batch or continuous process. It is also suitable for the liquid portion of the system to be formulated (e.g., mixed) on the surface of the polishing pad or on the surface of the substrate, through delivery of the components of the liquid portion of the system from two or more distinct sources, whereby the components meet at the surface of the polishing pad or at the surface of the substrate. In this regard, the flow rate at which the components of the liquid portion of the system are delivered to the polishing pad or to the surface of the substrate (i.e., the delivered amount of the particular components of the system) can be altered prior to the polishing process and/or during the polishing process, such that the polishing selectivity and/or viscosity of the system is altered. Moreover, it is suitable for the particular components of the liquid portion of the system being delivered from two or more distinct sources to have different pH values, or alternatively to have substantially similar, or even equal, pH values, prior to delivery to the surface of the polishing pad or to the surface of the substrate. It is also suitable for the particular components being delivered from two or more distinct sources to be filtered either independently or to be filtered jointly (e.g., together) prior to delivery to the surface of the polishing pad or to the surface of the substrate.

EXAMPLES

The following examples further illustrate the present invention but, of course, should not be construed as in any way limiting its scope.

The tantalum wafers referenced in all of the following examples and the copper wafers referenced in all but one of the following examples (i.e., Example 4) were tantalum blanket films and copper blanket films, respectively. The silicon dioxide wafers referenced in all of the following examples were blanket films with a thickness of approximately 9000 Å. All blanket films were deposited on a silicon substrate.

The copper, tantalum, and silicon dioxide wafers in the following examples (hereinafter collectively referred to as "test wafers") were each polished with an IPEC472 polishing machine. The polishing pads used in all but one of the following examples (i.e., Example 4) were Rodel® IC1000 polishing pads stacked on Rodel® SUBA IV pads. The polishing pads used in Example 4 were Rodel® IC1000 polishing pads, without stacked

Rodel® SUBA IV pads. The test wafers in all but one of the following examples (i.e., Example 4) were polished using a down force of about 20 kPa (3 psi), a back pressure of 0 kPa (0 psi), a table speed of 50 rpm, and a wafer holder speed of 30 rpm. The test wafers of Example 4 were polished using a down force of about 20 kPa (3 psi), a back pressure of about 14 kPa (2 psi), a table speed of 55 rpm, and a wafer holder speed of 30 rpm.

Test wafer removal rates were determined by directly measuring the thickness of each test wafer before and after polishing using a Tencor Surfscan® UV 1050 machine and a Tencor RS-75.

The systems in all but one of the following examples (i.e., Example 7) were adjusted to the target pH with ammonium hydroxide (NH_4OH), unless otherwise noted.

EXAMPLE 1

This example illustrates that the polishing rate of a first metal layer achievable by the system of the present invention is dependent on the presence and identity of the polishing additive in the system.

Copper wafers were polished separately with three different polishing systems (designated Systems 1A-1C) with 2 wt.% alumina (specifically, Cabot's Semi-Sperse® W-A355 product), 1 wt.% oxidizing agent (specifically, H_2O_2), 2.2 wt.% polishing additive (specifically, aminotri(methylenephosphonic acid) (i.e., Dequest® 2000 product)), either 0 M, 0.037 M, or 0.33 M ammonia (i.e., 0 wt.% NH_3, about 0.06 wt.% NH_3, and about 0.56 wt.% NH_3, respectively), and 0.08 wt.% film-forming agent (specifically, triazole), wherein each of the systems was pH-adjusted to 8.5 with HNO_3 or KOH.

For comparison purposes, the test wafers also were polished with a comparative system ("comparative") with 2 wt.% alumina (specifically, Cabot's Semi-Sperse® W-A355 product), wt.% oxidizing agent (specifically, H_2O_2), 0.33 M ammonia (i.e., about 0.56 wt.% NH_3), and 0.08 wt.% film-forming agent (specifically, triazole), wherein the system was pH-adjusted to 8.5 with HNO_3.

Following use of the systems, the removal rate (RR) of copper, tantalum, and SiO_2 by each system was determined, as well as the relative removal of copper to tantalum ("Cu:Ta"), with the resulting data set forth in Table 1.

Table 1:

System	Polishing Additive	NH_3 [M]	Cu RR [Å/min]
Comparative	None	0.33	180
1A	2.2 wt.% Dequest® 2000	None	1657
1B	2.2 wt.% Dequest® 2000	0.037	2527
1C	2.2 wt.% Dequest® 2000	0.33	6448

As is apparent from the data set forth in Table 1, the copper removal rates exhibited by systems containing a polishing additive (Systems 1A-1C) were greater than the copper removal rate of the comparative system that did not contain a polishing additive. Moreover, the copper removal rate exhibited by the system containing a polishing additive and 0.33 M NH_3 (System 1C) was greater than the copper removal rate of the system containing a polishing additive and 0.037 M NH_3 (System 1B), which, in turn, was greater than the copper removal rate of the system with a polishing additive and no NH_3 (System 1A).

These results demonstrate the significance of the presence of a polishing additive in the context of the present inventive system, as well as a combination of the polishing additive with a particular concentration of a source of ammonia, on the polishing rate achievable by the present inventive system and method.

EXAMPLE 2

This example illustrates that the polishing rate of a first metal layer achievable by the system of the present invention is dependent on the presence and identity of the polishing additive in the system.

Copper wafers were polished separately with five different polishing systems (designated Systems 2A-2E) with 2 wt.% alumina (specifically, Cabot's Semi-Sperse® W-A355 product), 1 wt.% oxidizing agent (specifically, H_2O_2), varying concentrations of a first polishing additive (specifically, 0.16 M ethylenediamine, 0.33 M 2-amino-1-butanol, 0.33 M aminoethylethanolamine, 0.33 M 2,2'-aminoethoxyethanol, or 0.33 M of a low molecular weight ethylenimine copolymer (i.e., Lupasol® FG)), 2.2 wt.% of a second polishing additive (specifically, aminotri(methylenephosphonic acid) (i.e., Dequest® 2000 product)), and 0.08 wt.% film-forming agent (specifically, triazole), wherein each of the systems had a pH of 8.5. Following use of the systems, the removal rate (RR) of copper by each system was determined, with the resulting data set forth in Table 2. The molecular structure of a portion of the first polishing additive of each system also is included in Table 2

and the XY- $NCR^1R^2CR^3R^4N$-X'Y' moiety, as discussed above, is in bold in the molecular structure of Table 2, if present in the polishing additive.

Table 2

System	1st Polishing Additive [M]	Molecular Structure	Cu RR [Å/min]
2A	0.16 M ethylenediamine	**H2NCH2CH2NH2**	>15000
2B	0.33 M aminoethylethanolamine	**H2NCH2CH2NH**CH2CH2OH	10815
2C	0.33 M Lupasol® FG	**H2N-[CH2CH2NH(R)]-NH2**	4985
2D	0.33 M 2,2'-aminoethoxyethanol	H2NCH2CH2OCH2CH2OH	3196
2E	0.33 M 2-amino-1-butanol	H3CCH2CH2CH(NH2)OH	2091

As is apparent from the data set forth in Table 2, the copper removal rates exhibited by systems containing a polishing additive that comprises the XY- $NCR^1R^2CR^3R^4N$-X'Y' moiety (Systems 2A-2C) were greater than the copper removal rates of the systems that contained a polishing additive that did not comprise the XY- $NCR^1R^2CR^3R^4N$-X'Y' moiety (Systems 2D-2E). Moreover, among the systems containing the XY- $NCR^1R^2CR^3R^4N$-X'Y' moiety (Systems 2A-2C), the copper removal rate exhibited by the system in which X, Y, X', and Y' were hydrogen atoms (i.e., two primary amino groups) (System 2A) was greater than the copper removal rate exhibited by the system in which X, Y, and X' were hydrogen atoms and Y' was ethanol (i.e., one primary amino group and one secondary amino group) (System 2B), which, in turn, was greater than the copper removal rate exhibited by the system comprising a ratio of primary:secondary:tertiary amino groups of about 1:0.82:0.53 (System 2C).

These results demonstrate the significance a polishing additive comprising the XY-NCR_2CR_2N-X'Y' moiety in the context of the present inventive system, as well as the significance of the ratio of primary:secondary:tertiary amino groups in the XY-NCR_2CR_2N-X'Y moiety of the polishing additive, on the polishing rate achievable by the present inventive system and method.

EXAMPLE 3

This example illustrates that the polishing rate of a first metal layer achievable by the system of the present invention is dependent on the presence and identity of the polishing additive in the system.

Copper wafers and tantalum wafers were polished separately with sixteen different polishing systems (designated Systems 3A-3P) with 3 wt.% alumina (specifically, Cabot's

Semi-Sperse® W-A355 product), 2.5 wt.% oxidizing agent (specifically, H_2O_2), and either 0.5 wt.% or 1 wt.% of a polishing additive (specifically, 1-diphosphonic acid (i.e., Dequest® 2010 product), diethylenetriaminepenta(methylenephosphonic acid) (i.e., Dequest® 2060 product), N-phosphonomethyliminodiacetic acid, Lupasol® FG, 1,3-diamino-2-propanol, 2-imino-4-thiobiuret, iminodiacetic acid, dimethylglyoxime, dipyridineamine, iminodiacetonitrile, guanidine nitrate, pyrazinecarbonitrile, thioglycolic(mercaptoacetic)acid, thiodipropanionic acid, 1 wt.% of an ethoxylated high molecular weight polyethylenimine (i.e., Lupasol® SC-61B), or a modified high molecular weight ethylenimine polymer (i.e., Lupasol® SKA)), wherein each of the systems had a pH of 5 (Systems 3C, 3F, 3H, 3I, 3K, 3L, 3O, and 3P) or a pH of 7.7 (Systems 3A, 3B, 3D, 3F, 3G, 3J, 3M, and 3N).

For comparison purposes, the test wafers also were polished with a control system ("control") with 3 wt.% alumina (specifically, Cabot's Semi-Sperse® W-A355 product) and 2.5 wt.% oxidizing agent (specifically, H_2O_2), wherein the control system had a pH of 7.7.

Following use of the systems, the removal rate (RR) of copper and tantalum by each system was determined, as well as the relative removal of copper to tantalum ("Cu:Ta"). The resulting data are set forth in Table 3.

Table 3:

System	Polishing Additive	Cu RR [Å/min]	Ta RR [Å/min]	Cu:Ta
Control	None	87	198	1:2
3A	1 wt.% Dequest® 2010	4777	406	12:1
3B	1 wt.% Dequest® 2060	7624	279	27:1
3C	1 wt.% N-phosphonomethyl-iminodiacetic acid	4333	314	14:1
3D	1 wt.% Lupasol® FG	733	13	56:1
3E	1 wt.% 1,3-diamino-2-propanol	2668	50	53:1
3F	1 wt.% 2-imino-4-thiobiuret	1216	95	13:1
3G	1 wt.% iminodiacetic acid	7738	533	15:1
3H	0.5 wt.% dimethylglyoxime	1153	273	4:1
3I	0.5 wt.% dipyridylamine	3022	264	11:1
3J	1 wt.% iminodiacetonitrile	243	446	1:1.8
3K	0.5 wt.% guanidine nitrate	281	289	1:1
3L	0.5 wt.% pyrazinecarbonitrile	246	323	1:1.3

3M	1 wt.% thioglycolic(mercaptoacetic) acid	552	263	2:1
3N	1 wt.% thiodipropanionic acid	652	250	2.6:1
3O	1 wt.% Lupasol® SC-61B	682	14	49:1
3P	0.5 wt.% Lupasol® SKA	480	15	32:1

As is apparent from the data set forth in Table 3, the ratio of copper removal to tantalum removal (i.e., the Cu:Ta removal selectivity) exhibited by systems containing a polishing additive (Systems 3A-3D) were greater than the Cu:Ta removal selectivity of the control polishing composition. Moreover, the Cu:Ta removal selectivity of the system containing Lupasol® FG (System 3D) was the greatest among the systems of Table 3.

These results demonstrate the significance of the presence and identity of the polishing additive in the context of the present inventive system on the polishing rate and selectivity achievable by the present inventive system and method.

EXAMPLE 4

This example illustrates that the polishing rate of a first metal layer achievable by the system of the present invention is dependent on the presence and identity of the polishing additive in the system.

Copper wafers and tantalum wafers were polished separately with six different polishing systems (designated Systems 4A-4F) with 5 wt.% silica (specifically, Cabot's Semi-Sperse® SC-E product), 2.5 wt.% oxidizing agent (specifically, H_2O_2), and either 0.5 wt.% or 1 wt.% of a polishing additive (specifically, potassium pyrophosphate ($K_4P_2O_7$), phosphonoacetic acid, 1-di-phosphonic acid (i.e., Dequest® 2010 product), aminotri(methylenephosphonic acid) (i.e., Dequest® 2000 product), a low molecular weight ethylenimine copolymer (i.e., Lupasol® FG), or a high molecular weight ethylene-imine homopolymer (i.e., Lupasol® P)), wherein each of the systems had a pH of 5 (Systems 4A, 4D, 4E, and 4F) or a pH of 7.7 (Systems 4B and 4C).

For comparison purposes, the test wafers also were polished with a control system ("control") with 5 wt.% silica (specifically, Cabot's Senti-Sperse® SC-E product), 2.5 wt.% oxidizing agent (specifically, H_2O_2), wherein the control system had a pH of 7.7.

Following use of the systems, the removal rate (RR) of copper and tantalum by each system was determined, as well as the relative removal of copper to tantalum ("Cu:Ta"). The resulting data are set forth in Table 4.

Table 4:

System	Polishing Additive	Cu RR [Å/min]	Ta RR [Å/min]	Cu:Ta
Control	none	306	383	1:1.3
4A	0.5 wt.% $K_4P_2O_7$	3918	798	5:1
4B	0.5 wt.% phosphonoacetic acid	3658	40	91:1
4C	0.5 wt.% Dequest® 2010	2532	66	38:1
4D	0.5 wt.% Dequest® 2000	5245	337	16:1
4E	1 wt.% Lupasol® FG	5784	9	643:1
4F	1 wt.% Lupasol® P	4297	5	860:1

As is apparent from the data set forth in Table 4, the ratio of copper removal to tantalum removal (i.e., the Cu:Ta removal selectivity) exhibited by systems containing a polishing additive (Systems 4A-4F) were greater than the Cu:Ta removal selectivity of the control polishing composition. Moreover, the Cu:Ta removal selectivity of the system containing Lupasol® FG and Lupasol® P (Systems 4E and 4F, respectively) was greater than the Cu:Ta removal selectivities of the systems containing $K_4P_2O_7$, phosphonoacetic acid, Dequest® 2010, and Dequest® 2000 (Systems 4A, 4B, 4C, and 4D, respectively).

These results demonstrate the significance of the presence and identity of the polishing additive in the context of the present inventive system on the polishing rate and selectivity achievable by the present inventive system and method.

EXAMPLE 5

This example illustrates that the polishing selectivity of a multi-layer substrate achievable by the system of the present invention is dependent on the presence and identity of the polishing additive and stopping compound in the system.

Copper wafers, tantalum wafers, and silicon dioxide (SiO_2) wafers were polished separately with eight different polishing systems (designated Systems 5A-5G) with 3 wt.% alumina (specifically, Cabot's Semi-Sperse® W-A355 product), 2.5 wt.% oxidizing agent (specifically, H_2O_2), varying concentrations of a polishing additive (specifically, 1.25 wt.% tartaric acid, 0.5 wt.% 1-di-phosphonic acid (i.e., Dequest® 2010 product), 0.75 wt.% aminotri(methylenephosphonic acid) (i.e., Dequest® 2000 product), 0.8 wt.% Dequest® 2010 product, or 2.5 wt.% Dequest® 2000 product), and varying concentrations of a stopping compound (specifically, 0.25 wt.% Lupasol® SKA, which contains 25% of an ethylenimine polymer (i.e., 0.06 wt.% polyethylenimine), 0.1 wt.% dicyanoimidazole, 0.5

wt.% Lupasol SKA (i.e., 0.12 wt.% polyethylenimine), 0.5 wt.% polyacylamide, or 0.5 wt.% 1,4-bis(3-aminopropyl) piperazine, or 0.5 wt.% Varisoft® 300, which contains cetyl trimethylammonium chloride, wherein each of the systems had a pH of 5 (System 5E) or a pH of 7.7 (Systems 5A-5D, 5F-5G). Moreover, System 5C contained 0.005 wt.% surfactant (specifically, Triton DF-16).

For comparison purposes, the test wafers also were polished with a control system ("control") with 3 wt.% alumina (specifically, Cabot's Semi-Sperse® W-A355 product) and 2.5 wt.% oxidizing agent (specifically, H_2O_2), wherein the control system had a pH of 7.7. Moreover, also for comparison purposes, the test wafers were polished with (i) a comparative system ("comparative 1") with 3 wt.% alumina (specifically, Cabot's Semi-Sperse® W-A355 product), 2.5 wt.% oxidizing agent (specifically, H_2O_2), and 1.25 wt.% polishing additive (specifically, tartaric acid), and with (ii) a comparative system ("comparative 2") with 3 wt.% alumina (specifically, Cabot's Semi-Sperse® W-A355 product), 2.5 wt.% oxidizing agent (specifically, H_2O_2), and 1 wt.% polishing additive (specifically, Dequest® 2010 product), wherein each of the comparative systems had a pH of 7.7.

Following use of the systems, the removal rate (RR) of copper, tantalum, and SiO_2 by each system was determined, as well as the relative removal of copper to tantalum ("Cu:Ta"). The resulting data are set forth in Table 5.

Table 5:

System	Polishing Additive	Stopping Compound	Cu RR [Å/min]	Ta RR [Å/min]	SiO_2 RR [Å/min]	Cu:Ta
Control	none	none	87	198	-	1:2
Comparative 1	1.25 wt.% tartaric acid	none	3615	133	53	27:1
Comparative 2	1 wt.% Dequest® 2010	none	4777	406	-	12:1
5A	1.25 wt.% tartaric acid	0.06 wt.% polyethylenimine	2375	19	12	125:1
5B	0.5 wt.% Dequest® 2010	0.1 wt.% dicyano-imidazole	3163	175	54	18:1
5C	0.75 wt.% Dequest® 2000	0.12 wt.% polyethylenimine	3265	28	16	117:1
5D	0.8 wt.% Dequest® 2010	0.12 wt.% polyethylenimine	2949	35	26	84:1
5E	0.75 wt.% Dequest® 2000	0.5 wt.% polyacylamide	6381	43	28	148:1
5F	2.5 wt.% Dequest® 2000	0.5 wt.% 1,4-bis-(3-aminopropyl) piperazine	3860	109	5.5	35:1
5G	2.5 wt.% Dequest® 2000	0.5 wt.% Varisoft® 300	2260	97.6	3.6	23:1

As is apparent from the data set forth in Table 5, the ratio of copper removal to tantalum removal (i.e., the Cu:Ta removal selectivity) exhibited by systems containing a polishing additive and a stopping compound (Systems 1A-1G) were greater than the Cu:Ta removal selectivity of both the control polishing system and of the comparative 2 polishing system, and were similar to or greater than the Cu:Ta removal selectivity of the comparative 1 polishing system. Moreover, the SiO_2 removal rate exhibited by systems containing a

polishing additive and a stopping compound (Systems 1A-1G) were similar to or less than the SiO_2 removal rate exhibited by the comparative 1 polishing system.

These results demonstrate the significance of the combination of a polishing additive and a stopping compound in the context of the present inventive system, as well as the effect of the particular polishing additive, in combination with the particular stopping compound, on the polishing rate and selectivity achievable by the present inventive system and method.

EXAMPLE 6

This example illustrates that the polishing selectivity of a multi-layer substrate achievable by the system of the present invention is dependent on the presence and identity of the polishing additive and stopping compound in the system.

Copper wafers, tantalum wafers, and silicon dioxide (SiO_2) wafers were polished separately with three different polishing systems (designated Systems 2A-2C) with 5 wt.% silica (specifically, Cabot's Cab-O-Sperse® SC-E product), 2.5 wt.% oxidizing agent (specifically, H_2O_2), varying concentrations of a polishing additive (specifically, 0.8 wt.% 1-di-phosphonic acid (i.e., Dequest® 2010 product), 0.75 wt.% aminotri(methylenephosphonic acid) (i.e., Dequest® 2000 product), or 0.75 wt.% diethylenetriaminepenta(methylenephosphonic acid) (i.e., Dequest® 2060 product)), and 0.5 wt.% stopping compound (specifically, 0.5 wt.% Lupasol® SKA, which contains 25% of an ethylenimine polymer (i.e., 0.12 wt.% polyethylenimine)), wherein each of the systems had a pH of 7.7. For comparison purposes, the test wafers also were polished with a control system ("control") with 5 wt.% silica (specifically, Cabot's Cab-O-Sperse® SC-E product) and 2.5 wt.% oxidizing agent (specifically, H_2O_2), wherein the control system had a pH of 8. Following use of the systems, the removal rate (RR) of copper, tantalum, and SiO_2 by each system was determined, as well as the relative removal of copper to tantalum ("Cu:Ta"), with the resulting data set forth in Table 6.

Table 6:

System	Polishing Additive	Stopping Compound	Cu RR [Å/min]	Ta RR [Å/min]	SiO_2 RR [Å/min]	Cu:Ta
Control	none	none	306	383	299	1:1.3
6A	0.8 wt.% Dequest® 2010	0.12 wt.% Lupasol® SKA	1789	13	5	138:1
6B	0.75 wt.% Dequest® 2000	0.12 wt.% Lupasol® SKA	1733	9	20	193:1
6C	0.75 wt.% Dequest® 2060	0.12 wt.% Lupasol® SKA	2132	7	12	305:1

As is apparent from the data set forth in Table 6, the ratio of copper removal to tantalum removal (i.e., the Cu:Ta removal selectivity) exhibited by systems containing a polishing additive and a stopping compound (Systems 6A-6C) were greater than the Cu:Ta removal selectivity of the control system that did not contain a polishing additive or a stopping compound. Moreover, the copper removal rate and the Cu:Ta removal selectivity of the system containing a stopping compound and Dequest® 2060 product (System 6C) were greater than the copper removal rate and the Cu:Ta removal selectivity of the system containing a stopping compound and Dequest® 2000 product (System 6B), which in turn were greater than the copper removal rate and the Cu:Ta removal selectivity of the system containing a stopping compound and Dequest® 2010 product (System 6A). Moreover, the SiO_2 removal rate exhibited by systems containing a polishing additive and a stopping compound (Systems 6A-6C) were greater than the SiO_2 removal rate of the control system that did not contain a polishing additive or a stopping compound.

These results demonstrate the significance of the combination of a polishing additive and a stopping compound in the context of the present inventive system, as well as the effect of the particular polishing additive, in combination with the stopping compound, on the polishing rate and selectivity achievable by the present inventive method.

EXAMPLE 7

This example illustrates that the polishing selectivity of a multi-layer substrate achievable by the system of the present invention is dependent on the identity of the stopping compound in the system.

Copper wafers, tantalum wafers, and silicon dioxide (SiO_2) wafers were polished separately with fourteen different polishing compositions with 3 wt.%

alumina (specifically, Cabot's Semi-Sperse® W-A355 product), 2.5 wt.% oxidizing agent (specifically, H_2O_2), 1 wt.% polishing additive (specifically, ammonium oxalate ($(NH_4)_2C_2O_4$)), and varying concentrations of a stopping compound (specifically, 0.2 wt.% isophoronediamine, 0.2 wt.% hexamethylenediamine, 0.2 wt.% N-cyclohexyl-1,3-propanediamine, 0.2 wt.% N-(3-aminopropyl)-1,3-propanediamine, 0.2 wt.% tetraethylenepentamine, 0.2 wt.% N,N,N',N'-tetramethyl-1,4-butanediamine, 0.5 wt.% propylamine, 0.2 wt.% 2-(2-aminoethoxy)ethanol, 2.0 wt.% 1,3-diamino-2-propanol, 1.0 wt.% thiomicamine, 3.0 wt.% 2-amino-l-butanol, 0.2 wt.% 4,7,10-trioxa-1,13-tridecanediamine, 0.2 wt.% lysine, 0.2 wt.% poly[bis(2-chloroether)-*alt*-1,3-bis(3-dimethylamino)propyl], wherein each of the systems had a pH of 7.6. For comparison purposes, the test wafers also were polished with a control system ("control") with 3 wt.% alumina (specifically, Cabot's Semi-Sperse® W-A355 product), 2.5 wt.% oxidizing agent (specifically, H_2O_2), and 1 wt.% polishing additive (specifically, ammonium oxalate $(NH_4)_2C_2O_4$), wherein the control system had a pH of 7.6. Following use of the polishing compositions, the relative tantalum (Ta) removal rate and the relative silicon dioxide (SiO_2) removal rate of each system were determined in comparison with the removal rates of the control system, with the resulting data set forth in Table 7.

Table 7:

System	Stopping Compound	Relative Removal Rate Ta	Relative Removal Rate SiO_2
Control	none	1	1
7A	0.2 wt.% isophoronediamine	0.17	-
7B	0.2 wt.% hexamethylenediamine	0.24	0.27
7C	0.2 wt.% N-cyclohexyl-1,3-propanediamine)	0.12	0.11
7D	0.2 wt.% N-(3-aminopropyl)-1,3-propanediamine	0.17	0.03
7E	0.2 wt.% tetraethylenepentamine	0.21	0.13
7F	0.2 wt.% N,N,N',N'-tetramethyl-1,4-butanediamine	-	0.37
7G	0.5 wt.% propylamine	0.17	-
7H	0.2 wt.% 2-(2-aminoethoxy)ethanol	0.71	-

7I	3.0 wt.% 2-amino-1-butanol	0.04	0.21
7J	0.2 wt.% 4,7,10-trioxa-1,13-tridecanediamine	0.28	0.22
7K	0.2 wt.% lysine	0.35	1.1
7L	0.2 wt.% poly[bis(2-chloroether)-*alt*-1,3-bis(3-dimethylamino)propyl]	-	0.33

As is apparent from the data set forth in Table 7, the relative tantalum removal rates exhibited by the evaluated polishing systems containing a polishing additive and a stopping compound were desirably less than the relative tantalum removal rate of the control polishing composition that did not contain both a polishing additive and a stopping compound. Moreover, the relative SiO_2 removal rates exhibited by all but one of the evaluated polishing systems containing a polishing additive and a stopping compound were desirably less than the relative SiO_2 removal rate of the control polishing system that did not contain both a polishing additive and a stopping compound.

These results demonstrate the significance of the presence of a stopping compound in the context of the present inventive system, as well as the effect of the particular stopping compound, on the removal rate and selectivity achievable by the present inventive method.

EXAMPLE 8

This example illustrates that the polishing selectivity of a multi-layer substrate achievable by the system of the present invention, as well as the minimization of surface defects by the system, is dependent on the identity of the stopping compound in the system.

Copper wafers, tantalum wafers, and silicon dioxide (SiO_2) wafers were polished separately with two different polishing systems (designated Systems 8A and 8B) with 3 wt.% alumina (specifically, Cabot's Semi-Sperse® W-A355 product), 2.5 wt.% oxidizing agent (specifically, H_2O_2), 1.25 wt.% polishing additive (specifically, tartaric acid), and either 0 wt.% or 0.06 wt.% stopping compound (specifically, an ethylenimine polymer (i.e., Lupasol® SKA)), wherein each of the systems had a pH of 7.7. Following use of the systems, the relative removal of copper to tantalum ("Cu:Ta"), copper dishing, and SiO_2 erosion were measured, with the resulting data set forth in Table 8. Wafer dishing of copper lines (i.e., copper dishing) and SiO_2 erosion were determined through use of a Tencor P-20 Long Scan Profiler. Copper dishing was measured at a 10 μm feature size and at a 50 μm feature size ("10 μm/50 μm"). SiO_2 erosion was measured for an array having a 2 μm line and a 4 μm pitch ("2 μm/4 μm array").

Table 8:

System	Polishing Additive	Stopping Compound	Cu:Ta	Cu Dishing [10 μm/50 μm]	SiO_2 Erosion [2 μm/4 μm array]
8A	1.25 wt.% tartaric acid	None	81:1	952 Å /1868 Å	896 Å
8B	1.25 wt.% tartaric acid	0.06 wt.% Lupasol® SKA	220:1	840 Å /1552 Å	714 Å

As is apparent from the data set forth in Table 8, the ratio of copper removal to tantalum removal (i.e., the Cu:Ta removal selectivity) exhibited by the system containing a polishing additive and a stopping compound (System 8B) were greater than the Cu:Ta removal selectivity exhibited by the system containing only a polishing additive (System 8A). Moreover, Cu dishing and SiO_2 erosion exhibited by the system containing a polishing additive and a stopping compound (System 4B) were less than the Cu dishing and SiO_2 erosion exhibited by the system containing only a polishing additive (System 8A).

These results demonstrate the significance of the presence of a stopping compound in the context of the present inventive system on the polishing selectivity achievable by the system, as well as the minimization of surface defectivity of the polished substrate by the system of the present invention.

All of the references cited herein, including patents, patent applications, and publications, are hereby incorporated in their entireties by reference.

While this invention has been described with an emphasis upon preferred embodiments, it will be obvious to those of ordinary skill in the art that variations of the preferred embodiments may be used and that it is intended that the invention may be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications encompassed within the spirit and scope of the invention as defined by the following claims.

CLAIMS

1. A system for polishing one or more layers of a multi-layer substrate that includes a first metal layer and a second layer comprising (i) a liquid carrier, (ii) at least one oxidizing agent, (iii) at least one polishing additive that increases the rate at which the system polishes at least one layer of the substrate, wherein the polishing additive is selected from the group consisting of pyrophosphates, condensed phosphates, diphosphonic acids, triphosphonic acids, polyphosphonic acids, phosphonoacetic acids and salts thereof, aminoethylethanolamine, polyethyleneimine, amino alcohols, amides, imines, imino acids, nitriles, nitros, thiols, thioesters, thioethers, carbothiolic acids, carbothionic acids, thiocarboxylic acids, thiosalicylic acids, and mixtures thereof, (iv) at least one passivation film-forming agent, and (v) a polishing pad and/or an abrasive.
2. The system of claim 1, wherein the liquid carrier is a nonaqueous solvent.
3. The system of claim 1, wherein the liquid carrier is water.
4. The system of claim 3, wherein the system comprises an abrasive suspended in the liquid carrier.
5. The system of claim 3, wherein the abrasive is fixed on the polishing pad.
6. The system of claim 3, wherein no abrasive is present in the system, and the polishing pad is a non-abrasive pad.
7. The system of claim 3, wherein at least one oxidizing agent is a peroxide, and at least one passivation film-forming agent comprises one or more 5-6 member heterocyclic nitrogen-containing rings.
8. The system of claim 3, wherein at least one polishing additive is selected from the group consisting of ethylene di-phosphonic acid, 1-hydroxyethylidene-1,1-di-phosphonic acid, and a mixture thereof.
9. The system of claim 8, wherein at least one oxidizing agent is a peroxide, and at least one passivation film-forming agent comprises one or more 5-6 member heterocyclic nitrogen-containing rings.
10. The system of claim 3, wherein at least one polishing additive is both (a) a compound selected from the group consisting of pyrophosphates, condensed phosphates, phosphonic acids and salts thereof, and (b) a compound selected from the group consisting of amines, amino alcohols, amides, imines, imino acids, nitriles, and nitros.
11. The system of claim 3, wherein at least one polishing additive is both (a) a compound selected from the group consisting of amines, amino alcohols, amides, imines, imino acids, nitriles, and nitros, and (b) a compound selected from the group consisting of thiols, thioesters, and thioethers, carbothiolic acids, carbothionic acids, thiocarboxylic acids, and thiosalicylic acids.

12. The system of claim 10, wherein at least one polishing additive is selected from the group consisting of 2-aminoethyl phosphonic acid, amino(trimethylenephosphonic acid), diethylenetriaminepenta(methylenephosphonic acid), hexamethylenediaminetetra(methylene phosphonic acid), and mixtures thereof.
13. The system of claim 3, wherein the system further comprises a source of ammonia.
14. The system of claim 13, wherein the system comprises (i) aminotri-(methylenephosphonic acid) and (ii) ammonia or an ammonium salt.
15. The system of claim 3, wherein the system further comprises at least one stopping compound.
16. The system of claim 3, wherein the system further comprises at least one polymeric compound that reduces the polishing rate of at least one layer associated with the substrate.
17. The system of claim 3, wherein at least one passivation film-forming agent is selected from the group consisting of 1,2,3-triazole, 1,2,4-triazole, benzotriazole, benzimidazole, benzothiazole, and hydroxy-, amino-, imino-, carboxy-, mercapto-, nitro-, urea-, thiourea-, or alkyl-substituted derivatives thereof.
18. The system of claim 3, wherein the abrasive is a metal oxide abrasive.
19. The system of claim 18, wherein the abrasive is selected from the group consisting of alumina, ceria, germania, silica, titania, zirconia, and coformed products thereof, and mixtures thereof.
20. The system of claim 19, wherein the abrasive is alumina.
21. The system of claim 1, wherein at least one polishing additive is iminodiacetic.
22. The system of claim 21 wherein the system further comprises at least one stopping compound.
23. The system of claim 21, wherein the system further comprises at least one polymeric compound that reduces the polishing rate of at least one layer associated with the substrate.
24. The system of claim 15, wherein the system further comprises ammonia or an ammonium salt.
25. A method of polishing a substrate comprising:

(i) contacting a surface of the substrate with a polishing system comprising:

(a) a liquid carrier,

(b) at least one oxidizing agent,

(c) at least one polishing additive that increases the rate at which the system polishes at least one layer of the substrate, wherein the polishing additive is selected from the group consisting of pyrophosphates, condensed phosphates, phosphonic acids and salts thereof, amines, amino alcohols,

amides, imines, imino acids, nitriles, nitros, thiols, thioesters, thioethers, carbothiolic acids, carbothionic acids, thiocarboxylic acids, thiosalicylic acids, and mixtures thereof, and

(d) a polishing pad and/or an abrasive, and

(ii) polishing at least a portion of the substrate therewith.

26. The method of claim 25, wherein the liquid carrier is a nonaqueous solvent.

27. The method of claim 25, wherein the liquid carrier is water.

28. The method of claim 27, wherein the system comprises an abrasive suspended in the liquid carrier.

29. The method of claim 27, wherein the system comprises an abrasive, and the abrasive is fixed on the polishing pad.

30. The method of claim 27, wherein no abrasive is present in the system, and the polishing pad is a non-abrasive pad.

31. The method of claim 27, wherein at least one polishing additive is selected from the group consisting of di-phosphonic acids, tri-phosphonic acids, poly-phosphonic acids, phosphonoacetic acids, and mixtures thereof.

32. The method of claim 31, wherein at least one oxidizing agent is a peroxide, and wherein the system further comprises at least one passivation film-forming agent comprising one or more 5-6 member heterocyclic nitrogen-containing rings.

33. The method of claim 31, wherein at least one polishing additive is selected from the group consisting of ethylene diphosphonic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, and a mixture thereof.

34. The method of claim 27, wherein at least one polishing additive is selected from the group consisting of primary amines, secondary amines, tertiary amines, hydroxylated amines, and mixtures thereof.

35. The method of claim 34, wherein at least one polishing additive comprises the structure XY-NCR^{1}R^{2}CR^{3}R^{4}N-X'Y', wherein X, Y, X', Y', R^1, R^2, R^3, and R^4 are selected from the group consisting of hydrogen (H) atoms, heteroatom-containing functional groups, C_1-C_{20} alkyl groups, heteroatom-containing C_1-C_{20} alkyl groups, cyclic groups, heteroatom-containing cyclic groups, aromatic groups, heteroatom-containing aromatic groups, and combinations thereof.

36. The method of claim 35, wherein at least one polishing additive comprises the structure XY-NCR^{1}R^{2}CR^{3}R^{4}N-X'Y', wherein X and X' are H atoms, and wherein Y, Y', R^1, R^2, R^3, and R^4 are selected from the group consisting of hydrogen (H) atoms, heteroatom-containing functional groups, alkyl groups, heteroatom-containing alkyl groups, cyclic groups, heteroatom-containing cyclic groups, aromatic groups, heteroatom-containing aromatic groups, and combinations thereof.

37. The method of claim 36, wherein at least one polishing additive comprises the structure XY-NCR^{1}R^{2}CR^{3}R^{4}N-X'Y', wherein X, Y, X', and Y' are H atoms, and wherein R^1, R^2, R^3, and R^4 are selected from the group consisting of hydrogen (H) atoms, heteroatom-containing functional groups, alkyl groups, heteroatom-containing alkyl groups, cyclic groups, heteroatom-containing cyclic groups, aromatic groups, heteroatom-containing aromatic groups, and combinations thereof.
38. The method of claim 35, wherein at least one polishing additive is selected from the group consisting of aminoethylethanolamine, polyethyleneimine, and a mixture thereof.
39. The method of claim 36, wherein at least one polishing additive is ethylenediamine.
40. The method of claim 37, wherein at least one oxidizing agent is a peroxide, and wherein the system further comprises at least one passivation film-forming agent comprising one or more 5-6 member heterocyclic nitrogen-containing rings.
41. The method of claim 27, wherein at least one polishing additive is both (a) a compound selected from the group consisting of pyrophosphates, condensed phosphates, phosphonic acids and salts thereof, and (b) a compound selected from the group consisting of amines, amino alcohols, amides, imines, imino acids, nitriles, and nitros.
42. The method of claim 27, wherein at least one polishing additive is both (a) a compound selected from the group consisting of amines, amino alcohols, amides, imines, imino acids, nitriles, and nitros, and (b) a compound selected from the group consisting of thiols, thioesters, and thioethers, carbothiolic acids, carbothionic acids, thiocarboxylic acids, and thiosalicylic acids.
43. The method of claim 41, wherein at least one polishing additive is selected from the group consisting of 2-aminoethyl phosphonic acid, amino(trimethylenephosphonic acid), diethylenetriaminepenta(methylenephosphonic acid), hexamethylenediaminetetra(methylene phosphonic acid), and mixtures thereof.
44. The method of claim 27 wherein the system further comprises a source of ammonia.
45. The method of claim 44, wherein the system comprises (i) aminotri-(methylenephosphonic acid) and (ii) ammonia or an ammonium salt.
46. The method of claim 27, wherein the system further comprises at least one stopping compound.
47. The method of claim 27, wherein the polishing additive is iminodiacetic acid.
48. The method of claim 47, wherein the system further comprises at least one stopping compound.
49. The method of claim 47, wherein the system further comprises at least one polymeric compound that reduces the polishing rate of at least one layer associated with the substrate.
50. The method of claim 47, wherein the system further comprises ammonia or an ammonium salt.

51. The method of claim 27, wherein the system further comprises at least one polymeric compound that reduces the polishing rate of at least one layer associated with the substrate.
52. The method of claim 27, wherein the system further comprises at least one passivation film-forming agent.
53. The method of claim 27, wherein the abrasive is a metal oxide abrasive.
54. The method of claim 53, wherein the abrasive is selected from the group consisting of alumina, ceria, germania, silica, titania, zirconia, and coformed products thereof, and mixtures thereof.
55. The method of claim 54, wherein the abrasive is alumina.
56. A method of polishing one or more layers of a multi-layer substrate that includes a first noble metal layer and a second layer comprising:

(i) contacting the substrate with a chemical-mechanical polishing system comprising:

(a) a liquid carrier,

(b) at least one oxidizing agent,

(c) at least one polishing additive that increases the rate at which the system polishes the noble metal layer of the substrate, wherein the polishing additive is selected from the group consisting of carboxylates and acids thereof, hydroxylates and acids thereof, carbonylates and acids thereof, pyrophosphates, condensed phosphates, phosphonic acids and salts thereof, amines, amino alcohols, amides, imines, imino acids and salts thereof, nitriles, nitros, thiols, thioesters, thioethers, carbothiolic acids and salts thereof, carbothionic acids and salts thereof, thiocarboxylic acids and salts thereof, sulfonic acids and salts thereof, thiosalicylic acids and salts thereof, and mixtures thereof, and

(d) a polishing pad and/or an abrasive, and

(ii) abrading at least a portion of the substrate to polish the substrate.

57. The method of claim 56, wherein the oxidizing agent is a per-compound.
58. The method of claim 56, wherein the noble metal is platinum, iridium, or ruthenium.
59. The method of claim 56, wherein the polishing additive is selected from the group consisting of oxalate salts, pyrophosphate salts, aminotri(methylenephosphonic acid), 1-diphosphonic acid, diethylenetriaminepenta(methylenephosphonic acid), amino acids, and thiodiacetic acid.