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(54) Title: PROCESS FOR REDUCING DISHING AND EROSION DURING CHEMICAL MECHANICAL PLANARIZATION

(57) Abstract: This invention is directed to a slurry system and process of metal removal from a substrate. This invention is useful for polishing a microelectronic device. This invention is especially useful for chemical mechanical planarization of a semiconductor wafer. The slurry system of the present invention includes a first slurry and a second slurry, wherein the first slurry has a higher abrasive concentration than the second slurry. The process of the present invention includes a first polish with the first slurry to partially remove metal from the substrate, and a second polish with the second slurry to further remove metal from the substrate

# PROCESS FOR REDUCING DISHING AND EROSION DURING CHEMICAL MECHANICAL PLANARIZATION

## BACKGROUND OF THE INVENTION

This application claims priority to United States patent application Serial Number 60/401,109 filed August 5, 2002, which application is incorporated herein by reference in its entirety.

## SUMMARY OF THE INVENTION

This invention is directed to a process of metal removal from a substrate. This invention is useful for polishing a microelectronic device. This invention is especially useful for chemical mechanical planarization of a semiconductor wafer.

Microelectronic devices such as semiconductor wafers are typically fabricated with copper interconnects. These copper interconnects are produced by a multi-step damascene process which consists of etching trenches into a dielectric material such as silicon dioxide, inlaying a barrier film such as tantalum into the trenches, and then filling the trenches with electroplating copper. Generally, a thick copper overburden is placed on top of the filled trenches. The application of this overburden typically does not result in a flat surface. Instead, there are low areas in the overburden corresponding to the filled-in trenches underneath and high areas corresponding to the space in-between the trenches (i.e., "step-height topography").

In order to place another interconnect level on the microelectronic device, removal of the copper overburden layer is required. Chemical mechanical planarization ("CMP") is a known technique for removing the copper overburden layer. During the CMP process, the copper overburden is cleared from the surface of the microelectronic device to reveal the actual interconnect patterns. In a typical chemical mechanical polishing process, the microelectronic device is placed in contact with a polishing pad. The pad is rotated while a force is applied to the backside of the microelectronic device. An abrasive-containing chemically-reactive solution commonly referred to as a "slurry", is applied to the pad during polishing. Typically, CMP polishing slurries contain an abrasive material, such as silica, alumina, ceria or mixtures thereof. The polishing process is facilitated by the rotational movement of the pad relative to the substrate as slurry is provided to the device/pad interface. Polishing is continued in this manner until the desired film thickness is removed.

Depending on the choice of abrasive, and other additives, the polishing slurry may be formulated to provide effective polishing to metal layers at desired polishing rates while minimizing surface imperfections, defects, corrosion, and erosion.

Processes for removal of copper overburden using an abrasive slurry is known in the art. A disadvantage in these known processes include the tendency of the pressure of the polishing pad to press the abrasive particles into the surface of the substrate, resulting in dishing within the trenches and erosion of the pattern on the substrate. It is desirable in the art to minimize such dishing and erosion. Thus, there is a need in the art for a method of efficiently removing the copper overburden while minimizing dishing within the trenches and erosion of the pattern on the substrate.

It is noted that, as used in this specification and the appended claims, the singular forms "a," "an," and "the" include plural referents unless expressly and unequivocally limited to one referent.

For the purposes of this specification, unless otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

The features that characterize the present invention are pointed out with particularity in the claims which are part of this disclosure. These and other features of the invention, its operating advantages and the specific objects obtained by its use will be more fully understood from the following detailed description and the operating examples.

It has been found that it is desirable to remove the step-height topography of the copper overburden in a first polishing step without clearing the entire overburden, such that a second step can be conducted to essentially clear the remaining overburden which is relatively free of step-height topography.

The present invention includes a slurry system comprising:

(a) a first slurry which comprises abrasive for partial removal of metal from a substrate; and

(b) a second slurry,

wherein said first slurry has higher concentration of said abrasive than said second slurry.

The present invention further includes a method comprising a first polish with a first slurry and a polishing pad. The first polish can remove a portion of the metal from the substrate. Residual metal remains on the substrate following completion of the first polish. In a non-limiting embodiment, the residual metal can at least partially form a layer or film. In a second polish with a second slurry and polishing pad, the substrate can be further polished with the second slurry which is less abrasive than the first slurry. The second polish at least partially removes the metal residual remaining on the substrate after the first polish.

The first polish can be terminated prior to all of the metal being removed from the substrate. When the first polish is terminated, residual metal remains on the substrate.

In a non-limiting embodiment, the metal can include copper, tantalum, silicon dioxide, or mixtures thereof. In a further non-limiting embodiment, the metal is copper.

It is contemplated that the use of an abrasive slurry for copper removal in the first step of the polishing process has a tendency to favor the high areas of the step-height topography, and thereby leaves residual copper which then can be removed by a second less-abrasive slurry. In an embodiment of the present invention, the second slurry can be abrasive-free.

A first slurry of the present invention includes a liquid and an abrasive. Suitable abrasives for use in the present invention can include metal oxides. Non-limiting examples of metal oxides can include but are not limited to alumina, titania, zirconia, gennania, silica, ceria and mixtures thereof. The amount of abrasive present in the first slurry can vary widely depending on the abrasive selected. In a non-limiting embodiment,

the abrasive can be present in an amount of from 0.1 to about 30.0 percent by weight, or from 0.5 to 12.0 percent by weight. In a further embodiment, the abrasive can be silica.

Various silicas and methods of their preparation are known to the skilled artisan. Suitable silicas for use in the present invention can be selected from the wide variety known in the art. In a non-limiting embodiment, the silica can be a precipitated silica. Various precipitated silicas and methods for their preparation are known to the skilled artisan. In a further non-limiting embodiment, the precipitated silica can be selected from those described in United States Patent Applications having Serial Nos. 09/882,549 and 09/882,548, both filed on June 14, 2001, currently pending in the United States Patent and Trademark Office; the relevant portions of which are incorporated herein by reference.

In another non-limiting embodiment, the abrasive slurry of the present invention includes silica having an aggregate of primary particles, said primary particles having an average diameter of at least seven (7) nanometers, wherein said aggregate has an aggregate size of less than one (1) micron; and a hydroxyl content of at least seven (7) hydroxyl groups per nanometer squared.

Silica can be prepared by a wide variety of methods known in the art. In general, silica can be prepared by combining an aqueous solution of a soluble metal silicate with an acid. The soluble metal silicate can include an alkali metal silicate such as but not limited to sodium or potassium silicate. Suitable acids can include mineral acids, organic acids, and carbon dioxide. The silicate/acid slurry then can be aged, and an acid or base can be added to the silicate/acid slurry. The resultant silica particles can be separated from the liquid portion of the mixture. The separated silica can be washed with water, the wet silica can be dried, and the dried silica can be separated from residues of other reaction products using conventional washing, drying and separating techniques known in the art.

In a non-limiting embodiment, the silica for use in the present invention, can be subjected to a particle size reduction technique. Various techniques for breaking down aggregates of primary particles within silica into smaller aggregates are known in the art. Non-limiting examples include but are not limited to wet milling and fluid energy milling. In a further non-limiting embodiment, the aggregates of primary particles of silica can be reduced using a double-jet cell process related to the apparatus and method disclosed in WO 00/39056 and United States Patent No. 5,720,551; the relevant portions of which are incorporated herein by reference.

As aforementioned, the first slurry of the present invention includes an abrasive and a liquid. In a non-limiting embodiment, the first abrasive slurry can be prepared in accordance with the process described in patent applications having Serial Nos. 09/882,549 and 09/882,548, both filed in the United States Patent and Trademark Office on June 14, 2001, which are currently pending; which relevant portions are incorporated herein by reference. In another non-limiting embodiment, the liquid can be water.

In addition to abrasive and water, the slurry can include an oxidant and a complexing agent. The presence of an oxidant in a slurry can be useful for oxidizing the substrate metal layer(s) to its corresponding oxide, hydroxide, or ions. In alternate non-limiting embodiments, an oxidant can be used to oxidize titanium to titanium oxide, tungsten to tungsten oxide, copper to copper oxide, and aluminum to aluminum oxide. The oxidant-containing slurry can be used to polish metals and metal-based components including but not limited to titanium, titanium nitride, tantalum, tantalum nitride, copper, tungsten, tungsten nitride, aluminum, aluminum alloys such as aluminum/copper alloys, gold, silver, platinum, ruthenium, and various mixtures and combinations thereof.

A wide range of oxidants can be used in the first slurry of the present invention. Suitable oxidants can include inorganic and organic per-compounds, and compounds containing an element in its higher or highest oxidation state. As used herein and the claims, the term "per-compound" means a compound containing at least one peroxy group (-0-0-). Non-limiting examples of compounds containing at least one peroxy group can include hydrogen peroxide and its adducts such as urea hydrogen peroxide and percarbonates, organic peroxides such as benzyl peroxide, peracetic acid, and di-t-butyl peroxide, monopersulfates ($SO_5$), dipersulfates ($S_200$), sodium peroxide, and mixtures thereof.

Non-limiting examples of oxidants containing an element in its higher oxidation state can include bromic acid, bromate salts, chloric acid, chlorate salts, chromate salts, iodic acid, iodate salts, periodic acid, periodate salts, perbromic acid, perbromate salts, perchloric acid, perchlorate salts, perboric acid, perborate salts, permanganate salts, cerium (IV) compounds such as but not limited to ammonium cerium nitrate, iron salts such as nitrates, sulfates, EDTA, and citrates, potassium ferricyanide, vanadium trioxide and the like, and aluminum salts.

In alternate non-limiting embodiments, the oxidant can be urea-hydrogen peroxide, hydrogen peroxide, or mixtures thereof. In another non-limiting embodiment, the oxidant can be hydrogen peroxide.

The amount of oxidant present in the first slurry can vary widely depending on the particular oxidant selected. In general, the amount should be sufficient for oxidizing the substrate metal laye(s) to its corresponding oxide, hydroxide, or ions. In alternate non-limiting embodiments, the oxidant can be present in an amount of 0.001 percent by weight or greater, or 0.01 percent by weight or greater, or 20.0 percent by weight or less, or 17.0 percent by weight or less, or 10.0 percent by weight or less.

Suitable complexing agents for use in the present invention can include organic acids and organic hydroxy acids. Non-limiting examples of organic acids can include but are not limited to dicarboxy, tricarboxy and polycarboxy acids, gluconic acid, lactic acid, citric acid, tartaric acid, malic acid, glycolic acid, malonic acid, oxalic acid, succinic acid, and phthalic acid. Non-limiting examples of organic hydroxy acids can include but are not limited to dicarboxy, tricarboxy and polycarboxy hydroxy acids. Further non-limiting examples of suitable complexing agents can include amino acids such as glycine, histidine, alanine, and aspartic acid; carboxylic acids of nitrogen-containing heterocycles such as picolinic acid, dipicolinic acid, quinolinic acid, 2-pyrazinecarboxylic acid, quinaldinic acid, and 2-quinoxalinecarboxylic acid; and organic bidentate ligands such as bipyridyl derivatives.

The amount of complexing agent used in the present invention can vary widely depending on the selection of the complexing agent. In a non-limiting embodiment, glycine can be used as a complexing agent in an amount such that it constitutes from 0.1 to 5 percent by weight of the slurry, or from 0.5 to 1 percent by weight. In another non-limiting embodiment, picolinic acid can be used as a complexing agent in an amount such that it constitutes from 0.1 to 5 percent by weight of the slurry, or from 0.5 to 1 percent by weight.

In other non-limiting embodiments, the first slurry of the present invention can include one or more of the following additives: polyvalent cation sequestrants, corrosion inhibitors, thickeners, stopping compounds, static etch controllers, accelerators, metal halides, surfactants, stabilizers and metal chelating agents.

In another non-limiting embodiment, the slurry of the present invention can include a polyvalent cation sequestrant. Suitable polyvalent cation sequestrants for use in the present invention can include various known compounds which bind to, complex with or otherwise sequester polyvalent metal cations. Non-limiting examples of polyvalent cation sequestrants can include carboxylic acids and polycarboxylic acids, amino acids, dipeptides and polyamino acids, polyimines, phosphoric acids and polyphosphoric acids. Further non-limiting examples can include glycine, histidine, aspartic acid, phytic acid, thermal polyaspartates, γ-amino-n-butyric acid, β-alanine, L-asparagine, 2-aminoisobutyric acid, citric acid, N-(phosphonomethyl)iminodiacetic acid, poly(dimethylsiloxane)-*graft*-polyacrylic acid, 4,5-imidazoledicarboxylic acid, aminotri(methylenephosphonic acid), polyethylenimine, acetic acid, aspartic acid-phenylalanine methyl ester, and 2-phosphono-1,2,4-butanetricarboxylic acid, a crosslinked polyacrylic acid commercially available from B.F. Goodrich under the tradename Carbopol, a polyacrylate commercially available from B.F. Goodrich under the tradename GOOD-RITE K-700, and mixtures thereof. In a non-limiting embodiment, Carbopol or GOOD-RITE K-700 can be used.

The polyvalent cation sequestrant can be present in an amount such that the copper polish rates are enhanced and static etch, corrosion, pitting, staining, instability of the silica dispersion, or disposal issues are not unduly increased. In alternate non-limiting embodiments, the silica-based slurry comprises a polyvalent cation sequestrant in an amount of from greater than 0 to 5% by weight, or from 0.001 to 1 percent by weight of the slurry composition.

In another non-limiting embodiment, the slurry of the present invention can include an anticorrosion agent or corrosion inhibitor. The corrosion inhibitor for use in the present invention can include a variety of known compounds which inhibit the corrosion or static etch rate of copper, such as but not limited to polycarboxylic acids, polyamino acids, amino acids, imines, azoles, carboxylated azoles, and mercaptans. Non-limiting examples of suitable corrosion inhibitors include benzotriazole, 4-carboxybenzotriazole, 5-carboxybenzotriazole, thermal polyaspartates, histidine, mercaptobenzotriazole, phytic acid, a crosslinked polyacrylic acid commercially available from B.F. Goodrich under the tradename Carbopol, a polyacrylate commercially available from B.F. Goodrich under the tradename GOOD-RITE K-700, and mixtures thereof.

In a non-limiting embodiment, phytic acid can be used in the present invention in varying amounts. In a further non-limiting embodiment, the amount of phytic acid can be such that it constitutes at least 0.01 percent by weight of the slurry, or at least 0.05 percent by weight, or from 0.05 to 0.1 percent by weight, or less than 0.2 percent by weight. Non-limiting examples of suitable commercially available phytic acid include water soluble corrosion inhibitors commercially available from King Industries, Incorporated, under the trade names of CDI 4302, 4303, and 4304, and CDX 2128 and 2165.

In a non-limiting embodiment, the corrosion inhibitor can be present in an amount such that static etch, corrosion and pitting are adequately decreased; copper polish rates are not unduly decreased; and staining, instability of the silica dispersion, excessive cost or disposal issues are not unduly increased.

In an embodiment, the corrosion inhibitor for use in the present invention can serve as a passivation film forming agent which forms a passivation layer on the surface of the substrate to be polished. The corrosion inhibitor forms a passivation layer on the surface of an electrical substrate layer. Once a passivation layer is formed, the passivation layer then can be disturbed to obtain a desirable polishing rate. The corrosion inhibitor can include a compound or combination of compounds that are capable of facilitating the formation of a passivation layer of metals and dissolution-inhibiting layers on the surface of a metal layer. Passivation of the substrate metal surface layer can prevent metal surface wet etching. Such film forming agents include nitrogen-containing heterocyclic compounds, wherein the compound comprises at least one 5 or 6 member heterocyclic ring with nitrogen as part of the ring. Examples of such nitrogen-containing 5 and 6 member ring compounds include 1,2,3-triazole, 1,2,4-triazole, benzotriazole, benzimidazole and benzothiazole and their derivatives with hydroxy, amino, imino, carboxy, mercapto, nitro- and alkyl-substituted groups, urea, and thiourea, and mixtures thereof. In an embodiment of the present invention, the passivation film forming agent comprises benzotriazole ("BTA"), 1,2,3-triazole, 1,2,4-triazole, and mixtures thereof.

In alternate non-limiting embodiments, the corrosion inhibitor or passivation film forming agent can comprise from greater than 0 to about 0.5 percent by weight of the silica-based slurry composition, or at least 0.001 percent by weight or greater, or at least 0.01 percent by weight or greater, or at least 0.1 percent by weight or greater, or less than

1 percent by weight, or less than 0.5 percent by weight, or less than 0.05 percent by weight.

The formation of a passivation layer of metals and dissolution-inhibiting layers on the surface of a metal layer of the substrate can be useful to minimize or prevent metal surface wet etching.

In another non-limiting embodiment, the slurry of the present invention can include a thickener. Suitable thickeners can include a wide variety of known thickeners in the art. In general a suitable thickener includes materials which stabilize the silica-based slurry to reduce settling. Non-limiting examples can include but are not limited to polyvinyl alcohols, polyacrylic acids, polysaccharides, hydroxy ethyl cellulose and modified hydroxyethylcellulose, polyethylene glycols, polypropylene glycols, copolymers of polyethylene and polypropylene glycols, alkylated polyethylene and polypropylene glycols, polyethylene imines, polyamino acids, polyacrylamides, and polyamic acids. Non-limiting examples of such suitable anionic polymers can include a crosslinked polyacrylic acid commercially available from B.F. Goodrich under the tradename Carbopol, a polyacrylate commercially available from B.F. Goodrich under the tradename GOOD-RITE K-700, Kelzan AR xanthan gum polysaccharide which is commercially available from CP Kelco, Natrosol 250 MMR hydroxyethylcellulose which is commercially available from Hercules, Airvol 523 polyvinyl alcohol which is commercially available from Air Products, and Polyox 3333 polyethylene oxide which is commercially available from Union Carbide, or mixtures thereof.

The thickener can be present in an amount such that the settling rate is adequately decreased, but viscosity is not unduly increased such that pumpability and filterability is compromised, or heat build during polishing becomes deleterious to the slurry performance. The amount of thickener used can vary depending on the thickener selected. In alternate non-limiting embodiments, the thickener can be present in an amount of from greater than 0 to 5% by weight, or from 0.001 to 1% by weight. In a further non-limiting embodiment, Carbopol can be present as a thickener in an amount of less than 0.5% by weight.

In a further non-limiting embodiment, the thickener can be shear-stable. As used herein and the claims, the term "shear-stable" means that under the shear of polishing, the

viscosity of the thickener will not sufficiently decrease (e.g., will decrease by not more than 75% of the viscosity prior to polishing).

In alternate non-limiting embodiments of the present invention, a polyvalent cation sequestrant, corrosion inhibitor, and optionally thickener can be added to the silica during the milling of the silica and/or when the particle size of the silica is reduced, as previously described herein; or milling and/or particle reduction of the silica has been completed.

In a non-limiting embodiment of the present invention, a polyvalent cation sequestrant, a corrosion inhibitor, and optionally a thickener, can be added to the slurry. In a further non-limiting embodiment, the polyvalent cation sequestrant, corrosion inhibitor and/or thickener are combined under mild agitation and then added to the slurry.

In another non-limiting embodiment, the slurry of the invention can include at least one stopping compound. The stopping compound can interact with a metal layer, an adhesion layer, and/or a dielectric layer of the substrate and suppress the removal rate of the layers underlying the layer being polished. The result can be such that the slurry polishes a first layer of a substrate and can be essentially stopped from polishing a second layer that is beneath the first layer. Suitable stopping compounds for use in the present invention can include a wide variety known in the art such as but not limited to polar compounds or polymers that contain polar moieties such as hydroxyl, amino, nitrogen-containing heterocycles, carboxyl, carbonyl, ethereal, sulphonyl, or phosphonyl moieties. Non-limiting examples can include polyvinyl alcohols, polyvinylpyrrolidones, polyvinylpyridines, polyethylene oxide, glycols or polyglycols, polycarboxylic acid derivatives, such as polyacrylic acid polymethyl acrylates. The term "essentially stopped" as used herein and the claims means that the polishing composition or slurry has a first layer to second layer polishing selectivity of about 5:1, or at least 10:1, or 100: 1. The selection of the stopping compound can be dependent on its chemical stability, interaction with other components of the slurry, and its effect on the colloidal stability of any abrasive particles employed.

In a non-limiting embodiment, the abrasive can be present in the slurry of the present invention in an amount of from 0 to 20.0 percent by weight, the anticorrosion agent can be present in an amount of from 0 to 1 percent by weight, and the stopping compound can be present in an amount of from 0 to 1 percent by weight.

In another non-limiting embodiment, the slurry can include a dispersant. Non-limiting examples of suitable dispersants include polycarboxylic acids such as polyacrylic acids, crosslinked polyacrylic acids and polymethacrylic acids; phosphonic acids such as but not limited to alkylphosphonic acids, arylphosphonic acids, polyphosphonic acids, and alkylaminophosphonic acids; polyaminoacids such as but not limited to polyaspartic acids.

In another non-limiting embodiment, the slurry can include a surfactant. Suitable surfactants for use in the present invention can include cationic, anionic and non-ionic surfactants. Suitable cationic surfactants can include but are not limited to aliphatic amines and aliphatic ammonium salts. Non-limiting examples of anionic surfactants can include carboxylic acid salts such as but not limited to fatty acid soaps, alkylether carboxylates, salts of alkyl and aryl sulfonic acids such as from alkylbenzenesulfonic acid, alkylnaphthalenesulfonic acid, and alpha-olefinsulfonic acids. Non-limiting examples of anionic surfactants can include but are not limited to salts of sulfonic acid esters such as higher alcohol sulfonic acid esters, alkylether sulfonic acids, and sulfonic acid ester salts of poyoxyethylene alkylphenylethers. In a non-limiting embodiment, anionic surfactants can include salts of phosphoric acid esters such as but not limited to alkyl phosphoric and arylphosphoric acid esters. Non-limiting examples of nonionic surfactants can include but are not limited to ethers such as polyethylene alkylethers, ether esters such as polyoxyethylene ethers of glycerin esters, and esters such as glycerin esters, and sorbitan esters.

In a non-limiting embodiment, the slurry of the present invention can include a stabilizer. Suitable stabilizers can include acetanilide, tin oxides, and free radical inhibitors such as but not limited to inorganic and organic nitrogen oxides.

Suitable dispersants include polycarboxylic acids such as polyacrylic acid, crosslinked polyacrylic acid and polymethacrylic acid; phosphonic acids such as alkylphosphonic acids, arylphosphonic acids, polyphosphonic acids, and alkylaminophosphonic acids; polyamino acids such as polyaspartic acids.

In a non-limiting embodiment, the oxidant and other non-abrasive components can be mixed into an aqueous medium, such as deionized or distilled water, under shear conditions until such components are sufficiently dissolved in the medium. Silica then can be added to the medium. In a non-limiting embodiment, the silica can be precipitated

silica. The composition then can be dispersed in a liquid such as water to prepare the slurry of the present invention.

In the present invention, the amount of copper removed in a first polishing step using a first slurry can vary widely depending on the composition of the first slurry, the length of polishing time, and the polishing conditions. In a non-limiting embodiment, the first slurry can remove less than 100% of the copper such that residual copper remains. In alternate non-limiting embodiments, the first slurry can remove from 10% to 95%, or from 20% to 90%, or from 25% to 85%, of the copper from the substrate. In a further non-limiting embodiment, the residual copper can be at least partially in the form of a layer or film.

The copper removal rate in the first step can vary widely depending on the composition of the first slurry, the length of polishing time, and the polishing conditions. In alternate non-limiting embodiments, the copper removal rate in the first step can be at least 2,500, or less than 10,000 angstroms per minute, at least 5,000 angstroms per minute, or less than 8,000 angstroms per minute.

The static etch rate can vary widely in the first polishing step. In a non-limiting embodiments, the static etch rate can be from 0% to 20% of the copper removal rate, or from 0.1% to 15%, or from 1% to 10%, of the copper removal rate.

In the present invention, after the first polishing step is essentially terminated, a second slurry can be used in a second polishing step. In a non-limiting embodiment, the first polish with the first slurry can be terminated and a second polish with a second slurry can be initiated without cleaning the first slurry from the substrate and/or polishing pad.

The various abrasives and their methods of preparation previously described for the first slurry can be utilized for the second slurry. In a non-limiting embodiment, the abrasive concentration in the second slurry can be less than the abrasive concentration in the first slurry. In alternate non-limiting embodiments, the abrasive concentration in the second slurry can be 0% or greater, or 10% or less, or 0.1% or greater, or 1% or greater, or 5% or less, by weight of the second slurry.

In alternate non-limiting embodiments, the various oxidants, complexing agents, and other optional additives previously described for the first slurry can be included in the second slurry.

In a non-limiting embodiment, the composition of the second slurry can be the same as the composition of the first slurry with the exception that the abrasive concentration in the second slurry is less than the abrasive concentration in the first slurry.

In a further non-limiting embodiment, the second slurry can be abrasive-free.

The second slurry for use in a second polishing step can be used to remove the residual copper remaining on the substrate following termination of the first polishing step with the first slurry. In general, a slurry having a low abrasive concentration or no abrasive, removes copper by relying on the abrasiveness of the polishing pad and residual abrasive from the first slurry used in the first polishing step. In a non-limiting embodiment, the copper removal rate for removing the residual copper using the second slurry can be less than the removal rate of the copper using the first slurry. In alternate non-limiting embodiments, the copper removal rate for removing the residual copper can be less than 50%, or less than 35%, or less than 25%, or less than 10%, of the removal rate of the copper using the first slurry.

The static etch rate using the second slurry in the second polishing step can be less than the static etch rate using the first slurry. In alternate non-limiting embodiments, the static etch rate in using the second slurry can be from 0 to 70%, or at least 10%, or at least 20%, or less than 70%, of the static etch rate in using the first slurry.

In a non-limiting embodiment, the slurry of the invention can be useful for chemical mechanical planarization (CMP) of substrates such as semiconductor wafers. In this embodiment, the first slurry of the present invention can be applied to the wafer substrate, and the wafer can be polished by conventional means using polishing equipment and a polishing pad known in the art. Suitable CMP equipment for use in the present invention can include but is not limited to IPEC 472, Applied Materials Mirra Mesa or Reflexion, Speedfam 676, Novellus Momentum, Lam Terres and Nikon CMP System NPS 2301. Further, the selection of a polishing pad can include Rodel's IC1400, IC1000 stacked on a SUBA IV, Polytex or PPG's FastPad.

In a non-limiting embodiment, the first slurry of the present invention can polish copper at a high rate while exhibiting a low polishing rate towards tantalum and other adhesion, dielectric or metal layers. The second slurry can then applied to the partially polished substrate. The second slurry can polish copper at a lower rate while exhibiting a higher polishing rate towards tantalum or other adhesion, dielectric, or metal layers. It is

contemplates that the selection of one or more additives can control the desired rate of removal in polishing specific metal, adhesion, or oxide layers at the high or low rate desired.

Upon completion of the polishing process using the slurries of the present invention, the substrate can be washed with deionized water or other solvents or cleaning solutions to remove the polishing slurry from the substrate. In a non-limiting embodiment, this washing process can be carried out prior to using the second slurry. Upon completion of the second polishing step, the second slurry can be washed from the substrate with deionized water or another solvent and the substrate can be ready for further processing.

In both polishing steps, the polishing slurries can be applied directly to the substrate, to a polishing pad, or to both in a controlled manner during substrate polishing. In a non-limiting embodiment, the slurry can be applied to the pad, the pad can be placed against the substrate, and the pad can be moved in relationship to the substrate to accomplish substrate polishing.

The slurries and process of the present invention can be used to provide effective polishing at desired polishing rates while minimizing surface imperfections and defects. Furthermore, the slurries and process of the present invention can be especially useful when it is desired to provide a high material removal rate during polishing while maintaining a low static etch rate to minimize dishing and erosion of imbedded features.

## EXAMPLES

In the experiments using copper pucks of 2.4-centimeter diameter as the metal sample, the average weight loss of the pucks was used to calculate the copper removal rate. The polishing pucks were weighed before polishing. After polishing, the pucks were once again weighed and the difference between the two values was used to calculate the weight loss due to polishing. The average weight loss of the three pucks was used to calculate the copper removal rate. The average weight loss per minute was calculated by dividing the average weight loss by the average polish time in minutes. The cross-sectional area of the puck and the density of copper was used to convert the average weight loss per minute to removal rate in nanometers or angstroms per minute.

A Stuers LabPol-V ™ polisher was used for polishing the pucks. Both the carrier and the polish table rotated counter-clockwise and were maintained at a speed of 60 rpm.

The pucks were held at a downward force of 30 N (approx. 9.8 psi). The slurry for puck polishing was supplied to the polisher at the center of the puck at a fixed flow rate. A polyurethane polishing pad was used for all the polishing experiments.

The term "pad reconditioning" as used herein refers to the removal of leftover slurry and products of polishing on the polishing pad. Without pad reconditioning the polishing rate decreases due to a glazing effect. Various recondition techniques known in the art may be used.

Reconditioning of the polishing pad was done using a SUBA™ 500 pad. The pad reconditioning sequence consisted of one (1) minute of cleaning using de-ionized water, 30 seconds of conditioning using hydrogen peroxide, one (1) minute of de-ionized water cleaning, 30 seconds of conditioning using citric acid, and one (1) minute of de-ionized water cleaning.

In the experiments using 200-millimeter copper blanket wafers and patterned wafers, the wafers were polished using a Westech 372M rotary CMP tool with a Rodel IC1400-A2 pad. Pad conditioning was performed between each wafer polish (*ex-situ conditioning*) with de-ionized water and a diamond-grit conditioning-wheel. Copper blanket wafers from either International SEMATECH or Montco Silicon Technologies, Inc. were employed as rate monitors. SEMATECH 854-006 patterned wafers were used for topography evaluation. All chemicals were ACS regent grade. De-ionized water was used for all solutions. Film thickness and profile of the copper wafers were measured by using Prometrix® RS-35 four-point probe metrology tool and Ambios Technology INC. XP-2 profilometer equipped with a stylus with a 2.5-micron radius tip.

**Example 1**

A slurry comprising benzotriazole, glycine, and hydrogen peroxide (with no added silica), Entry 1, was compared with slurries that were of the same composition with the exception of varying silica concentrations. The pucks were polished for three (3) minutes with a slurry feed rate of 60 milliliters per minute. The data demonstrates that the copper removal rates for the samples containing silica are higher than the copper removal rate for the sample containing no silica. Copper removal rates for polishing copper pucks are reported in Table 1. It is recognized that the copper removal rates shown in Table 1 do not linearly decrease with an increase in silica concentration. It is believed that the

relationship between the silica concentration and copper removal rate demonstrated in this example is due at least in part to the fluctuations in pH of the samples.

**Table 1**

| Entry | Silica (wt%) | pH *-log* $[H_3O^+]$ | Hydrogen peroxide (wt%) | BTA (mM) | Copper Removal Rate (nm/min) |
|---|---|---|---|---|---|
| 1 | 0 | 5.63 | 3 | 1 | 207 |
| 2 | 1 | 6.47 | 3 | 1 | 626 |
| 3 | 2 | 6.72 | 3 | 1 | 499 |
| 4 | 3 | 6.84 | 3 | 1 | 508 |
| 5 | 4 | 6.86 | 3 | 1 | 379 |
| 6 | 5 | 6.79 | 3 | 1 | 420 |
| 7 | 6 | 6.76 | 3 | 1 | 462 |
| 8 | 7 | 6.75 | 3 | 1 | 520 |
| 9 | 8 | 6.72 | 3 | 1 | 545 |

**Example 2**

A solution comprising benzotriazole, glycine, and hydrogen peroxide (with no added silica), Entry 1, was compared with slurries that contained increasing silica concentrations in a similar solution. Pucks were polished for one (1) minute with slurry feed rate of 100 milliliters per minute. Similar to the previous example, the data demonstrates that the copper removal rates for the samples containing silica are higher than the copper removal rate for the sample containing no silica. Copper removal rates for polishing copper pucks are reported in Table 2. It is recognized that the copper removal rates shown in Table 1 do not linearly decrease with an increase in silica concentration. It is believed that the relationship between the silica concentration and copper removal rate demonstrated in this example is due at least in part to the fluctuations in pH of the samples. Furthermore, it is demonstrated that the copper removal rates decrease with an increase in slurry flow rate.

**Table 2**

| Entry | Silica (wt%) | pH *-log* $[H_3O^+]$ | Hydrogen peroxide (wt%) | BTA (mM) | Copper Removal Rate (nm/min) |
|---|---|---|---|---|---|
| 1 | 0.0 | 6.08 | 3 | 1 | 68 |
| 2 | 0.1 | 6.34 | 3 | 1 | 201 |
| 3 | 0.2 | 6.49 | 3 | 1 | 207 |
| 4 | 0.3 | 6.65 | 3 | 1 | 199 |
| 5 | 0.5 | 6.79 | 3 | 1 | 213 |
| 6 | 1.0 | 7.02 | 3 | 1 | 252 |
| 7 | 2.0 | 7.14 | 3 | 1 | 241 |
| 8 | 3.0 | 7.21 | 3 | 1 | 237 |
| 9 | 4.0 | 7.25 | 3 | 1 | 272 |
| 10 | 5.0 | 7.39 | 3 | 1 | 233 |

**Example 3**

The slurries in this example are similar to the previous Example 2 slurries with the exception that the hydrogen peroxide concentration was increased (from 3% to 5% by weight) to lower the copper removal rate when silica is absent. A solution comprising benzotriazole, glycine, and hydrogen peroxide (with no added silica), Entry 1, was compared with slurries that contained increasing silica concentrations in a similar solution. The pucks were polished for three (3) minutes with slurry feed rate of 60 milliliters per minute. The data demonstrates that the copper removal rates for the samples containing silica are higher than the copper removal rate for the sample containing no silica. Further, it is demonstrated that the copper removal rate for a slurry containing only one percent by weight of silica is not significantly different from the copper removal rate for a slurry containing 8 percent by weight of silica. Copper removal rates for polishing copper pucks are reported in Table 3.

**Table 3**

| Entry | Silica (wt%) | pH *-log* $[H_3O^+]$ | Hydrogen peroxide (wt%) | BTA (mM) | Copper Removal Rate (nm/min) |
|---|---|---|---|---|---|
| 1 | 0 | 5.67 | 5 | 1 | 94 |
| 2 | 1 | 6.39 | 5 | 1 | 400 |
| 3 | 2 | 6.61 | 5 | 1 | 351 |
| 4 | 3 | 6.71 | 5 | 1 | 332 |
| 5 | 4 | 6.67 | 5 | 1 | 291 |
| 6 | 5 | 6.81 | 5 | 1 | 279 |
| 7 | 6 | 6.74 | 5 | 1 | 302 |
| 8 | 7 | 6.72 | 5 | 1 | 325 |
| 9 | 8 | 6.68 | 5 | 1 | 390 |

**Example 4**

The slurries in this example were prepared according to Example 1, with the exception that the pH value was adjusted to remain constant. Adjustments of pH were made with either sulfuric acid or potassium hydroxide. Each slurry was comprised of glycine (1 weight percent), benzotriazole (1 millimolar), and hydrogen peroxide (3 weight percent). The affect of silica concentration on copper removal rate at various pH values was evaluated by polishing the copper pucks for one (1) minute with slurry feed rate of 60 milliliters per minute. The results demonstrate that for a particular silica concentration, the copper removal rate varies with varying levels of pH. Results are shown in Table 4.

**Table 4**

| Silica | Copper Removal Rate (Å/min) | | | |
|---|---|---|---|---|
| (wt%) | pH 3 | pH 4 | pH 5 | pH 6 |
| 0 | 259 | 106 | 176 | 151 |
| 1 | 434 | 488 | 412 | 342 |
| 2 | 597 | 537 | 483 | 393 |
| 3 | 705 | 617 | 528 | 451 |
| 4 | 801 | 644 | 565 | 520 |

**Example 5**

Copper polishing in two phases was performed with 200 mm copper blanket wafers. These wafers were comprised of a silicon metal wafer with a stack of thin film layers. The stack comprised a layer of thermal oxide (5,000Å) on the silicon metal, a layer of tantalum metal (250Å) on the thermal oxide, and a copper layer on top (15,000Å). In each case, a wafer was polished in a first phase for 60 seconds with an aqueous slurry (200 milliliters per minute) that contained silica (8 weight percent), benzotriazole (1 millimolar), glycine (1 weight percent), and hydrogen peroxide (3 weight percent). After this first-phase polish, the slurry flow ceased, and the polish was continued with either deionized water or an aqueous solution comprising benzotriazole (1 millimolar), glycine (1 weight percent), and hydrogen peroxide (3 weight percent) without silica. All polishing was performed with 4 psig down force, 1 psig carrier back pressure, and 60 rpm table velocity. Copper removal rates were determined using an Prometrix RS-35™ 4-point probe, and are reported in Table 5 as an average value from 49 measurements across the wafer diameter. These results demonstrate that little additional copper is removed by continuing to polish with water in the second phase. However, a significant copper removal rate is maintained in the second phase by polishing with a chemical solution without abrasive and relying on residual abrasive in the pad from the first phase.

**Table 5**

| Case | Phase 1 total time (sec) | Phase 2 | Phase 2 total time (sec) | Total copper removed (Å) | Incremental copper removed by Phase 2 (Å/min) |
|---|---|---|---|---|---|
| 1 | 60 | - | - | 2891 | - |
| 2 | 60 | DI water | 120 | 3036 | 73 |
| 3 | 60 | Chemical solution | 180 | 8490 | 1866 |

**Example 6**

Copper polishing in two phases was performed with 200 mm copper blanket wafers. These wafers were comprised of a silicon metal wafer with a stack of thin film layers. The stack comprised a layer of thermal oxide (5,000Å) on the silicon metal, a layer of tantalum metal (250Å) on the thermal oxide, and a copper layer on top (15,000Å). In each case, a wafer was polished in a first phase for 60 seconds with an aqueous slurry that contained silica (11 weight percent), benzotriazole (1 millimolar), glycine (1 weight percent), and hydrogen peroxide (5 weight percent). After this first-phase polish, the slurry flow ceased, and the polish was continued with either deionized water or an aqueous solution comprising benzotriazole, glycine, and hydrogen peroxide without silica. The silica-free chemical composition of the solutions that were used for Phase 2 was varied as shown in Table 6. Polishing conditions and liquid pH were held constant throughout both polishing phases (down force 4 psig, table velocity 70 rpm, carrier velocity 68 rpm, carrier back pressure 0 psig, slurry flow rate 190 ml/min, pH 5). Copper removal rates were determined using an Prometrix RS-35™ 4-point probe, and are reported in Table 5 as an average value from 49 measurements across the wafer diameter. The results demonstrate that in this example there is no significant additional copper removed by continuing to polish without silica in the second phase. The results also demonstrate that copper removal rate in Phase 2 (i.e., second polishing step) may be varied independently from the copper removal rate in Phase 1 (i.e., first polishing step).

**Table 6**

| Entry | Phase 2 polish time (sec) | Glycine (wt%) | Hydrogen peroxide (wt%) | BTA (mM) | De-ionized Water | Copper removed (Å) | Incremental Phase 2 copper removal rate (Å/min) |
|---|---|---|---|---|---|---|---|
| 1 | - | - | - | - | - | 6023 | - |
| 2 | 60 | - | - | - | 100% | 6485 | 462 |
| 3 | 60 | 1 | 5 | 1 | bulk | 9314 | 3291 |
| 4 | 60 | 1 | 5 | 3 | bulk | 8569 | 2546 |
| 5 | 60 | 1 | 8 | 1 | bulk | 9488 | 3465 |
| 6 | 60 | 1 | 8 | 3 | bulk | 7815 | 1792 |
| 7 | 60 | 1 | 6.5 | 2 | bulk | 8287 | 2264 |

**Example 7**

Copper polishing in two phases was performed with 200 mm copper blanket wafers. These wafers were comprised of a silicon metal wafer with a stack of thin film layers. The stack comprised a layer of thermal oxide (5,000Å) on the silicon metal, a layer of tantalum metal (250Å) on the thermal oxide, and a copper layer on top (15,000Å). In each case, a wafer was polished in a first phase for 60 seconds with an aqueous slurry that contained silica (11 weight percent), benzotriazole (1 millimolar), glycine (1 weight percent), and hydrogen peroxide (5 weight percent). After this first-phase polish, the slurry flow ceased, and the polish was continued for 60 seconds with an aqueous solution comprising benzotriazole, glycine, and hydrogen peroxide without silica. The silica-free chemical composition of the solutions that were used for Phase 2 was varied as shown in Table 7. Polishing conditions and liquid pH were held constant throughout both polishing phases (down force 3 psig, table velocity 70 rpm, carrier velocity 68 rpm, carrier back pressure 0 psig, slurry flow rate 190 ml/min, pH 5). Copper removal rates were determined using an Prometrix RS-35™ 4-point probe, and are reported in Table 5 as an average value from 49 measurements across the wafer diameter. The results demonstrate that the copper removal rate in Phase 2 (i.e., the second polishing step) may be varied independently of the copper removal rate in Phase 1 (i.e., the first polishing step)..

**Table 7**

| Entry | Phase 2 polish time (sec) | Glycine (wt%) | Hydrogen peroxide (wt%) | BTA (mM) | De-ionized Water | Copper removed (Å) | Incremental Phase 2 copper removal rate (Å/min) |
|---|---|---|---|---|---|---|---|
| 1 | - | - | - | - | - | 5122 | - |
| 2 | 60 | 1 | 5 | 3 | bulk | 6250 | 1128 |
| 3 | 60 | 1 | 8 | 1 | bulk | 7383 | 2261 |
| 4 | 60 | 1 | 8 | 3 | bulk | 6022 | 880 |
| 5 | 60 | 1 | 6.5 | 2 | bulk | 6209 | 1087 |

**Example 8**

Copper polishing in two phases was performed with 200 mm copper blanket wafers. These wafers were comprised of a silicon metal wafer with a stack of thin film layers. The stack comprised a layer of thermal oxide (5,000Å) on the silicon metal, a layer of tantalum metal (250Å) on the thermal oxide, and a copper layer on top (15,000Å). In each case, a wafer was polished in a first phase for 60 seconds with an aqueous slurry that contained silica (11 weight percent), benzotriazole (1 millimolar), glycine (1 weight percent), and hydrogen peroxide (5 weight percent). After this first-phase polish, the slurry flow ceased, and the polish was continued with an aqueous solution comprising benzotriazole (3 millimolar), glycine (1 weight percent), and hydrogen peroxide (8 weight percent), without silica. Polishing conditions and liquid pH were held constant throughout both polishing phases (force of 3psi, table velocity 70 rpm, carrier velocity 68 rpm, carrier back pressure 0 psig, slurry flow rate 190 ml/min, pH 5). Individual wafers were polished for each Phase 2 time interval. Copper removal rates were determined using a Prometrix RS-35™ 4-point probe, and are reported in Table 8 as an average value from 49 measurements across the wafer diameter. The data show that the pad remains sufficiently abrasive from the Phase 1 (i.e., the first polishing step) polishing conditions to maintain a relatively constant removal rate in Phase 2 (i.e., the second polishing step) for at least 4 minutes.

**Table 8**

| Phase 2 Time (min) | Copper removed (Å) | Incremental Copper Removed (Å/min) |
|---|---|---|
| 0 | 5122 | - |
| 1 | 6002 | 880 |
| 2 | 6972 | 925 |
| 3 | 7707 | 862 |
| 4 | 8537 | 854 |

**Example 9**

A SEMATECH 854 patterned wafer was polished 105 seconds with a slurry which comprised silica (11 weight percent), hydrogen peroxide (5 weight percent), glycine ( 1 weight percent) and benzotriazole (1 milliMolar). Polishing was continued for an additional 285 seconds with a liquid that comprised hydrogen peroxide (8 weight percent), glycine (1 weight percent) and benzotriazole (3 milliMolar), but no silica. Visual inspection revealed that the copper overburden was greater than 95% cleared from the wafer. Dishing was measured for several features for 9 separate dies that spanned the diameter of the wafer surface. The average dishing values for these features are described in Table 9. The results demonstrate that a two-phase polish to remove copper overburden, which uses a reactive liquid which contains no abrasive in the last phase, can reduce line dishing when compared to similar polishing that uses abrasive-containing slurry throughout the entire polish.

**Table 9**

| Feature<br>Copper line width_Oxide line width (μm) | 5_5 | 10_10 | 20_20 | 50_50 | 100_100 |
|---|---|---|---|---|---|
| Average Dishing (Å) | 1163 | 1511 | 1601 | 1911 | 2544 |
| Dishing Standard Deviation (Å) | 316 | 379 | 379 | 609 | 869 |

**Example 10**

The abrasive used in this example was silica that was surface-modified by reaction with dichlorodimethylsilane. A SEMATECH 854 patterned wafer was polished 95 seconds with a slurry which comprised surface-modified silica (11 weight percent), hydrogen peroxide (5 weight percent), glycine (1 weight percent) and benzotriazole (1 milliMolar). Polishing was continued for an additional 275 seconds with a liquid which comprised hydrogen peroxide (8 weight percent), glycine (1 weight percent) and benzotriazole (3 milliMolar), but no surface-modified silica. Visual inspection revealed that the copper overburden was greater than 95% cleared from the wafer. Dishing was measured for several features for 9 separate dies that spanned the diameter of the wafer surface. The average dishing values for these features is described in Table 10. The results demonstrate that using a surface-modified abrasive in the first phase of the copper polish can further reduce line dishing when compared to similar polishing with an unmodified abrasive. Data acquired for one 50_50 micron feature in a die in the middle of the wafer radius, indicated that dishing after 215 seconds of polishing in the second liquid-only phase was about 52% of the final value after 275 seconds. These data indicate that this mutiphase process has a wide overpolish window.

**Table 10**

| Feature<br>Copper line width_Oxide line width (μm) | 5_5 | 10_10 | 20_20 | 50_50 | 100_100 |
|---|---|---|---|---|---|
| Average Dishing (Å) | 697 | 887 | 830 | 1001 | 1611 |
| Dishing Standard Deviation (Å) | 372 | 320 | 342 | 543 | 785 |

**Example 11**

A SEMATECH 854 patterned wafer was polished with down force of 4.5 psig for 105 seconds with an aqueous slurry which comprised silica (11 weight percent), hydrogen peroxide (4 weight percent), glycine (1 weight percent) and benzotriazole (1 milliMolar). Polishing was continued with down force of 1 psig for an additional 90 seconds with the same aqueous slurry. Visual inspection revealed that the copper overburden was greater than 95% cleared from the wafer. Dishing was measured for several features for 3 separate dies that spanned the radius of the wafer surface. The average dishing values for

these features is described in Table 11. These results demonstrate that a two-phase polish to remove copper overburden, in which polishing conditions are made progressively milder only by reducing mechanical force, but a silica containing slurry is employed throughout the entire polishing process, produces higher dishing.

**Table 11 Untreated**

| Feature<br>Copper line width_Oxide line width (μm) | 10_10 | 50_50 | 100_100 |
|---|---|---|---|
| Average Dishing (Å) | 2915 | 2982 | 3227 |
| Dishing Standard Deviation (Å) | 321 | 633 | 587 |

**Example 12**

The abrasive used in the slurry of this example was silica that was surface-modified by reaction with dichlorodimethylsilane. A SEMATECH 854 patterned wafer was polished with 3.5 psig downforce for 90 seconds with an aqueous slurry which comprised surface-modified silica (11 weight percent), hydrogen peroxide (5 weight percent), glycine (1 weight percent) and benzotriazole (1 milliMolar). Polishing was continued with 1 psig downforce for an additional 120 seconds with the same aqueous slurry. Visual inspection revealed that the copper overburden was greater than 95% cleared from the wafer. Dishing was measured for several features for 3 separate dies that spanned the radius of the wafer surface. The average dishing values for these features is described in Table 12. These results demonstrate that a two-phase polish to remove copper overburden, in which polishing conditions are made progressively milder only by reducing mechanical force, but a silica containing slurry is employed throughout the entire polishing process, produces higher dishing.

**Table 12**

| Feature<br>Copper line width_Oxide line width (μm) | 10_10 | 50_50 | 100_100 |
|---|---|---|---|
| Average Dishing (Å) | 2653 | 2152 | 2824 |
| Dishing Standard Deviation (Å) | 932 | 870 | 1265 |

Static Etch Rates for Slurries used in the Polishing Examples

**Example 13**

Slurry (400 milliLiters) comprising silica (11 weight percent), hydrogen peroxide (4 weight percent), glycine (1 weight percent), and benzotriazole ( 1 milliMolar) at pH 5 was poured into a glass dish (30 *x* 22 *x* 6 cm). The slurry was stirred with a magnetic bar and warmed using a Nuova™ heatable stir plate from Thermolyne Company. Temperature was adjusted and allowed to equilibrate to 23 °C as measured with a thermometer (-10 to 100 °C range). Slurry stirring was stopped. A 200 mm blanket copper wafer was pre-weighed on a TR-2102™ balance from Denver Instruments and placed in the slurry. After standing 20 minutes, the wafer was removed from the slurry, rinsed with deionized water, rinsed with isopropanol, dried, and re-weighed on the same balance. Weight loss was determined by the weight difference between the pre-weighed and re-weighed wafer. The wafer weight loss was 140 mg, which corresponds to a copper thickness loss of 250 Å/min.

**Example 14**

Slurry (400 milliLiters) comprising silica (11 weight percent), hydrogen peroxide (4 weight percent), glycine (1 weight percent), and benzotriazole ( 1 milliMolar) at pH 5 was poured into a glass dish (30 *x* 22 *x* 6 cm). The slurry was stirred with a magnetic bar and warmed using a Nuova™ heatable stir plate from Thermolyne Company. Temperature was adjusted and allowed to equilibrate to 55 °C as measured with a thermometer (-10 to 100 °C range). Slurry stirring was stopped. A 200 mm blanket copper wafer was pre-weighed on a TR-2102™ balance from Denver Instruments and placed in the slurry. After standing 5 minutes, the wafer was removed from the slurry, rinsed with deionized water, rinsed with isopropanol, dried, and re-weighed on the same balance. Weight loss was determined by the weight difference between the pre-weighed and re-weighed wafer. The wafer weight loss was 100 mg, which corresponds to a copper thickness loss of 710 Å/min.

**Example 15**

Slurry (400 milliLiters) comprising hydrogen peroxide (8 weight percent), glycine (1 weight percent), and benzotriazole ( 3 milliMolar) at pH 5 was poured into a glass dish (30 *x* 22 *x* 6 cm). The slurry was stirred with a magnetic bar and warmed using a Nuova™ heatable stir plate from Thermolyne Company. Temperature was adjusted and allowed to equilibrate to 23 °C as measured with a thermometer (-10 to 100 °C range). Slurry stirring was stopped. A 200 mm blanket copper wafer was pre-weighed on a TR-2102™ balance from Denver Instruments and placed in the slurry. After standing 20 minutes, the wafer was removed from the slurry, rinsed with deionized water, rinsed with isopropanol, dried, and re-weighed on the same balance. Weight loss was determined by the weight difference between the pre-weighed and re-weighed wafer. The wafer weight loss was 10 mg, which corresponds to a copper thickness loss of 18 Å/min.

**Example 16**

Slurry (400 milliLiters) comprising hydrogen peroxide (8 weight percent), glycine (1 weight percent), and benzotriazole ( 3 milliMolar) at pH 5 was poured into a glass dish (30 *x* 22 *x* 6 cm). The slurry was stirred with a magnetic bar and warmed using a Nuova™ heatable stir plate from Thermolyne Company. Temperature was adjusted and allowed to equilibrate to 55 °C as measured with a thermometer (-10 to 100 °C range). Slurry stirring was stopped. A 200 mm blanket copper wafer was pre-weighed on a TR-2102™ balance from Denver Instruments and placed in the slurry. After standing 5 minutes, the wafer was removed from the slurry, rinsed with deionized water, rinsed with isopropanol, dried, and re-weighed on the same balance. Weight loss was determined by the weight difference between the pre-weighed and re-weighed wafer. The wafer weight loss was 10 mg, which corresponds to a copper thickness loss of 71 Å/min.

We claim:

1.A slurry system for removal of metal from a substrate comprising:

(c) a first slurry which comprises abrasive and provides for partial removal of said metal from said substrate; and

(d) a second slurry which provides for further removal of said metal from said substrate,

wherein said first slurry has higher concentration of said abrasive than said second slurry.

2. The slurry system of claim 1 wherein said metal is selected from copper, tantalum, silicon dioxide, or mixtures thereof.

3. The slurry system of claim 1 wherein said metal is copper.

4. The slurry system of claim 1 wherein said second slurry is abrasive free.

5. The slurry system of claim 1 wherein said abrasive is selected from alumina, titania, zirconia, gennania, silica, ceria, or mixtures thereof.

6. The slurry system of claim 3 wherein said abrasive is silica.

7. The slurry system of claim 4 wherein said abrasive is precipitated silica.

8. The slurry system of claim 1 wherein said abrasive is present in an amount of from 0.1 to 30 percent by weight of said first slurry.

9. The slurry system of claim 4 wherein said silica has an aggregate of primary particles, said primary particles having an average diameter of at least seven (7) nanometers, wherein said aggregate has an aggregate size of less than one (1) micron, and a hydroxyl content of at least seven (7) hydroxyl groups per nanometer squared.

10. The slurry system of claim 1 wherein at least one of said first and second slurries further comprise an oxidant.

11. The slurry system of claim 8 wherein said oxidant is selected from inorganic and organic per-compounds, bromic acid, chloric acid, nitrates, sulfates, or mixtures thereof.

12. The slurry system of claim 8 wherein said oxidant is selected from hydrogen peroxide, urea-hydrogen peroxide, or mixtures thereof.

13. The slurry system of claim 1 wherein at least one of said first and second slurries further comprise a material selected from complexing agent,

anticorrosion agent, stopping compound, polyvalent cation sequestrant, thickener, or mixtures thereof.

14. The slurry system of claim 1 wherein at least one of said first and second slurries further comprises an acid selected from picolinic acid, dipicolinic acid, qunolinic acid, and mixtures thereof.

15. The slurry system of claim 1 wherein at least one of said first and second slurries further comprises a polyvalent cation sequestrant and a anticorrosion agent.

16. The slurry system of claim 1 wherein at least one of said first and second slurries further comprises a polyvalent cation sequestrant, a anticorrosion agent, and a thickener.

17. The slurry system of claim 1 wherein said first slurry leaves residual metal on said substrate.

18. The slurry system of claim 3 wherein said first slurry leaves residual copper on said substrate.

19. The slurry system of claim 17 wherein said second slurry at least partially removes said residual copper from said substrate.

20. The slurry system of claim 18 wherein said second slurry at least partially removes said residual copper from said substrate.

21. A method for removal of copper comprising:

(a) applying to a substrate a first slurry which comprises an abrasive;

(b) applying to said substrate a second slurry,

wherein said first slurry has higher concentration of said abrasive than said second slurry.

22. The method of claim 21 wherein said first slurry removes a portion of said copper from said substrate, and leaves residual copper on said substrate.

23. The method of claim 21 wherein said second slurry at least partially removes said residual copper from said substrate.

24. A method for polishing a microelectronic substrate comprising:

(a) performing a first polish with a first slurry and polishing pad, wherein said first slurry comprises abrasive; and

(b) performing a second polish with a second slurry and polishing pad wherein said first slurry has higher concentration of said abrasive than said second slurry.

25. The method of claim 24 wherein said first polish provides for partial removal of metal from said substrate and leaves residual portions of said metal on said substrate.

26. The method of claim 25 wherein said second polish provides for at least partial removal of said residual portions of said metal from said substrate.

27. The method of claim 25 wherein said metal is selected from copper, tantalum and silicon dioxide.

28. The method of claim 24 wherein said first polish is completed prior to applying said second slurry.

29. The method of claim 24 further comprising the step of washing said substrate after completion of said first polish and prior to initiation of said second polish.