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(54) Title: COMPOSITION AND METHOD FOR COPPER CHEMICAL MECHANICAL PLANARIZATION

(57) Abstract: A family of slurries are disclosed which are useful in modifying exposed surfaces of wafers for semiconductor fabrication along with methods of modifying exposed surfaces of wafers for semiconductor fabrication utilizing such a family of working slurries, and semiconductor wafers.



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COMPOSITION AND METHOD FOR COPPER CHEMICAL MECHANICAL PLANARIZATION

BACKGROUND OF THE INVENTION

Field of the Invention

- 5 This invention relates to an improved composition of slurries and a process for the chemical mechanical polishing or planarization of semiconductor wafers. More specifically, it relates to compositions of slurries containing sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide, that are employed in the polishing of silicon wafers used to produce semiconductor chips.

10 Discussion of the Prior Art

During integrated circuit manufacture, semiconductor wafers used in semiconductor fabrication typically undergo numerous processing steps, including deposition, patterning, and etching steps.

- Details of these manufacturing steps for semiconductor wafers are reported by
15 Tonshoff et al., "Abrasive Machining of Silicon", published in the Annals of the International Institution for Production Engineering Research, (Volume 39/2/1990), pp. 621-635. In each manufacturing step, it is often necessary or desirable to modify or refine an exposed surface of the wafer in order to prepare the wafer for subsequent fabrication or manufacturing steps.

- 20 In conventional semiconductor device fabrication schemes, a silicon wafer is subjected to numerous processing steps that deposit uniform layers of two or more discrete materials which together form a single layer of what will become a multi-layer structure. In this process, it is common to apply a uniform layer of a first material to the wafer itself or to an existing layer of an intermediate construct by any
25 of the means commonly employed in the art, to etch pits into or through that layer, and then to fill the pits with a second material. Alternatively, features of approximately uniform thickness comprising a first material may be deposited onto the wafer, or onto a previously fabricated layer of the wafer, usually through a mask, and then the regions adjacent to those features may be filled with a second material to

complete the layer. Following the deposition step, the deposited material or layer on a wafer surface generally needs further processing before additional deposition or subsequent processing occurs. When completed, the outer surface is substantially globally planar and parallel to the base silicon wafer surface. A specific example of such a process is the metal Damascene processes.

In the Damascene process, a pattern is etched into an oxide dielectric (e.g., SiO₂) layer. After etching, optional adhesion and or barrier layers are deposited over the oxide surface. Typical barrier layers may include tantalum, tantalum nitride, titanium nitride or titanium, or tungsten. Next, a metal (e.g., copper) is deposited over or on top of the adhesion and or barrier layers. The copper metal layer is then modified, refined or finished by removing the copper metal and regions of the adhesion and or barrier layer on the surface of the underlying dielectric. Typically, enough surface metal is removed so that the outer exposed surface of the wafer comprises both metal and an oxide dielectric material. A top view of the exposed wafer surface would reveal a planar surface with copper metal corresponding to the etched pattern and dielectric material adjacent to the copper metal. The copper (or other metal) and oxide dielectric material(s) located on the modified surface of the wafer inherently have different hardness values and susceptible to controlled corrosion. The method to modify the surface of the semiconductor may be a combination of a physical and chemical process. Such a process is called chemical mechanical planarization (CMP). An abrasive CMP process used to modify a wafer produced by the Damascene process must be engineered to simultaneously modify the metal (e.g., copper) and dielectric materials without scratching the surface of either material. The abrasive process must create a planar outer exposed surface on a wafer having an exposed area of a metal and an exposed area of a dielectric material.

Chemical mechanical polishing (or planarization) (CMP) is an area in semiconductor processing undergoing rapid changes. CMP provides global (millimeter-sized dimensions) and local (micron to nanoscale-sized) planarization on the wafer surface. This planarity improves the coverage of the wafer with dielectric materials and metals (e.g., copper) and increases lithography, etching and deposition process latitudes. Various equipment companies are advancing CMP technology through improvements in the engineering aspects of CMP while chemical companies are focusing on

consumables such as slurries and polishing pads. For example, conventional CMP methods for modifying or refining exposed surfaces of structured wafers uses techniques that polish a wafer surface with a slurry containing a plurality of loose abrasive particles dispersed in an aqueous medium. Typically this slurry is applied to a polishing pad and the wafer surface is then ground or moved against the pad in order to remove the desired material from the wafer surface. Generally, the slurry may also contain chemical agents that react with the wafer surface.

A relatively new alternative to CMP slurry methods uses an abrasive pad to planarize a semiconductor surface and thereby eliminate the need for the foregoing slurries containing polishing particles.

This alternative CMP process is reported in U.S. Patent Number 5,958,794. The abrasive pad has a textured abrasive surface that includes abrasive particles dispersed in a binder. During polishing, the abrasive pad is contacted with a semiconductor wafer surface, often in the presence of a working slurry containing no additional abrasive particles, with a motion adapted to modify a single layer of material on the wafer and thus provides a planar, uniform wafer surface. The working slurry is applied to the surface of the wafer to chemically modify or otherwise facilitate the removal of a material from the surface of the wafer under the action of the abrasive article.

Working slurries of the prior art useful in the process described above, either in conjunction with the aforementioned slurries or the abrasive pad, are typically aqueous slurries of a variety of additives including complexing agents, oxidizing agents, passivating agents, surfactants, wetting agents, buffers, viscosity modifiers or combinations of these additives. Additives may also include agents that are reactive with the second material, e.g., metal or metal alloy conductors on the wafer surface such as oxidizing, reducing, passivating, or complexing agents. Examples of such working slurries may be found, for example, in U.S. Patent Number 6,194,317.

Variables that may affect wafer CMP processing include the selection of the appropriate contact pressure between the wafer surface and abrasive article, type of slurry medium, relative speed and relative motion between the wafer surface and the abrasive article, and the flow rate of the slurry medium. These variables are

interdependent, and are selected based upon the individual wafer surface being processed.

CMP processes for modifying the deposited metal layer until the barrier layer or oxide dielectric material is exposed on the wafer outer surface leaves little margin for error

5 because of the sub-micron dimensions of the metal features found on the wafer surface. The removal rate of the deposited metal should be relatively fast to minimize the need for additional expensive CMP tools, and the metal must be completely removed from the areas that were not etched. The metal remaining in the etched areas must be limited to discrete areas while being continuous within those areas or zones to
10 ensure proper conductivity. In short, the metal modification process must be uniform, controlled, and reproducible on a sub-micron to nano-scale dimension.

In the CMP processes mentioned above, dishing performance, scratches or defects and removal rate of the metal are measurements of CMP performance. These performance measurements may depend on the use of the foregoing working slurries.

15 Dishing is a measure of how much metal, such as copper, is removed from bond pads or wire traces below the plane of the intermediate wafer surface as defined by the difference in height between the copper and the tops of the barrier or dielectric layers following removal of the blanket copper or copper plus barrier layer. Removal rate refers to the amount of material removed per unit time. Removal rates greater than at
20 least about 1000 Å per minute are preferred. Lower removal rates, such as a few hundred angstroms per minute (Å/min) or less, are less desirable because they tend to create increases in the overall manufacturing costs (cost of ownership) associated with wafer manufacture.

To minimize dishing and increase removal rates of layered surface materials on
25 semiconductor devices, it is important to engineer slurries with components in narrow concentration ranges and pH values. The pH of the slurries used in polishing of semiconductor devices is dependent upon the composition of the surface layer to be polished. In most cases, it is necessary to engineer a slurry with a proper pH to effectively produce an oxide layered surface at the same rate the mechanical action of
30 abrasion removes this layered oxide. For copper polishing slurries, U.S. Pat. No. 6,117,783 shows the importance of a pH of about 6.0 to form a copper (I) oxide, Cu₂O. Cuprous oxide can form only in near-neutral to slightly basic media. In low pH

slurries, a protective oxide may not form on the copper surface thus increasing the propensity for aggressive attack by the oxidizing agent on copper metal. In high pH slurries, removed copper may precipitate from solution resulting in un-wanted particulate matter adhering to the wafer surface. Therefore, copper-polishing slurries
5 must be formulated within a narrow pH window to ensure a high yield after CMP.

Prior art related to CMP includes the following:

U.S. Pat. No. 4,233,112 discloses the use of polysulfides as catalysts for hydrogen peroxide, useful in accelerating the dissolution of copper from circuit boards. This early disclosure allowed extrapolation to removal of copper from wafers, the basis of
10 much of the prior art.

Removal rate acceleration by sulfur compounds has been a major focus of many patent filings. WO01/44396 describes slurries containing mercaptans, disulfides and glycolates, which demonstrated accelerated copper removal rates. WO01/12740 describes organosulfur compounds that enhance the removal rate and WO01/12741
15 describes organosulfur corrosion accelerants in compositions also containing corrosion "stoppers".

U.S. Pat. No. 6,117,795 discloses organosulfur compounds as corrosion inhibitors for metal removal compositions. U.S. Pat. No. 6,068,879 discloses the utility of similar compounds in post-etch cleaners.

20 U.S. Pat. No. 5,073,577 discloses stable emulsions of high molecular weight polysulfides, which can be cured to produce sealants.

In Production of Sulfide Minerals by Sulfate-Reducing Bacteria During Microbiologically Influenced Corrosion of Copper, McNeil, Jones, and Uttle show that non-adherent layers of chalcocite (Cu_2S) are formed on copper surfaces under
25 some conditions. A Pourbaix diagram is published which details conditions under which copper sulfides and oxides are stable.

It would be desirable to provide improvements in chemical mechanical planarization by providing working slurries useful in modifying exposed intermediate copper surfaces of structured wafers for semiconductor fabrication and to methods of

modifying the exposed copper intermediate surfaces of such wafers for semiconductor fabrication, preferably with improved, sustainable, copper removal rates and utilizing the foregoing family of working slurries. It would be especially desirable to provide working slurries that are more stable than commercially available slurries. It would
5 also be desirable to provide working slurries that are useful in the aforementioned methods and resulting in the fabrication of copper containing structured wafers with better planarity and fewer defects.

SUMMARY OF THE INVENTION

The present invention is a slurry useful for modify exposed intermediate surfaces of
10 structured wafers for semiconductor fabrication, a method of modifying exposed intermediate surfaces of structured wafers for semiconductor fabrication utilizing such a family of working slurries, and semiconductor wafers made according to the foregoing process. The term slurry is used because it is familiar to one skilled in the art. However, for the present invention, the slurry may or may not contain abrasive
15 polishing particles or any other solid not totally dissolved. Furthermore, the term slurry may only refer to sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide.

This invention is an improved composition of slurries and process for the chemical mechanical polishing or planarization of semiconductor wafers, in which the slurry is
20 a composition containing sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide for use in modifying or refining intermediate surfaces of structured wafers suited for semiconductor fabrication. The sulfur compounds, including elemental sulfur of the present invention can be encapsulated with organic or inorganic materials to inhibit the conversion reaction of copper to
25 copper sulfide only when pressure or physical action, such as between a polishing pad and a wafer, is present.

In one aspect, the invention provides a working slurry useful in modifying a copper surface of a wafer suited for fabrication of a semiconductor device, the slurry being comprised of: a) a sulfur compound, including elemental sulfur capable of converting
30 copper to copper sulfide b) an activator to enhance the uniformity of the surface modification and/or c) a phase transfer agent to enhance the removal of copper (I) or

copper(II) sulfide from the surface d) optionally, a liquid carrier, e) optionally, an oxidizing agent, f) optionally, inorganic polishing particles, g) optionally, a chelating agent, h) optionally, a buffering agent i) optionally, a passivating agent, j) optionally, surfactants, emulsifying agents, viscosity modifiers, wetting agents, lubricants, soaps, and the like, k) optionally, a stopping compound to increase metal polishing selectively, and l) optionally a co-solvent.

Another embodiment of the invention is a method of modifying a surface of a wafer suited for fabrication of a semiconductor device comprising the steps of: a) providing a wafer comprising a first material having a surface etched to form a pattern and a second material deposited over the surface of the first material; b) contacting the second material of the wafer with polishing pad in the presence of the working slurry containing a sulfur compound, including elemental sulfur capable of converting copper to copper sulfide; and c) relatively moving the wafer or polishing pad while the second material is in contact with a polishing pad until an exposed surface of the wafer is planar and comprises at least one area of exposed first material and one area of exposed second material.

The invention also includes articles of manufacture that contain metal surfaces produced from slurries of this invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention teaches compositions useful for removal of copper and its alloys from surfaces such as those used in wafer fabrication. Also part of the invention is the use of said compositions in the process of Chemical Mechanical Planarization for manufacturing semiconductor wafers.

CMP slurries of the invention are characterized in significant part by containing sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide. Without being bound by theory, it is believed that the sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide can modulate the copper removal rate in the desired range to effectively promote formation of a copper (I) or copper (II) sulfide layer that is subsequently abraded from the surface of the electronic device. In addition, the sulfur compounds, including

elemental sulfur capable of converting copper to copper sulfide of this invention are characterized by producing an insoluble copper-sulfide complex which minimizes the propensity for copper deposition back onto the silicon device.

- 5 The sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide is optionally encapsulated in a material to inhibit the conversion reaction of copper to copper sulfide. The encapsulating material inhibits the reaction until it is broken or ruptured as through pressure or physical action. The pressure or physical action is typically provided by the interaction of a polishing pad and the wafer surface. The encapsulation materials can be a lignin sulfonate, fatty amine, 10 fatty ester or other surfactant type materials, or an inorganic material such as clay, which will form an encapsulating barrier around the sulfur compounds, including elemental sulfur yet which will rupture or break when subjected to pressure or physical action. The presence of such an encapsulating material provides increased control over the removal process.
- 15 Compositions of the invention contain a) sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide, b) an activator to enhance the uniformity of the surface modification and/or, c) a phase transfer agent to enhance the removal of copper (I) or copper (II) sulfide from the surface and optionally an aqueous, organic or mixed aqueous-organic liquid carrier optionally an oxidizing 20 agent, optionally inorganic polishing particles, optionally a chelating agent, optionally a buffering agent, optionally a passivating agent, optionally surfactants, optionally viscosity modifiers, optionally wetting agents, optionally lubricants, optionally soaps, and the like.

- 25 As discussed above, solutions of the invention containing sulfur compounds, including elemental sulfur, capable of converting copper to copper sulfide are particularly effective in various CMP slurries to effectively remove copper and copper alloy layers found in electronic devices. In particular, slurries of this invention containing sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide are useful for the removal of copper on integrated circuits such as 30 that produced in Damascene structures.

The sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide are vehicles to deliver sulfur to the copper surface and any material which achieves this purpose falls within the scope of the invention. Preferred is elemental sulfur, ideally with a small particle size. In one embodiment of this invention, a preferred particle size distribution would be such that 95% of the particles would have a diameter of less than about 15 micrometers, preferably less than about 10 micrometers, more preferably less than about 2 micrometers, and most preferably less than about 1 micrometer. Some examples of sulfur compounds which describe the invention but in no way limit the invention are mono and dithiocarbamates, thioacids, ash and ashless dithiophosphates as well as a variety of other sulfur bearing phosphorous materials, inorganic sulfides, organic sulfides and organometallic sulfides. The term sulfide embraces the class of sulfides and can be a mono, di, or polysulfide.

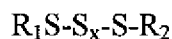
In another embodiment of this invention, very large sulfur particles (e.g., > 15 micrometers) can also act as abrasives to enhance the removal of both copper metal and formed copper sulfides. Combinations of the large particles and smaller particles described above may offer particularly advantageous synergies.

Submicron scale sulfur particles with controlled particle size distributions can be obtained by various milling techniques. A preferred method of generating sulfur particles with sub-micron particle sizes is wet milling and microfluidization. For example, sulfur particles with particle size distribution $D_{95}/D_{50}/D_{10}$ of about 450/50/10 μm can be wet- or dry-milled using a planetary ball mill to provide sulfur particles with particle size distribution $D_{95}/D_{50}/D_{10}$ of about 11/4.0/0.58 μm . These milled particles can be then further wet milled and microfluidized optionally multiple time in series to provide sulfur particles with a particle size distribution of $D_{95}/D_{50}/D_{10}$ of about 0.84/0.42/0.24 μm suitable for use in the present invention.

It is well documented that sulfur may exist in several allotropic forms, including various morphologies of cyclic-octasulfur, e.g., α -form, β -form, γ -form as well as oligomeric or polymeric sulfur (e.g., Crystex sulfur). It is further recognized by the inventors that these various sulfur allotropes exhibit different physico-chemical behaviors, e.g., solubilities, mass transport properties, and phase partitioning

properties. Selection of a sulfur having predominately one particular allotrope, or an appropriate mixture of allotropes, may offer advantages in the CMP process of this invention.

- Preferably, CMP slurries of this invention generally comprise elemental sulfur. A
5 variety of disulfide or polysulfides may also be introduced along with the elemental sulfur or alone as:



wherein R_1 and R_2 are independently an organic or inorganic functional group. These polysulfide species may also be formed in-situ .

- 10 The organic moieties may include hydrocarbons or functional groups such as hydrogen, amines, hydroxyl, carboxyl, halogen, sulfonyl, alkyl, aryl, alkaryl or combinations thereof. Inorganic functional groups may include alkali or alkaline earth metal salts or ammonium salts or combinations thereof. The rank of the polysulfide, the average x in the above structure, may vary from zero to twenty-four. The preferred
15 polysulfide is hydroethylpolysulfide.

- The sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide may be suitably present in a wide concentration range. Preferably, the sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide concentration is maintained at such concentrations to effectively maintain the
20 active sulfide at the desired concentration for copper sulfide formation and assist in precipitation of the removed copper. Preferably, the sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide compositions have a concentration range from about 0.0010% to about 100%, more preferably from about 0.5% to about 75% and still more preferably from about 1.0% to about 50%.

- 25 In addition to the sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide, the CMP slurry of the present invention contains an activator to enhance the uniformity of the surface modification and/or a phase transfer agent to enhance the removal of copper (I) or copper (II) sulfide from the surface. The

activator and phase transfer agent may be present in the slurry alone or in combination.

The activator is added in a concentration sufficient to achieve a uniform attack on the copper substrate but not so much as to cause a high static etch rate in the absence of external pressure. This concentration is preferably in the range of about 0.01 to 1% w/w, more preferably about 0.2 to 0.8 % w/w. The activator enhances the uniformity of reaction of the sulfur compounds, including elemental sulfur with the metal on the surface. Especially in cases where elemental sulfur is used, the reaction on the surface can be non-uniform due to the particulate nature of the sulfur and the presence of the activator provides for a uniform formation of a copper (I) or copper (II) sulfide layer on the surface. The activator is a material capable of reacting with elemental sulfur to form a species with anionic sulfur. Examples may include nucleophilic anions such as thiosulfate, sulfite, isocyanate, mercaptides, alkyl or aryl polysulfide anions, thioureas, trithiocarbonates, dithiocarbonates, monothiocarbonates, xanthates, monothiocarbamates, dithiocarbamates, amines, alkoxides and the like. The corresponding cation associated with the aforementioned anions include hydronium, ammonium, phosphonium, substituted ammonium or phosphonium, or other metal ions. The preferred anions for this invention include thiosulfate or sulfite, while the preferred cations include ammonium, substituted ammonium, potassium, cuprous ion and cupric ion, and any of these ions in combination with complexing agents.

The phase transfer agent is added in a concentration sufficient to achieve a minimal but uniform residue of copper sulfides on the surface after polishing. This concentration is preferably in the range of about 0.001 to 1% w/w, more preferably about 0.03 to 0.8% w/w. The phase transfer agent enhances the removal of the copper (I) or copper (II) sulfide layer formed on the surface by the action of the sulfur compounds, including elemental sulfur. The phase transfer agent is a material that acts to enhance transport of anionic species into the forming copper sulfide surface film, or that act to transport the anionic species through the copper sulfide film. While not be bound by any theory, it is thought that these phase transfer agents accelerate mass transfer of the anionic species from the aqueous slurry into the more hydrophobic copper sulfide phase, thus allowing more rapid reaction of the anions with the copper sulfides or with sulfur particles occluded in the copper sulfide phase.

The net effect is more efficient transport of the anions into and through the copper sulfide phase to enhance the mechanical removal of the copper sulfide phase.

The phase transfer agents of this invention include cationic quaternary ammonium or phosphonium species. The cationic ammonium or phosphonium species include, but
5 are not limited to ammonium or phosphonium species with any combination of four alkyl or aryl substituents, N, N'-dialkylimidizolium species, and other positively-charged heterocyclic compounds. The preferred phase transfer agents of this invention include trioctyl methylammonium, tributyl ammonium and tetrabutylammonium cations. The cationic phase transfer agents may be added into
10 the slurry in the form of salts derived from any number of anionic species, including halides, sulfates, sulfonates, phosphates, alkyl- or aryl phosphonates, carbonates, carboxylates, hydroxides, and peroxy analogs of these anionic species.

In addition, the CMP slurry may contain secondary oxidizing agent to promote copper removal. Without being limited by theory, the secondary oxidants are thought to
15 convert sulfur in the divalent state e.g., species containing $-S_x-Cu-S_x-Cu-$, or $Cu-S_x-Cu$ functionality where $x = 1, 2$, or greater; to form more oxidized sulfur species; e.g., sulfite, sulfate, thiosulfate, polythionate(s); which are in turn more soluble in the slurry media and thus more easily removed during polishing.

An alternative mode of action for the secondary oxidant is to oxidize anionic sulfur
20 species back to a disulfide or polysulfide form, e.g., $Z^1-S^- + Z^2-S^- \rightarrow Z^1-S-S-Z^2$, where Z^1 and Z^2 represent homo-sulfur, polythionate, or any number of metal-sulfur species.

In either of the above cases, conversion of the anionic species to a di/polysulfide or oxygenated form can act to decrease the concentration of anionic sulfur species, and
25 thus inhibit attack on the copper surface. Thus, the secondary oxidant could serve as a rate controlling agent operating in combination with the sulfur particles, activator(s), and/or phase transfer agent(s) to provide a balanced level of copper removal. Formed sulfides or polythionates can obviously be reactivated at some later time in a given polishing cycle via reaction with one of the activator species.

A third possible mode of action is direct oxidation of exposed copper surfaces to form dense and potentially impermeable copper oxide deposits or films on the surface. Such films would then act to slow or fully inhibit copper removal by the sulfur species.

- 5 Suitable chemical oxidizing agents, if used, include hydrogen peroxide, cupric chloride; persulfates of ammonium, sodium and potassium; ferric chloride; potassium ferricyanide; nitric acid, potassium nitrate, ammonium molybdate potassium iodate, hydroxylamine, diethylhydroxylamine, OXONE, transition metal complexes such as ferricyanide, ammonium ferric EDTA, ammonium ferric citrate, ferric citrate,
10 ammonium ferric oxalate and combinations thereof.

- The concentration of the oxidizing agent in deionized water may range from about 0.01 to 50% by weight, preferably 0.02 to 40% by weight. Where hydrogen peroxide is used as the oxidizing agent, it is typically present in an aqueous solution at a concentration (weight percentage) within the range from about 0.01% to about 15%,
15 preferably from about 0.5% to about 7.5% and most preferably from about 1.0% to about 5.0%.

- The CMP slurry can optionally contain additives such as a polishing particles, a primary and secondary buffer, chelating agents, passivating agents, surfactants, emulsifying agents, viscosity modifiers, wetting agents, lubricants, soaps, an organic
20 or inorganic co-solvent and the like.

- The optional polishing particles may be inorganic or organic abrasive particles. These abrasive particulates may be used to increase the removal rate of the copper metal and/or the dielectric. Examples of such inorganic particulates include: SiO_2 , Al_2O_3 , CeO_2 , zirconia, calcium carbonate, cerium salts, garnet, silicates and titanium dioxide.
25 The average particle size of these inorganic particulates should be less than about 1,000 Angstroms, preferably less than about 500 Angstroms and more preferably less than about 250 Angstroms. In one embodiment, the polishing particles may comprise colloidal or fumed silicas. At high levels the added abrasives may become a primary polishing media that abrades copper metal, copper sulfides and dielectric. However,
30 at lower concentrations, the added abrasives may primarily act to remove copper sulfides from the surface.

Preferably, the working slurry contains less than 10% by weight, preferably less than 5% by weight and more preferably less than 3% by weight inorganic particulates.

Although abrasive particles may be added to the CMP slurry, CMP processes utilizing three-dimensional abrasive particles fixed to an abrasive polishing pad will preferably provide for substantially abrasive-free slurry.

Moreover, the polishing of wafers in this invention may involve no polishing particles, either in the slurry of this invention or fixed to the polishing pad.

The slurry of this invention may also contain a buffering agent. Buffers may be added to the working slurry to assist in pH-control. As mentioned above, the pH can have a significant effect on the nature of the copper surface, and the copper removal rate. The most preferred buffers are compatible with semiconductor, post-CMP cleaning needs as well as having reduced potential impurities such as alkali metals. In addition, the most preferred buffers could be adjusted to span the pH range from acidic to near-neutral to basic. Mono, di and polyprotic acids may act as buffers, and when fully or partially de-protonated with bases such as ammonium hydroxide. Ammonium salts of the acids are preferred but other alkali and alkaline earth metal salts of the carboxylic acids may be used. Representative examples include salts of carboxylic acids, for example, mono-carboxylic acids, di-carboxylic acids, tri-carboxylic acids, and polycarboxylic acids. Preferred containing compounds include, for example, malonic acid, oxalic acid, citric acid, tartaric acid, succinic acid, malic acid, adipic acid, salts thereof, and mixtures thereof. Nitrogen containing compounds that may buffer the slurry include: aspartic acid, glutamic acid, histidine, lysine, arginine, ornithine, cysteine, tyrosine, and camosine, bis(2-hydroxyethyl)iminotris(hydroxymethyl)methane, tris(hydroxymethyl)aminomethane. N-(2-acetamido)-2-iminodiacetic acid, 1,3-bis[tris(hydroxymethyl)methylamino]propane, triethanolamine, N-tris(hydroxymethyl)methylglycine, N,N-bis(2-hydroxyethyl)glycine and glycine. Monoammonium or diammonium hydrogen phosphates may also be used in the slurry of the invention.

The pH range may vary from about 2 to about 13, preferably from about 3 to 12 and most preferably from about 4 to 11.

The slurry of this invention may also comprise a copper-chelating agent. Copper removal from the wafer surface may be enhanced with the use of a complexing or chelating agent in the CMP slurry of the invention. The oxidation and dissolution of copper is enhanced by the addition of complexing agents that bond to copper to
5 increase the solubility of dissolved copper metal or copper oxides in the organic or aqueous medium.

In the working slurries of the present invention, the complexing agent is always present at a concentration from about 0.01 to 50% by weight. During the planarization of copper; the preferred complexing agents are acids or salts of: citric, iminodiacetic,
10 2-aminoethyl phosphonic acid, aminotri(methylenephosphonic acid) 1-hydroxyethylidene-1, 1-phosphonic acid and diethylenetri-aminepenta(methylenephosphonic acid), and glycine. The concentration of the chelating agents in the slurry may range from 0.001% to about 50% by weight, preferably from 0.5% to about 10% by weight and most preferably from 1% to about
15 10% by weight.

The slurry of this invention may also comprise a passivating agent (i.e., corrosion inhibitor). Corrosion inhibitors or passivating agents are well known for copper. Copper is known to be somewhat passivated by cuprous oxide, especially at neutral or mildly alkaline pH. The addition of passivating agents to the working slurry may
20 protect areas of a copper surface not yet in contact with the abrasive article from premature, excessive removal by the oxidizing agent or control the concentration of the oxidizing agent reacting with the exposed metal surface. The best-known and most widely used inhibitors for copper are tolyltriazole, mercaptobenzothiazole, benzotriazole, hydroxybenzotriazoles and their derivatives known as azole
25 derivatives.

The amount and type of passivating agent will depend in part on the desired planarization criteria (removal rate, surface finish and planarity). Depending on the activity of the passivating agent in the particular slurry composition, the preferred concentration in the working slurry (weight percentage) is within the range between
30 about 0.0001% and about 0.20%, preferably between about 0.050% and about 0.15% and more preferably between about 0.050% and about 0.10%.

The slurry of the invention may also comprise viscosity modifiers to achieve a desired viscosity of about 5 centipoise to about 25 centipoise. Examples of viscosity modifiers include polyoxTM available from Union Carbide and CarpoolTM available from B.F. Goodrich. Those skilled in the art will appreciate that surfactants, viscosity
5 modifiers and other known additives may be added to the working slurry as may be required in a particular application.

The slurry of the invention may also comprise a stopping 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 adsorb to the first metal layer, the second
10 layer, and/or one or more additional layers of a multi-layer substrate and at least partially inhibit the removal of the layer(s) by the slurry of the present invention. Preferably, the stopping compound at least partially inhibits the removal of the second layer by the slurry. The term "at least partially inhibits" as used herein means that the system has a polishing selectivity of the first metal layer:second layer of at least about
15 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. Suitable stopping compounds also include, for example, cationically
20 charged nitrogen-containing compounds selected from the group of compounds comprising amines, imines, amides, imides, polymers thereof, and mixtures thereof, wherein the stopping compound is not a sulfur-containing compound or an azole compound. Cationically charged as used herein means that a fraction (e.g., >1%) of the stopping compound is protonated at the operating pH of the system of the present
25 invention. Preferred stopping compounds also are oppositely charged from the surface charge of the metallic layer that is not to be polished.

The slurry of the invention may contain various co-solvents to assist in solubilizing sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide. The solvent may be entirely water or entirely organic depending upon the
30 composition of the sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide. Mixtures of water and an appropriate organic solvent may also be used within the scope of the invention. Suitable organic solvents

include methanol, ethanol, isopropanol, tetrahydrofuran, dimethylsulfoxide, acetonitrile, dimethylformamide, *N*-methylpyrrolidin-2-one among others.

The slurry of the invention may contain various emulsifying agents.

5 It may also be advantageous to provide mechanical or hydrodynamic shear during preparation and handling of the slurry described in this invention, both to mix the reagents and to inhibit agglomeration of the sulfur particles or other solids. Such shear can be obtained via mechanical stirring or via treatment with ultra-sonic vibration, the latter be a preferred embodiment.

10 The slurry of the invention can be used from about 10° C to about 70°C, more preferably from about 15° C to about 60° C and most preferably from about 20° C to about 50° C.

The method of present invention for modifying a surface of a wafer suited for fabrication of a semiconductor device comprises the steps of:

- 15 a. providing a wafer comprising a first material having a surface etched to form a pattern and a second material deposited over the surface of the first material;
- b. contacting the second material of the wafer with slurry of the invention used in conjunction with a polishing pad, the slurry comprising a plurality of loose abrasive particles dispersed in the slurry; and
- 20 c. relatively moving the wafer while the slurry and polishing pad are in contact with the exposed surface of the wafer until the wafer is planar and comprises at least one area of exposed first material and one area of exposed second material.

25 The method is preferably directed to modifying intermediate surfaces of a structured wafer. The first material is typically a dielectric material with an intermediate material or adhesion/barrier layer applied thereover. Some suitable intermediate materials or adhesion barrier layers include tantalum, titanium, tantalum nitride, titanium nitride. Other suitable intermediate materials or adhesion/barrier layers include metals, nitrides, and silicides. The designs associated with the first material include patterned areas, grooved areas, and vias, as well as other structures that make up a completed

semiconductor device. The second material is typically a conductive material selected from titanium, silver, aluminum, tungsten, copper, or alloys thereof. The present method is particularly adapted to modifying conductive surfaces of materials having resistivity values typically less than about 0.1 ohm-cm. In general, preferred dielectric materials will have dielectric constants less than about 5.

In this aspect, the working slurry containing sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide and optionally the inorganic particles is as described above.

The movement between the wafer and the polishing pad occurs under pressure in the general range from about 0.1 to about 25 psi, preferably in a range from about 0.2 to about 15 psi and most preferably in a range from about 0.1 to about 6 psi. The wafer and polishing pad may be rotated and/or moved against each other in a circular fashion, spiral fashion, a non-uniform manner, an elliptical fashion such as a figure eight or a random motion fashion. The wafer holder or the base may also oscillate or vibrate, such as by transmitting ultrasonic vibrations through the holder or base. For example, either the polishing pad or the wafer or both the polishing pad and the wafer are rotated relative to the other as well as being moved linearly along relative centers of the wafer and pad. The rotational motion or speed of rotation between the wafer and polishing pad may be between 1 rpm to 10,000 rpm. Preferred rotational speeds for the pad are at a speed between 10 rpm to 1,000 rpm, and more preferably between 10 rpm to 250 rpm and most preferably between 10 rpm to 60 rpm. Preferred rotational speeds for the wafer are between 2 rpm to 1,000 rpm, more preferably between 5 rpm to 500 rpm, and still more preferred between 10 rpm to 100 rpm. The pressure and/or physical action between the wafer and polishing pad allows intimate contact between the sulfur particles of the slurry and the copper substrate. In the absence of this induced intimate contact between sulfur and copper, the inventors observed very little reaction between suspended sulfur particles in the slurry and the copper substrate.

In the case of encapsulated sulfur particles, the pressure and/or physical action may further serve to rupture or break the encapsulation of the sulfur component. Thus, the use of an encapsulant for the sulfur provides an additional means of controlling the activity of the sulfur component.

The CMP slurries of the invention may be used without the inorganic polishing particles mixed in the aqueous medium. Rather, a fixed abrasive pad whereby a fixed three-dimensional abrasive pad having numerous abrasive particles extending throughout at least a portion of its thickness, is used such that removing some of the particles during planarization exposes additional abrasive particles capable of performing the planarization function. A preferred abrasive polishing pad comprises a plurality of abrasive particles fixed and dispersed in a binder.

In this fixed abrasive polishing method, contact and motion is maintained between the fixed abrasive pad and the wafer until an exposed surface of the wafer is planar and comprises at least one area of exposed second or conductive material and at least one area of exposed first or dielectric material, and the exposed area of conductive material and the exposed area of dielectric material lay in a single plane. The dielectric material may be covered by one or more intermediate materials such as an adhesion or barrier layer. Usually, the exposed dielectric material surface is essentially free of the intermediate material after removal of the excess conductive material. Alternatively, removal of the metal layer may expose only the surfaces of the intermediate material. Continued modification may then expose on the surface of the wafer the dielectric material and the metal layer.

The abrasive pad used with the slurries of this invention may be circular in shape, e.g., in the form of an abrasive disc. The outer edges of the circular abrasive disc are preferably smooth or, alternatively, may be scalloped. The abrasive article may also be in the form of an oval or of any polygonal shape such as triangular, square, rectangular, and the like. Alternatively, the fixed abrasive pad may be in the form of a belt or in the form of a roll, typically referred to in the CMP polishing industry as abrasive tape rolls. Abrasive tape rolls may be indexed during the modification process. The abrasive article may be perforated to provide openings through the abrasive coating and/or the backing to permit the passage of the slurry medium before, during or after use.

The interface pressure between the abrasive article and wafer surface (i.e., the contact pressure) is typically less than about 30 pounds per square inch (psi), preferably less than about 15 psi, more preferably less than about 6 psi. Also, two or more processing conditions within a planarization process may be used. For example, a first processing

segment may comprise a higher interface pressure than a second processing segment. Rotation and translational speeds of the wafer and/or the abrasive pad also may be varied during the planarization process.

Recessed portions of the abrasive pad may act as channels to help distribute the working slurry over the entire wafer surface. The recessed portions may also act as channels to help remove the worn abrasive metallic sulfide particles and other debris from the wafer and abrasive article interface. The recessed portions may also prevent the phenomenon known in the art as "stiction" where the abrasive article tends to stick to or become lodged against the wafer surface.

- 5 Methods directed toward producing uniform wear rates across the surface of the object being polished and or across the surface of the polishing pad are discussed in U.S. Pat. Nos. 5,177,908; 5,234,867; 5,297,364; 5,486,129; 5,230,184; 5,245,790; and 5,562,530. These methods may be adapted for use in the present invention. Variations of the wafer planarization process which employ either a continuous belt or a supply roll of sheet pad material in conjunction with a slurry may also be employed by substituting a belt or roll of textured, three-dimensional abrasive composite and working slurry of this invention.

- The amount of the working slurry of the invention applied to the wafer surface is preferably sufficient to aid in the removal of copper or copper oxide layer from the surface. In most cases, there is sufficient slurry from the working slurry of the invention. It will also be appreciated that some planarization applications may require that a second slurry be present at the planarization interface in addition to the slurry of this invention. This second slurry may be the same as the first slurry, or it may be different. The flow rate for dispersing the working slurry typically ranges from about 10 to 1,000 milliliters/minute, preferably 10 to 500 milliliters/minute, and more preferably between about 25 to 250 milliliters/minute.

- The surface finish of the wafer may be evaluated by known methods. One preferred method is to measure the R_t or R_a value of the wafer surface that provides a measure of "roughness" and may indicate scratches or other surface defects. The wafer surface is preferably modified to yield an R_t value of no greater than about 1000 Angstroms,

more preferably no greater than about 100 Angstroms, and even more preferably no greater than about 50 Angstroms.

There can be numerous process steps for a single semiconductor wafer. Therefore, a relatively high removal rate of metal layer is desired. With the CMP slurry of the invention described herein, the removal rate will typically be at least 1000 Angstroms per minute, preferably at least 2000 Angstroms per minute, more preferably at least 3000 Angstroms per minute, and most preferably at least 4000 Angstroms per minute. The removal rate of the metal may vary depending upon the CMP tool and the type of wafer surface being processed. Although it is generally desirable to have a high removal rate, the removal rate preferably will not be so high as to compromise the desired surface finish and/or topography of the wafer surface or make the control of the planarization process difficult.

A preferred slurry composition in accordance with the present invention comprises about 2 weight % sulfur in the form of sulfur particles with a particle size distribution such that 95% of the particles have a nominal diameter less than 2 micrometers, about 0.005 to 0.05 weight % tributyl methylammonium chloride phase transfer catalyst, about 0.5 weight % ammonium thiosulfate activator, about 0.5 weight % of a dispersing agent/surfactant such as Tween-20, about 0.5 weight % ammonium persulfate secondary oxidizer and about 0.4 weight % colloidal silica abrasive.

Without being bound to any particular theory or mode of action, the use of an activator such as ammonium thiosulfate or ammonium sulfite provides for a reaction with the sulfur component which is believed to generate small amounts of a water-soluble ionic sulfur species which can attack the copper surface in a uniform fashion. The activator anions may also react directly with sulfur-rich portions of the formed copper sulfide(s) on the surface to cleave sulfur-sulfur bonds. The addition of a phase transfer catalyst, such as tributyl methylammonium chloride, tetrabutylammonium bromide and trioctyl methylammonium chloride to the slurry enhanced the permeation of the sulfur, activator anions, and secondary oxidant anions through the formed copper sulfide(s) on the wafer surface, allowing more efficient reaction of these species with the sulfur components of the formed copper sulfide, thus loosening the adhesion of the copper sulfide(s) to the copper surface. Thus, the activator, phase

transfer catalyst, and secondary oxidant are believed to enhance copper removal rates while providing for a uniform post polish surface uniformity.

The relative advantages of the sulfur-based slurry as compared to a commercial CMP slurry can be summarized as follows:

	Sulfur-Based Slurry of The Present Invention		Fujimi PL-7103® Copper CMP Slurry
Polishing Conditions	1 psi & 1 m/s	1.5 psi & 1 m/s	1.5 psi & 1 m/s
Static Etch Rate	Non-Detectable		>50 Å/min
Shear Force*	24 lb _f	36 lb _f	44 lb _f
Coefficient of Friction*	0.5	0.5	0.6
Removal Rate	4400 Å/min	6600 Å/min	2500 Å/min
Selectivity* (Cu/TEOS, Cu/Ta, Cu/TaN)	Infinitely High		≈ 100
* Per experimental data collected on Araca APD-500 polisher with 200 mm wafers			

5 EXAMPLES

The invention is further illustrated in the non-limiting examples set forth below.

Example 1

Copper blanket wafers were polished with sulfur based slurries. These results demonstrate that the sulfur is an effective polishing agent for the removal of copper,
 10 giving removal rates that are superior to commercial H₂O₂ and abrasive CMP slurries.

Dispersed Sulfur (% w/w)	Polishing Downforce (psi)	Removal Rate (Å/min)	Surface Roughness (Ra, nm)
2	0.5	9,489	78
1	2	13,336	105
1	0.5	5,204	71
0.5	2	5,218	100

Example 2

Copper pattern wafers would be polished and treated in one step with a slurry consisting of sulfur particles, optionally encapsulated, in the range of 1-3% w/w,
 15 dispersed in an aqueous media using a surfactant such as Tween -20, 0.5% activator e.g., ammonium thiosulfate, 0.05-0.5% phase transfer agent e.g., tributyl methylammonium chloride, 0.5% secondary oxidant e.g, ammonium persulfate,

blended with a suspension of abrasive particles. During polishing down to the tantalum nitride barrier layer, copper removal rates would be expected to be on the same order as observed with commercial H_2O_2 /abrasive slurries.

Example 3

- 5 Copper pattern wafers would be polished and treated in two steps:

Step 1 would involve removal of the bulk of the copper using a slurry similar to that described in Example 2. Here the polishing would be performed such that most, but not all, of the copper overburden would be removed.

- 10 Step 2 would consist of a final polish using a traditional chemical-mechanical planarization slurry containing an oxidizing agent (H_2O_2 , persulfate salt, or other oxidant) and abrasive particles such that the residual copper and any copper sulfides would be removed down to the barrier layer.

- This two-step approach could be used in those cases where any permeation of the sulfur into the trenches of the pattern wafer, or where the presence of residual copper sulfide(s) on the polished surfaces, cannot be tolerated.
- 15

Example 4: The effect of sulfur particle size.

- Sulfur particles (Akron Dispersions) with particle size distribution $D_{95}/D_{50}/D_{10} \approx 450/50/10 \mu\text{m}$ were wet-milled using a planetary ball mill to provide sulfur particles with particle size distribution $D_{95}/D_{50}/D_{10} \approx 11/4.0/0.58 \mu\text{m}$. The wet-milled particles
- 20 were then subjected to additional wet-milling, then microfluidized (Microfluidics M110-EH-30 processor) four times in series to afford sulfur particles with a particle size distribution of $D_{95}/D_{50}/D_{10} \approx 0.84/0.42/0.24 \mu\text{m}$.

- Using a laboratory CMP polisher (Araca Inc.; APD-500) equipped with force acquisition software and data analysis software (Araca FSX-500), 200-mm copper
- 25 blanket wafers were polished with slurries consisting of 2% dispersed sulfur in deionized water. A Rohm & Haas 20-inch IC1020 M-groove pad was used for the polishing. Prior to the addition of the sulfur slurry, the pad was initially conditioned with a 3M A165 disc rotating at 95 rpm and sweeping at 10 cycles/min. The results

for the submicron sulfur particles and the larger dry-milled particles are tabulated below. The submicron particles provided a higher removal rate (RR) and reduced non-uniformity (RRNU). Despite the higher uniformity offered by the submicron particles, the residual copper sulfide films on the copper wafer were also thicker, showing the potential advantage of a larger particle acting as an abrasive.

Slurry	COF	RR [$\text{\AA}/\text{min}$]	RRNU [%]	Residual Cu-S Film Thickness [$\text{\AA}$]
2% Submicron Particles	0.291	5829	34%	1871 (Grey Cu-S film)
2% Wet-Milled Particles	0.221	2837	64%	574 (Brown Cu-S film)
COF = Coefficient of Friction, RR = Removal Rate, RRNU = Removal Rate Non-Uniformity Polishing Conditions: Polishing pressure 1 psi, sliding velocity = 1 m/s, polishing time = 60 seconds, slurry flow rate = 150 mL/min				

Example 5

The high selectivity of the sulfur slurry towards copper vs. TEOS and TaN barrier layers is illustrated herein. 200-mm copper, TEOS, and TaN blanket wafers were polished with a slurry comprised of 2% wet-milled and microfluidized sulfur particles dispersed in deionized water containing 0.7% Tween-20 surfactant. The sulfur particles were prepared similar to Example 4 but with 20 minutes of wet milling. The blanket wafers were polished as in Example 4. The results with the different wafers clearly show the high removal rates achieved on the copper wafers and the imperviousness of the TEOS and TaN surfaces to attack by sulfur.

Wafer	Polishing Time (s)	COF	RR [$\text{\AA}/\text{min}$]	RRNU [%]
Cu	45	0.239	5504	120
Cu	60	0.212	9445	31
TEOS	60	0.166	Not Measurable	Not Applicable
TEOS	60	0.185	Not Measurable	Not Applicable
TaN	60	0.166	Not Measurable	Not Applicable
TaN	60	0.170	Not Measurable	Not Applicable
COF = Coeff. of Friction, RR = Removal Rate, RRNU = RR Non-Uniformity Polishing Conditions: Polishing pressure 1.5 psi, sliding velocity = 1 m/s, slurry flow rate = 150 mL/min				

Examples 6

The effects of various combinations of ammonium thiosulfate (AT) activator, tributyl methyl ammonium chloride (TBMAC) phase transfer agent, and ammonium persulfate (APS) secondary oxidant, and added silica abrasives is illustrated herein using the procedure outlined in Example 4. The combination of ammonium

thiosulfate activator and TBMAC phase transfer catalyst results in a more uniform attack of the copper surface as shown by the lower non-uniformity (RRNU) results and thicker copper sulfide residues, however with concomitant lower removal rates.

Combining ammonium persulfate (APS) secondary oxidant with a low level of AT
 5 activator and TBMAC phase transfer catalyst further reduced the removal rate but afforded better uniformity and reduced residual film copper sulfide film thickness relative to the sulfur-only slurry. Increasing the amount of AT in the presence of the same levels of APS and TBMAC resulted in an increase in the removal rate, a slight decrease in the non-uniformity relative to the sulfur-only slurry, but also increased the
 10 residual copper-sulfide film after polishing. Adding abrasive particles (fumed silica) restored the removal rate with only a minor penalty in non-uniformity and copper sulfide residual film.

Example 7:

Replacement of the fumed silica abrasive in Example 6 with a commercially-
 15 available colloidal silica slurry afforded dramatic decreases in removal rate and surface uniformity as compared to a simple sulfur slurry. Combining the dispersed sulfur, TBMAC, AT, and colloidal silica in this slurry afforded an extremely high removal rate (9449 Å/min) Adding APS secondary oxidant to the same composition reduced the removal rate to a still quite acceptable 4187 Å/min and substantially
 20 reduced the copper sulfide residue, but at penalty of increased non-uniformity.

Slurry	COF	RR [Å/min]	RRNU [%]	Residual Cu-S Film Thickness [Å]
2% Dispersed Sulfur	0.272	6138	33.2%	1712 (Grey Cu-S film)
2% Dispersed Sulfur + 0.05% TBMAC + 0.1% AT	0.333	3713	14.6%	2690 (Grey Cu-S film)
2% Dispersed Sulfur + 0.05% TBMAC + 0.1% AT + 0.5% APS	0.308	2934	12.7	648 (Brown Cu-S film)
2% Dispersed Sulfur + 0.05% TBMAC + 0.1% AT + 1.0% APS	0.319	2467	7.7	586 (Brown Cu-S film)
2% Dispersed Sulfur + 0.05% TBMAC + 0.1% AT + 1.0% APS + 5% Fumed Silica	0.394	5679	12.7	711 (Brown Cu-S film)

2% Dispersed Sulfur	0.268	5708	35.7%	1706 (Grey Cu-S film)
2% Dispersed Sulfur + 0.05% TBMAC + 0.5% AT + 0.5% APS	0.381	6322	10.1	1706 (Grey Cu-S film)
2% Dispersed Sulfur + 0.4% Colloidal Silica	0.341	67	74.7%	Not Available
2% Dispersed Sulfur + 0.4% Colloidal Silica + 0.5% APS	0.326	464	23.9	Not Available
2% Dispersed Sulfur + 0.05% TBMAC + 0.5% AT + 0.4% Colloidal Silica	0.488	9449	8.4	2447 (Grey Cu-S film)
2% Dispersed Sulfur + 0.05% TBMAC + 0.5% AT + 0.5% APS + 0.4% Colloidal Silica	0.380	4187	33.6	324 (Light brown Cu-S film)
COF = Coeff. of Friction, RR = Removal Rate, RRNU = RR Non-Uniformity Polishing Conditions: Polishing pressure 1.0 psi, sliding velocity = 1 m/s, polishing time = 60 seconds, slurry flow rate = 150 mL/min				

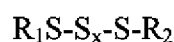
While the present invention has been described with respect to particular embodiments thereof, it is apparent that numerous other forms and modifications of this invention will be obvious to those skilled in the art. The appended claims and this invention generally should be construed to cover all such obvious forms and

5 modifications which are within the true spirit and scope of the present invention.

What is claimed is:

1. A slurry useful in planarizing a surface of a wafer suited for fabrication of a semiconductor device, the slurry being comprised of:
 - a) sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide,
 - b) an additive selected from the group consisting of an activator, a phase transfer agents and mixtures thereof,
 - c) optionally, a liquid carrier,
 - d) optionally, an oxidizing agent,
 - e) optionally, inorganic polishing particles,
 - f) optionally, a chelating agent,
 - g) optionally, a buffering agent,
 - h) optionally, a passivating agent,
 - i) optionally, surfactants, emulsifying agents, viscosity modifiers, wetting agents, lubricants, soaps, and the like,
 - j) optionally a stopping compound to increase metal polishing selectively, and
 - k) optionally, a co-solvent.

2. The slurry of claim 1 wherein the sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide is selected from the group consisting of elemental sulfur, disulfide or polysulfide having the structure:



wherein R_1 and R_2 are independently an organic or inorganic moiety and x is an integer from 0 to 24 and mixtures thereof.

3. The slurry of claim 2 wherein R_1 and R_2 are independently an organic moiety that may include hydrocarbons or functional groups such as a hydrogen, amines, hydroxyl, carboxyl, halogen, sulfonyl, alkyl, aryl, alkaryl or combinations thereof.
4. The slurry of claim 2 wherein R_1 and R_2 are independently an inorganic functional group selected from an alkali or alkaline earth metal salts or ammonium salts or combinations thereof.

5. The slurry of claim 2 wherein the polysulfide is hydroxyethylpolysulfide.
6. The slurry of claim 1 wherein the sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide has a concentration from 0.0010% to 100%.
7. The slurry of claim 1, wherein the inorganic polishing particles are selected from SiO_2 , Al_2O_3 , CeO_2 , zirconia, calcium carbonate, cerium salts, garnet, silicates and titanium dioxide.
8. The slurry of claim 1 wherein the pH is between 2 to 13.
9. The slurry of claim 1 wherein said sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide have a particle size distribution such that 95% of the particles have a diameter less than about 15 micrometers.
10. The slurry of claim 1 wherein said sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide have a particle size distribution such that 95% of the particles have a diameter less than about 2 micrometers.
11. The slurry of claim 1 wherein said sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide have a particle size distribution such that 95% of the particles have a diameter less than about 1 micrometer.
12. The slurry of claim 1 wherein said sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide are encapsulated with an organic or inorganic material.
13. The slurry of claim 9 wherein said sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide having a particle size distribution such that 95% of the particles have a diameter less than about 15 micrometers is provided by wet milling, microfluidization or combinations thereof.
14. The slurry of claim 1 wherein said sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide comprises particles having a diameter

less than about 15 micrometers and particles having a diameter greater than about 15 micrometers.

15. The slurry of claim 1 wherein said sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide are the allotropic form of the sulfur.

16. The slurry of claim 1 wherein said inorganic polishing particles are selected from the group consisting of colloidal silica, fumed silica and mixtures thereof.

17. The slurry of claim 15 wherein said allotropic form of the sulfur is selected from α -sulfur, β -sulfur, γ -sulfur, an oligomeric sulfur, a polymeric sulfur or mixtures thereof.

18. The slurry of claim 1 wherein said slurry is mixed via mechanical shear, hydrodynamic shear or combinations thereof.

19. A method of modifying a surface of a wafer suited for the fabrication of a semiconductor device comprising the steps of:

a) providing a wafer comprising a first material having a surface etched to form a pattern and a second material deposited over the surface of the first material;

b) contacting the second material of the wafer with polishing pad in the presence of the working slurry containing sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide and an additive selected from the group consisting of an activator, a phase transfer agents and mixtures thereof; and

c) relatively moving the wafer or polishing pad while the second material is in contact with a polishing pad until an exposed surface of the wafer is planar and comprises at least one area of exposed first material and one area of exposed second material.

20. The method of claim 19 wherein the slurry contains polishing particles.

21. The method of claim 19 wherein the polishing particles are fixed on the polishing pad.
22. The method of claim 19 wherein the polishing comprises a slurry and a polymer pad, the slurry comprising a plurality of loose abrasive particles dispersed in a slurry, the slurry contacting the metal layer of the wafer by the application of the polishing pad.
23. The method of claim 22 wherein the first material is a dielectric material and the second material is a conductive material.
24. The method of claim 22, wherein the wafer further comprises a barrier layer covering the dielectric material.
25. The method of claim 22, wherein the metal layer is a conductive metal selected from the group consisting of titanium, silver, aluminum, tungsten, tantalum, tantalum nitride, tungsten nitride, tantalum oxide, tungsten oxide, silica, copper, or alloys thereof.
26. The method of claim 22 wherein high impingement water is used to remove the abraded copper sulfide particles.
27. The method of claim 22 wherein ultrasonic radiation is used to assist in copper sulfide removal from the wafer surface.
28. The method of claim 19 wherein said sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide have a particle size distribution such that 95% of the particles have a diameter less than about 15 micrometers.
29. The method of claim 19 wherein said sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide have a particle size distribution such that 95% of the particles have a diameter less than about 2 micrometers.
30. The method of claim 19 wherein said sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide have a particle size distribution such that 95% of the particles have a diameter less than about 1 micrometer.

31. The method of claim 28 wherein said sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide having a particle size distribution such that 95% of the particles have a diameter less than about 15 micrometers is provided by wet milling, microfluidization or combinations thereof.
32. The method of method 19 wherein said sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide comprises particles having a diameter less than about 15 micrometers and particles having a diameter greater than about 15 micrometers.
33. The method of claim 19 wherein said sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide are encapsulated with an organic or inorganic material.
34. The method of claim 19 wherein said slurry containing sulfur compounds, including elemental sulfur capable of converting copper to copper sulfide and an additive selected from the group consisting of an activator, a phase transfer agents and mixtures thereof is mixed via mechanical shear, hydrodynamic shear or combinations thereof.

INTERNATIONAL SEARCH REPORT

International application No.

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A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C09K 3/14 (2009.01)

USPC - 51/298

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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USPC - 51/298

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
451/28 (keyword-limited:see terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Google, Google Patents, PUBWEST (PGPB, USPT, USOC, EPAB, JPAB)

Search Terms Used: Chemical mechanical polishing, (copper or Cu), (Sulfide and conversion), compounds, allotropic, (abrasive particles or polishing particles), additives, activator, abrasive, (silica or colloidal silica), ultrasonic, distribution, 95%, 15 micrometers.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6,911,393 B2 (NOSOWITZ et al.) 28 June 2005 (28.06.2005) col 8, ln 9 - ln 21, Abstract, col 6, ln 5 - ln 44, col 9, ln 41 - ln 43, claim 12 - claim 17, col 5, ln 15 - ln 26.	1-34
Y	US 6,121,143 A (MESSNER et al.) 19 September 2000 (19.09.2000) col 12, ln 66 to col 13, ln 7, col 18 - ln 12 - ln 22.	1-34

☐ Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

02 September 2009 (02.09.2009)

Date of mailing of the international search report

15 SEP 2009

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