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(54) **POLISHING SLURRY AND METHOD FOR CHEMICAL-MECHANICAL POLISHING OF COPPER**

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(57) **ABSTRACT**

The claimed invention involves a novel aqueous polishing slurry for chemical-mechanical polishing that is effective for polishing copper at high polish rates. The aqueous slurry according to the present invention comprises particles of MoO<sub>2</sub> in an oxidizing agent. A method for polishing copper by chemical-mechanical polishing includes contacting copper with a polishing pad and an aqueous slurry comprising particles of MoO<sub>2</sub> in an oxidizing agent.

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## POLISHING SLURRY AND METHOD FOR CHEMICAL-MECHANICAL POLISHING OF COPPER

### TECHNICAL FIELD

[0001] This invention relates to chemical-mechanical polishing processes in general and more specifically to a molybdenum oxide slurry and method for the chemical-mechanical polishing of copper.

### BACKGROUND

[0002] Chemical-mechanical polishing (CMP) is the term used to refer to a process that are used in semiconductor manufacture. As its name implies, the CMP process is typically used in semiconductor processing to polish (e.g., planarize) the surface of the semiconductor wafer. The CMP process is relatively new in that, until recently, conventional processes were sufficient with the comparatively low circuit densities involved. However, increases in circuit densities (e.g., the transition from wafers having 0.25 micron features to 0.18 micron features) have forced the need to develop new processes for planarizing the wafer, of which CMP has become favored. Similarly, the more recent shift away from aluminum interconnect technology to copper interconnect technology has further favored the use of CMP to polish (e.g., planarize) semiconductor wafers.

[0003] Briefly, the chemical-mechanical polishing (CMP) process involves scrubbing a semiconductor wafer with a pad in the presence of a chemically reactive slurry that contains abrasive particles. As its name implies, the polishing action of the chemical-mechanical polishing (CMP) process is both chemical and mechanical. Chemicals aid in material removal by modifying the surface film while abrasion between the surface particles, pad, and the modified film facilitates mechanical removal. It is believed that this synergistic interplay between the chemical and mechanical components in the process is the key to effective polishing of the CMP process.

[0004] While the CMP process is being increasingly used in semiconductor manufacturing processes, the CMP process remains poorly understood, and the exact mechanisms through which the process works have not been determined. For example, while certain parameters for the CMP process have been developed that are satisfactory for wafers utilizing aluminum interconnect technology, those same process parameters have not proven to be particularly satisfactory for use with wafers utilizing copper interconnect technology. One important requirement of a successful CMP slurry for copper is a high polish rate. High polish rates lead to shorter copper overburden polishing times.

### SUMMARY OF THE INVENTION

[0005] The following summary is provided as a brief overview of the claimed product and process. It shall not limit the invention in any respect, with a detailed and fully-enabling disclosure being set forth in the Detailed Description of Preferred Embodiments section. Likewise, the invention shall not be restricted to any numerical parameters, processing equipment, chemical reagents, operational conditions, and other variables unless otherwise stated herein.

[0006] The claimed invention involves a novel aqueous polishing slurry for chemical-mechanical polishing that is effective for polishing copper at high polish rates. The aqueous slurry according to the present invention comprises particles of  $\text{MoO}_2$  in an oxidizing agent.

[0007] Embodiments of slurries may contain  $\text{MoO}_2$  in amounts ranging from about 0.5% to about 10% by weight particles of  $\text{MoO}_2$  and the oxidizing agent may comprise ferric nitrate ( $\text{Fe}(\text{NO}_3)_3$ ), nitric acid ( $\text{HNO}_3$ ), potassium iodide (KI), potassium iodate ( $\text{KIO}_3$ ) and mixtures thereof. Additional oxidizing agents may include hydroxylamine hydrochloride ( $(\text{NH}_2\text{OH})\text{Cl}$ ) and potassium permanganate ( $\text{KMnO}_4$ ).

[0008] Embodiments of slurries according to the present invention may also be provided with an anionic surfactant comprising polyacrylic acid (PAA), a carboxylic acid or its salt, a sulfuric ester or its salt, a sulfonic acid or its salt, a phosphoric acid or its salt, a sulfosuccinic acid or its salt, and mixtures thereof. Other embodiments of slurries according to the present invention may be provided with a cationic surfactant comprising any one or a mixture of a primary amine or its salt, a secondary amine or its salt, a tertiary amine or its salt, and a quaternary amine or its salt.

[0009] Still yet other embodiments of aqueous slurries may be provided with a copper passivating agent which may comprise any one or a mixture of heterocyclic organic compounds including benzotriazole (BTA), triazole, and benzimidazole. Further embodiments of slurries may contain any combination of these surfactants and passivating agents.

[0010] Additional embodiments of slurries according to the present invention may also be provided with amounts of molybdenum sulfide ( $\text{MoS}_2$ ) as a lubricant. Aqueous slurries can optionally include acids or bases for adjusting the pH within an effective range of from about 1 to 14. Yet additional embodiments of slurries according to the invention may also be provided with supplemental metal oxide particles. Such supplemental metal oxide particles used in the aqueous slurry may comprise any one or a mixture of silica, ceria, alumina, zirconia, titania, magnesia, iron oxide, tin oxide, and germania.

[0011] The present invention also includes a novel method of polishing copper by chemical-mechanical polishing. The method of the present invention comprises polishing copper using a polishing pad and an aqueous slurry comprising  $\text{MoO}_2$  particles and an oxidizing agent.

[0012] Embodiments of slurries may contain  $\text{MoO}_2$  in amounts ranging from about 0.5% to about 10% by weight particles of  $\text{MoO}_2$  and the oxidizing agent may comprise any one or a mixture of ferric nitrate ( $\text{Fe}(\text{NO}_3)_3$ ), nitric acid ( $\text{HNO}_3$ ), potassium iodide (KI), or potassium iodate ( $\text{KIO}_3$ ). Additional oxidizing agents may comprise any one or a mixture of hydroxylamine hydrochloride ( $(\text{NH}_2\text{OH})\text{Cl}$ ) and potassium permanganate ( $\text{KMnO}_4$ ).

[0013] Embodiments of slurries according to the present invention may also be provided with an anionic surfactant comprising polyacrylic acid (PAA), a carboxylic acid or its salt, a sulfuric ester or its salt, a sulfonic acid or its salt, a phosphoric acid or its salt, a sulfosuccinic acid or its salt, and mixtures thereof. Other embodiments of slurries according to the present invention may be provided with a cationic

surfactant comprising any one or a mixture of a primary amine or its salt, a secondary amine or its salt, a tertiary amine or its salt, and a quaternary amine or its salt.

[0014] Still yet other embodiments of aqueous slurries may be provided with a copper passivating agent which may comprise any one or a mixture of heterocyclic organic compounds including benzotriazole (BTA), triazole, and benzimidazole. Further embodiments of slurries may contain any combination of these surfactants and passivating agents.

[0015] Embodiments of slurries according to the present invention may also be provided with amounts of molybdenum sulfide ( $\text{MoS}_2$ ) as a lubricant. Aqueous slurries can optionally include acids or bases for adjusting the pH within an effective range of from about 1 to 14. Yet additional embodiments of slurries according to the invention may also be provided with supplemental metal oxide particles. Such supplemental metal oxide particles used in the aqueous slurry may comprise any one or a mixture of silica, ceria, alumina, zirconia, titania, magnesia, iron oxide, tin oxide, and germania.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0016] Broadly described, embodiments of aqueous polishing slurries according to the present invention may comprise a molybdenum oxide ( $\text{MoO}_2$ ) polishing material and an oxidizing agent. The  $\text{MoO}_2$  polishing material may be present in an amount of about 0.5 to about 10 wt. %, such as about 1 to about 3 wt. %, and more preferably in an amount of about 3 wt. %. The molybdenum oxide polishing material may comprise fine particles of  $\text{MoO}_2$  having a mean particle size in the range of about 25 nanometers (nm) to about 1 micron, such as about 25 nanometers to about 560 nm, and more preferably about 50 to 200 nm, as measured by a Horiba laser scattering analyzer.

[0017] The  $\text{MoO}_2$  particles may be produced from a variety of molybdenum-containing precursor materials, such as, for example, ammonium molybdates and related compounds, as well as molybdenum oxides prepared from a variety of processes known in the art, wherein molybdenum precursors and products can be made in particles within the size ranges specified herein. Alternatively particles of  $\text{MoO}_2$  may be reduced in size to the ranges specified herein by any of a variety of milling methods known in the art, such as attrition milling assisted by the use of appropriate reagents.

[0018] By way of example, embodiments of slurries according to the present invention may utilize particles of  $\text{MoO}_2$  produced from a precursor material comprising nano-particles of  $\text{MoO}_3$ . Nano-particles of  $\text{MoO}_3$  are commercially available from the Climax Molybdenum Company of Ft. Madison, Iowa (US). Alternatively, nano-particles of  $\text{MoO}_3$  may be produced in accordance with the teachings provided in U.S. Pat. No. 6,468,497 B1, entitled "Method for Producing Nano-Particles of Molybdenum Oxide," which is hereby incorporated herein by reference for all that it discloses.

[0019] Regardless of whether the nano-particles of  $\text{MoO}_3$  are obtained commercially or manufactured in accordance with the teachings provided in U.S. Pat. No. 6,468,497 B1, identified above, the  $\text{MoO}_2$  particles comprising the polish-

ing material may be produced by heating nano-particles of  $\text{MoO}_3$  for a time sufficient to convert substantially all of the  $\text{MoO}_3$  to  $\text{MoO}_2$ . More specifically, the nano-particles of  $\text{MoO}_3$  may be heated in a reducing atmosphere (e.g., hydrogen) to a temperature in the range of about 400 to about 700° C. (550° C. preferred). Times may be in the range of about 30 to about 180 minutes, as may be required to reduce  $\text{MoO}_3$  to  $\text{MoO}_2$  in sufficient quantities. Heating may be accomplished in a rotary furnace, although other types of furnaces may be used. If necessary, the resulting  $\text{MoO}_2$  product may then be ground to produce an  $\text{MoO}_2$  polishing material having a mean particle diameter within the ranges specified herein. A particle classification step may optionally be used to ensure that the resulting  $\text{MoO}_2$  polishing material lacks particles that may cause damage during polishing.

[0020] The oxidizing agent may comprise any one or a mixture of ferric nitrate ( $\text{Fe}(\text{NO}_3)_3$ ), nitric acid ( $\text{HNO}_3$ ), potassium iodide (KI), and potassium iodate ( $\text{KIO}_3$ ). Ferric nitrate oxidizing agent may be present in concentrations ranging from about 0.05 to about 0.2 molar (M)  $\text{Fe}(\text{NO}_3)_3$ , such as about 0.1 to about 0.2M  $\text{Fe}(\text{NO}_3)_3$ , and more preferably in a concentration of about 0.2 M  $\text{Fe}(\text{NO}_3)_3$ . Nitric acid oxidizing agent may be present in amounts ranging from about 0.5 to about 2 wt. %  $\text{HNO}_3$ , such as about 1 to about 2 wt. %  $\text{HNO}_3$ , and more preferably in an amount of about 2 wt. %  $\text{HNO}_3$ . Potassium iodide oxidizing agent may be present in amounts ranging from about 0.5 to about 5 wt. % KI, such as about 1 to about 5 wt. % KI, and more preferably in an amount of about 3 wt. % KI. Potassium iodate oxidizing agent may be present in amounts ranging from about 1 to about 5 wt. %  $\text{KIO}_3$ , such as about 1 to about 3 wt. %  $\text{KIO}_3$ , and more preferably in an amount of about 3 wt. %  $\text{KIO}_3$ .

[0021] Additional oxidizing agents may comprise any one or a mixture of hydroxylamine hydrochloride ( $(\text{NH}_2\text{OH})\text{Cl}$ ) and potassium permanganate ( $\text{KMnO}_4$ ). Hydroxylamine hydrochloride oxidizing agent may be present in amounts ranging from about 1 to about 5 wt. %  $(\text{NH}_2\text{OH})\text{Cl}$ , such as about 2 to about 4 wt. %  $(\text{NH}_2\text{OH})\text{Cl}$ , and more preferably in an amount of about 3 wt. %  $(\text{NH}_2\text{OH})\text{Cl}$ . Potassium permanganate oxidizing agent may be present in amounts ranging from about 1 to about 5 wt. %  $\text{KMnO}_4$ , such as about 2 to about 4 wt. %  $\text{KMnO}_4$ , and more preferably in an amount of about 3 wt. %  $\text{KMnO}_4$ . However, the polishing rates with slurries containing hydroxylamine hydrochloride and potassium permanganate are generally lower than with the other oxidizing agents identified herein.

[0022] Embodiments of slurries according to the present invention may also be provided with an anionic surfactant or a cationic surfactant. The anionic surfactant used in the aqueous slurry may comprise any one or a mixture of polyacrylic acid (PAA), a carboxylic acid or its salt, a sulfuric ester or its salt, a sulfonic acid or its salt, a phosphoric acid or its salt, and a sulfosuccinic acid or its salt. The cationic surfactant used in the aqueous slurry may comprise any one or a mixture of a primary amine or its salt, a secondary amine or its salt, a tertiary amine or its salt, and a quaternary amine or its salt. Optionally, the aqueous slurry may be provided with a copper passivating agent which may comprise any one or a mixture of heterocyclic organic compounds including benzotriazole (BTA), triazole, and benzimidazole. Further, the slurry may contain any combination of these surfactants and passivating agents.

[0023] A preferred anionic surfactant is polyacrylic acid (PAA). A preferred cationic surfactant is cetyl pyridinium chloride (CPC). A preferred copper passivating agent is benzotriazole (BTA). The addition of PAA improved slurry dispersability and surface quality. It is believed that the addition of PAA modifies the surface charge of the molybdenum oxide particles such that interaction between the molybdenum oxide particles and copper is favorable, leading to an increase in the polish rate. Polyacrylic acid (PAA) surfactant may be present in amounts ranging from about 0.1 to about 4 wt. % PAA, such as about 0.5 to about 1 wt. % PAA, and more preferably in an amount of about 1 wt. % PAA. The cationic surfactant cetyl pyridinium chloride (CPC) may be present in amounts ranging from about 0.01 to about 1 wt. % CPC, such as about 0.05 to about 0.5 wt. % CPC, and more preferably in an amount of about 0.1 wt. % CPC. Benzotriazole (BTA) copper passivating agent may be present in concentrations ranging from about 0.5 to about 10 milli-molar (mM) BTA, such as about 1 to about 5 mM BTA, and more preferably in a concentration of about 1 mM BTA.

[0024] Embodiments of slurries according to the present invention may also be provided with amounts of molybdenum sulfide ( $\text{MoS}_2$ ) as a lubricant. It has been found that the addition of molybdenum sulfide particles increases the polish rate of copper for slurries containing  $\text{KIO}_3$  and PAA. Molybdenum sulfide particles may have mean diameters in the range of about 0.01 to about 1 micron. Molybdenum sulfide particles may be present in amounts ranging from about 0.1 to about 10 wt. %  $\text{MoS}_2$ , such as about 0.5 to about 5 wt. %  $\text{MoS}_2$ , and more preferably in an amount of about 1 wt. %  $\text{MoS}_2$ . Molybdenum sulfide particles having the size ranges herein are commercially available from the Climax Molybdenum Company of Ft. Madison, Iowa (US).

[0025] The pH of embodiments of slurries according to the present invention may be in the range of about 1 to about 14, such as a pH in the range of about 3 to about 7, and preferably having a pH of 4. The pH of embodiments of slurries according to the present invention may be adjusted by the addition of suitable acids (e.g., hydrochloric acid (HCl)) or bases (e.g., potassium hydroxide (KOH)), as would be known by persons having ordinary skill in the art.

[0026] Yet additional embodiments of polishing slurries according to the invention may also be provided with supplemental metal oxide particles. Such supplemental metal oxide particles used in the aqueous slurry may comprise any one or a mixture of silica, ceria, alumina, zirconia, titania, magnesia, iron oxide, tin oxide, and germania.

[0027] Embodiments of slurries according to the present invention exhibit high polish rates for copper when used in the CMP process. More particularly, when potassium iodate ( $\text{KIO}_3$ ) was used as an oxidizing agent in the molybdenum oxide slurries very high copper disk and copper film polish rates (e.g., up to ~1000 and 470 nm/min, respectively, were obtained, as detailed in the following examples. Addition of PAA enhanced the film polish rate to about 667 nm/min. Further, when molybdenum sulfide particles were added to slurries containing  $\text{KIO}_3$  and PAA, copper film polish rates of about 750 nm/min were obtained.

[0028] While polish rates with the  $\text{KIO}_3$ -based slurries of the present invention are high for copper, the post-polish surface of the copper tended to be covered with a thick,

uneven misty layer with roughness values as high as about 150 nm as measured by a non-contact optical profilometer. If the post-polish surface quality is desired to be higher, the CMP polishing step may be followed by a buffing step. In one embodiment, the buffing step involved additionally polishing the copper surface with a dilute suspension of  $\text{H}_2\text{O}_2$ , glycine, BTA, and colloidal silica in de-ionized water at a pH of 4. The advantage of using an  $\text{H}_2\text{O}_2$ -based buffing step is that  $\text{H}_2\text{O}_2$  reacts spontaneously with molybdenum oxide, thus removing residual amounts of molybdenum oxide that may remain on the surface. Very clean and smooth copper surfaces were obtained after subsequent buffing, some with roughness values as low as 0.35 nm as measured by a non-contact optical profilometer.

[0029] Polishing selectivity of one embodiment of a slurry of the present invention between Cu, Ta, and silicon oxide ( $\text{SiO}_2$ ) was determined to be 235:1:1 for Cu:Ta: $\text{SiO}_2$ , as presented in Example 24.

[0030] Examples 25 and 26 involve the addition of ethylene diamine tetra acetic acid (EDTA) to test the complexing ability of EDTA with copper ions. The polish rates for the two specified slurry compositions are presented in Table 5.

[0031] In order to provide further information regarding the invention, the following examples are provided. The examples present below are representative only and are not intended to limit the invention in any respect.

#### EXAMPLES 1-15

[0032] Slurries of examples 1-15 were used to polish a copper disk having a diameter of 1.25 inches. The CMP polisher was a Struers DAP® with an IC-1400, k-groove polishing pad. The carrier remained stationary (i.e., was not rotated). The rotation rate of the platen was 90 revolutions per minute (rpm). The down-force placed on the copper disk was 6.3 pounds per square inch (psi). The slurry flow rate was 60 ml/min. The amount of copper removed from the surface of the disk by CMP was determined by measuring the weight difference of the copper disk both before and after polishing, taking into consideration the density of the Cu material, the area of the disk that was polished, and the polishing time. This was then converted into the rate of removal in terms of nm of copper removed per minute.

[0033] The slurries of examples 1-10 all contained 3 wt. % molybdenum oxide ( $\text{MoO}_2$ ) in deionized water. The mean particle size of molybdenum oxide for examples 1-10 was 1 micron (1000 nm). The mean particle size of molybdenum oxide for examples 11-15 was 150 nm. Various amounts and types of oxidizing agents were added, as identified in Table 1. Example 11 contained 1.5 wt. %  $\text{MoO}_2$  with 3 wt. % hydroxylamine hydrochloride ( $(\text{NH}_2\text{OH})\text{Cl}$ ) as an oxidizing agent. Example 12 contained 1.5 wt. %  $\text{MoO}_2$  with 3 wt. % potassium permanganate ( $\text{KMnO}_4$ ) as the oxidizing agent. Examples 13-15 all contain 3 wt. %  $\text{KIO}_3$  with varying amounts of  $\text{MoO}_2$ , as noted. The pH of slurries for examples 1-15 was adjusted to 4.0 by the addition of hydrochloric acid (HCl) or potassium hydroxide (KOH). The slurry compositions and polishing rates for the copper disk are presented in Table 1.

TABLE 1

Example	Slurry Composition	Mean Particle Size (nm)	pH	Polish Rate (nm/min)
1	3% MoO <sub>2</sub> + 0.05 M Fe (NO <sub>3</sub> ) <sub>3</sub>	1000	4	69
2	3% MoO <sub>2</sub> + 0.1 M Fe (NO <sub>3</sub> ) <sub>3</sub>	1000	4	88
3	3% MoO <sub>2</sub> + 0.2 M Fe (NO <sub>3</sub> ) <sub>3</sub>	1000	4	230
4	3% MoO <sub>2</sub> + 0.5% HNO <sub>3</sub>	1000	4	348
5	3% MoO <sub>2</sub> + 1% HNO <sub>3</sub>	1000	4	221
6	3% MoO <sub>2</sub> + 2% HNO <sub>3</sub>	1000	4	353
7	3% MoO <sub>2</sub> + 3% KI	1000	4	157
8	3% MoO <sub>2</sub> + 1% KIO <sub>3</sub>	1000	4	123
9	3% MoO <sub>2</sub> + 2% KIO <sub>3</sub>	1000	4	345
10	3% MoO <sub>2</sub> + 3% KIO <sub>3</sub>	1000	4	1014
11	1.5% MoO <sub>2</sub> + 3% (NH <sub>2</sub> OH) Cl	150	4	68
12	1.5% MoO <sub>2</sub> + 3% KMnO <sub>4</sub>	150	4	31
13	1% MoO <sub>2</sub> + 3% KIO <sub>3</sub>	150	4	169
14	2% MoO <sub>2</sub> + 3% KIO <sub>3</sub>	150	4	524
15	3% MoO <sub>2</sub> + 3% KIO <sub>3</sub>	150	4	862

## EXAMPLES 16-18

**[0034]** Slurries of examples 16-18 were used to polish a copper film deposited on a silicon substrate by sputter deposition. The copper film had a diameter of 6 inches. The CMP polisher was a Westech Model 372 with an IC-1400, k-groove polishing pad. The carrier was rotated at a rate of 40 rpm. The platen was rotated at 40 rpm. The down-force placed on the copper film was 6 pounds per square inch (psi). The slurry flow rate was set at 200 ml/min.

**[0035]** The amount of copper removed from the surface of the silicon substrate by CMP was determined by measuring the sheet resistance of the Cu film both before and after polishing at 17 points spread across the film utilizing a home-made paper mask and a 4-point probe. Sheet resistance was measured at the same points on the film before and after polishing. The measured sheet resistances both before and after polishing were then converted to respective film thicknesses before and after polishing based on the resistivity of the Cu material, the current applied, and the voltage across the 4-point probe. The difference between the starting and final thicknesses as 17 points were calculated, an average thickness loss was obtained which was then divided by the polish time to give the polish rate in nm/min.

**[0036]** The slurries all contained 3 wt. % molybdenum oxide (MoO<sub>2</sub>) in deionized water and with a potassium iodate (KIO<sub>3</sub>) oxidizing agent present in an amount of 3 wt. %. The mean particle size of the molybdenum oxide for examples 16-18 was 1 micron (1000 nm). Example 17 added 1 wt. % PAA to the slurry. Example 18 added 1 wt. % PAA and 1 wt. % molybdenum sulfide (MoS<sub>2</sub>) to the slurry. The pH of the slurries of examples 16-18 was adjusted to 4.0 by the addition of hydrochloric acid (HCl) or potassium hydroxide (KOH). The slurry compositions and polishing rates for the copper film are presented in Table 2.

TABLE 2

Example	Slurry Composition	Mean Particle Size (nm)	pH	Polish Rate (nm/min)
16	3% MoO <sub>2</sub> + 3% KIO <sub>3</sub>	1000	4	471
17	3% MoO <sub>2</sub> + 3% KIO <sub>3</sub> + 1% PAA	1000	4	667
18	3% MoO <sub>2</sub> + 3% KIO <sub>3</sub> + 1% PAA + 1% MoS <sub>2</sub>	1000	4	750

## EXAMPLES 19-23

**[0037]** Slurries of examples 19-23 were used to polish a copper film deposited on a silicon substrate by sputter deposition. The copper film had a diameter of 6 inches. The CMP polisher was a Westech Model 372 with an IC-1400, k-groove polishing pad. The carrier was rotated at a rate of 75 rpm. The platen was also rotated at 75 rpm. The down-force placed on the copper film was 4 pounds per square inch (psi). The slurry flow rate was set at 200 ml/min.

**[0038]** The amount of copper removed from the surface of the silicon substrate by CMP was determined by measuring the sheet resistance of the Cu film both before and after polishing at 17 points spread across the film utilizing a home-made paper mask and a 4-point probe. Sheet resistance was measured at the same points on the film before and after polishing. The measured sheet resistances both before and after polishing were then converted to respective film thicknesses before and after polishing based on the resistivity of the Cu material, the current applied, and the voltage across the 4-point probe. The difference between the starting and final thicknesses as 17 points were calculated, an average thickness loss was obtained which was then divided by the polish time to give the polish rate in nm/min.

**[0039]** The slurries all contained 3 wt. % molybdenum oxide (MoO<sub>2</sub>) in deionized water and with a potassium iodate (KIO<sub>3</sub>) oxidizing agent present in an amount of 3 wt. %. The mean particle diameter of the molybdenum oxide for examples 19-23 was 150 nm. Example 20 added 1 mM benzotriazole (BTA) to the slurry. Example 21 added 1 wt. % polyacrylic acid (PAA) to the slurry. Example 22 added 0.1 wt. % cetyl pyridinium chloride (CPC) to the slurry. Example 23 added 2 wt. % PAA and 1 mM BTA to the slurry. The pH of the slurries of examples 19-23 was adjusted to 4.0 by the addition of hydrochloric acid (HCl) or potassium hydroxide (KOH). The slurry compositions and polishing rates for the copper film are presented in Table 3.

TABLE 3

Example	Slurry Composition	Mean Particle Size (nm)	pH	Polish Rate (nm/min)
19	3% MoO <sub>2</sub> + 3% KIO <sub>3</sub>	150	4	695
20	3% MoO <sub>2</sub> + 3% KIO <sub>3</sub> + 1 mM BTA	150	4	471
21	3% MoO <sub>2</sub> + 3% KIO <sub>3</sub> + 1% PAA	150	4	997
22	3% MoO <sub>2</sub> + 3% KIO <sub>3</sub> + 0.1% CPC	150	4	913

TABLE 3-continued

Example	Slurry Composition	Mean Particle Size (nm)	pH	Polish Rate (nm/min)
23	3% MoO <sub>2</sub> + 3% KIO <sub>3</sub> + 2% PAA + 1 mM BTA	150	4	660

## EXAMPLE 24

**[0040]** Silicon wafers (6 inch diameter) having a 0.3 micron Ta layer deposited by sputter deposition and wafers having a 1 micron SiO<sub>2</sub> layer applied by thermal oxidation were separately polished with a polishing slurry. The amount of copper and Ta removed was determined using a four-point probe, and SiO<sub>2</sub> removed from the surface of the silicon wafer by CMP was measured using an optical interferometer, in order to determine the rate of removal in terms of nm of material removed per minute.

**[0041]** The slurry utilized comprised 3 wt % molybdenum oxide (MoO<sub>2</sub>) in deionized water with potassium iodate (KIO<sub>3</sub>) oxidizing agent present in an amount of 3 wt. %. The mean particle size of the molybdenum oxide for example 24 was 1 micron (1000 nm). The CMP polisher was a Westech Model 372 with an IC-1400, k-groove polishing pad. The carrier was rotated at a rate of 40 rpm. The platen was also rotated at 40 rpm. The down-force placed on the copper film was 6 pounds per square inch (psi). The slurry flow rate was 200 ml/min. The slurry composition and polishing rates for Cu, Ta, and SiO<sub>2</sub> are presented in Table 4.

TABLE 4

Example	Slurry Composition	Cu Polish Rate (nm/min)	Ta Polish Rate (nm/min)	SiO <sub>2</sub> Polish Rate (nm/min)
24	3% MoO <sub>2</sub> + 3% KIO <sub>3</sub>	471	2	2

## EXAMPLES 25 and 26

**[0042]** Slurries of examples 25 and 26 were used to polish a copper disk having a diameter of 1.25 inches. The CMP polisher was a Struers DAP® with an IC-1400, k-groove polishing pad. The carrier remained stationary (i.e., was not rotated). The rotation rate of the platen was 90 revolutions per minute (rpm). The down-force placed on the copper disk was 6.3 pounds per square inch (psi). The slurry flow rate was 60 ml/min. The amount of copper removed from the surface of the disk by CMP was determined by measuring the weight difference of the copper disk both before and after polishing, taking into consideration the density of the Cu material, the area of the disk that was polished, and the polishing time. This was then converted into the rate of removal in terms of nm of copper removed per minute.

**[0043]** The slurries of examples 25 and 26 all contained 3 wt. % molybdenum oxide (MoO<sub>2</sub>) in deionized water. The mean particle size of molybdenum oxide for both examples 25 and 26 was 1 micron (1000 nm). Various amounts and types of oxidizing agents were added, as identified in Table 5. Slurries of both examples included the addition of 1 wt.

% ethylene diamine tetra acetic acid (EDTA) to test the complexing ability of EDTA with copper ions. The slurry compositions and polishing rates for the copper disk are presented in Table 5.

TABLE 5

Example	Slurry Composition	Mean Particle Size (nm)	pH	Polish Rate (nm/min)
25	3% MoO <sub>2</sub> + 3% KI + 1% EDTA	1000	4	146
26	3% MoO <sub>2</sub> + 3% KI + 1% KMnO <sub>4</sub> + 1% EDTA	1000	4	259

**[0044]** In conclusion, the claimed product and process collectively represent an important development in CMP technology. The product and process discussed above are novel, distinctive, and highly beneficial from a technical and utilitarian standpoint. Having herein set forth preferred embodiments of the present invention, it is anticipated that suitable modifications can be made thereto which will nonetheless remain within the scope of the invention. The invention shall therefore only be construed in accordance with the following claims:

1. An aqueous polishing slurry for chemical-mechanical polishing, comprising particles of MoO<sub>2</sub> and an oxidizing agent.
2. The aqueous polishing slurry of claim 1, wherein said polishing slurry comprises about 0.5% to about 10% by weight particles of MoO<sub>2</sub>.
3. The aqueous polishing slurry of claim 1, wherein said polishing slurry comprises about 1% to about 3% by weight particles of MoO<sub>2</sub>.
4. The aqueous polishing slurry of claim 1, wherein said polishing slurry comprises about 3% by weight particles of MoO<sub>2</sub>.
5. The aqueous polishing slurry of claim 1, wherein the particles of MoO<sub>2</sub> have a mean particle size in the range of about 25 nanometers to about 1 micron.
6. The aqueous polishing slurry of claim 1, wherein the particles of MoO<sub>2</sub> have a mean particle size in the range of about 25 nanometers to about 560 nanometers.
7. The aqueous polishing slurry of claim 1, wherein the particles of MoO<sub>2</sub> have a mean particle size in the range of about 50 nanometers to about 200 nanometers.
8. The aqueous polishing slurry of claim 1, wherein said oxidizing agent comprises one or more selected from the group consisting of ferric nitrate, nitric acid, potassium iodide, and potassium iodate.
9. The aqueous polishing slurry of claim 1, wherein said oxidizing agent comprises one or more selected from the group consisting of hydroxylamine hydrochloride and potassium permanganate.
10. The aqueous polishing slurry of claim 1, wherein said oxidizing agent is potassium iodate.
11. The aqueous polishing slurry of claim 1, further comprising an acid or a base for adjusting the pH of said polishing slurry within the range of from about 1 to about 14.
12. The aqueous polishing slurry of claim 1, further comprising an acid or a base for adjusting the pH of said polishing slurry within the range of from about 3 to about 7.

13. The aqueous polishing slurry of claim 1, further comprising an acid or a base for adjusting the pH of said polishing slurry to about 4.

14. The aqueous polishing slurry of claim 1, wherein said polishing slurry further comprises an anionic surfactant.

15. The aqueous polishing slurry of claim 14, wherein said anionic surfactant comprises one or more selected from the group consisting of polyacrylic acid, a carboxylic acid or its salt, a sulfuric ester or its salt, a sulfonic acid or its salt, a phosphoric acid or its salt, and a sulfosuccinic acid or its salt.

16. The aqueous polishing slurry of claim 14, wherein said anionic surfactant is polyacrylic acid.

17. The aqueous polishing slurry of claim 1, wherein said polishing slurry further comprises a cationic surfactant.

18. The aqueous polishing slurry of claim 17, wherein said cationic surfactant comprises one or more selected from the group consisting of a primary amine or its salt, a secondary amine or its salt, a tertiary amine or its salt, and a quaternary amine or its salt.

19. The aqueous polishing slurry of claim 17, wherein said cationic surfactant is cetyl pyridinium chloride.

20. The aqueous polishing slurry of claim 1, further comprising a copper passivating agent.

21. The aqueous polishing slurry of claim 20, wherein said copper passivating agent comprises a heterocyclic organic compound.

22. The aqueous polishing slurry of claim 20, wherein the copper passivating agent comprises one or more selected from the group consisting of benzotriazole, triazole, and benzimidazole.

23. The aqueous polishing slurry of claim 1 further comprising supplemental metal oxide particles.

24. The aqueous polishing slurry of claim 23, wherein said supplemental metal oxide particles comprise one or more selected from the group consisting of silica, ceria, alumina, zirconia, titania, magnesia, iron oxide, tin oxide, and germania.

25. The aqueous polishing slurry of claim 1, wherein said polishing slurry further comprises molybdenum sulfide particles.

26. The aqueous polishing slurry of claim 1, wherein said polishing slurry further comprises about 0.1% to about 10% by weight molybdenum sulfide particles.

27. The aqueous polishing slurry of claim 1, wherein said polishing slurry further comprises about 0.5% to about 5% by weight molybdenum sulfide particles.

28. The aqueous polishing slurry of claim 1, wherein said polishing slurry further comprises about 1% by weight molybdenum sulfide particles.

29. The aqueous polishing slurry of claim 1, wherein said slurry further comprises ethylene diamine tetra acetic acid.

30. A method for producing MoO<sub>2</sub>, comprising:

providing a supply of MoO<sub>3</sub>;

heating said supply of MoO<sub>3</sub> in a reducing atmosphere to a temperature in the range of about 400° C. to about 700° C. for a time in the range of about 30 minutes to about 180 minutes.

31. The method of claim 30, wherein said reducing atmosphere comprises hydrogen.

32. A method for polishing copper by chemical-mechanical polishing comprising polishing copper using a polishing pad and an aqueous slurry comprising MoO<sub>2</sub> and an oxidizing agent.

33. The method of claim 32, wherein said slurry comprises about 0.5% to about 10% by weight particles of MoO<sub>2</sub>.

34. The method of claim 32, wherein said slurry comprises about 1% to about 3% by weight particles of MoO<sub>2</sub>.

35. The method of claim 32, wherein said slurry comprises about 3% by weight particles of MoO<sub>2</sub>.

36. The method of claim 32, wherein the particles of MoO<sub>2</sub> have a mean particle size in the range of about 25 nanometers to about 1 micron.

37. The method of claim 32, wherein the particles of MoO<sub>2</sub> have a mean particle size in the range of about 25 nanometers to about 560 nanometers.

38. The method of claim 32, wherein the particles of MoO<sub>2</sub> have a mean particle size in the range of about 50 nanometers to about 200 nanometers.

39. The method of claim 32, wherein said oxidizing agent comprises one or more selected from the group consisting of ferric nitrate, nitric acid, potassium iodide, and potassium iodate.

40. The method of claim 32, wherein said oxidizing agent comprises one or more selected from the group consisting of hydroxylamine hydrochloride and potassium permanganate.

41. The method of claim 32, wherein said oxidizing agent is potassium iodate.

42. The method of claim 32, further comprising an acid or a base for adjusting the pH of said slurry within the range of from about 1 to about 14.

43. The method of claim 32, further comprising an acid or a base for adjusting the pH of said slurry within the range of from about 3 to about 7.

44. The method of claim 32, further comprising an acid or a base for adjusting the pH of said slurry to about 4.

45. The method of claim 32, wherein said slurry further comprises an anionic surfactant.

46. The method of claim 45, wherein said anionic surfactant comprises one or more selected from the group consisting of polyacrylic acid, a carboxylic acid or its salt, a sulfuric ester or its salt, a sulfonic acid or its salt, a phosphoric acid or its salt, and a sulfosuccinic acid or its salt.

47. The method of claim 45, wherein said anionic surfactant is polyacrylic acid.

48. The method of claim 32, wherein said polishing slurry further comprises a cationic surfactant.

49. The method of claim 48, wherein said cationic surfactant comprises one or more selected from the group consisting of a primary amine or its salt, a secondary amine or its salt, a tertiary amine or its salt, and a quaternary amine or its salt.

50. The method of claim 48, wherein said cationic surfactant is cetyl pyridinium chloride.

51. The method of claim 32, further comprising a copper passivating agent.

52. The method of claim 51, wherein said copper passivating agent comprises a heterocyclic organic compound.

53. The method of claim 51, wherein the copper passivating agent comprises one or more selected from the group consisting of benzotriazole, triazole, and benzimidazole.

54. The method of claim 32 further comprising supplemental metal oxide particles.

**55.** The aqueous polishing slurry of claim 54, wherein said supplemental metal oxide particles comprise one or more selected from the group consisting of silica, ceria, alumina, zirconia, titania, magnesia, iron oxide, tin oxide, and germania.

**56.** The method of claim 32, wherein said slurry further comprises molybdenum sulfide particles.

**57.** The method of claim 32, wherein said slurry further comprises about 0.1% to about 10% by weight molybdenum sulfide particles.

**58.** The method of claim 32, wherein said slurry further comprises about 0.5% to about 5% by weight molybdenum sulfide particles.

**59.** The method of claim 32, wherein said slurry further comprises about 1% by weight molybdenum sulfide particles.

**60.** The method of claim 32, further comprising additionally polishing the copper with a dilute suspension of H<sub>2</sub>O<sub>2</sub>, glycine, BTA, and colloidal silica in de-ionized water at a pH of 4.

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