# SLURRY COMPOSITION FOR USE IN CHEMICAL MECHANICAL POLISHING OF METAL WIRING

## Technical Field

The present invention relates, in general, to a slurry composition for use in chemical mechanical polishing(CMP) processes in manufacturing semiconductor devices, in detail, to a CMP slurry composition for planarization of tungsten layer of device wafers.

## Background Art

Metals including tungsten have diverse applicability in manufacturing integrated circuits. For example, metal layers can be formed to interconnect numerous conductive devices positioned on a siliconwafer or to constitute them. Currently, integrated circuits are produced by mounting appropriate devices such as a diode and a transistor on and/or in a siliconwafer. At this time, processes for forming separate layers of insulating material and conductive material throughout the surface of the device are repeated. In an integrated circuit, characteristics of a contact hole or via depend on the nature of the insulating material, and the via is filled with conductive materials so as to provide a vertical contact that penetrates the insulating material and contacts appropriate parts of the devices mounted on the

wafer. While aluminum is useful as a wiring material, it is inadequate to fill the inside of a via completely. Typically, a via is filled with tungsten that can be adapted to a CVD(chemical vapor deposition) process. In the course of chemical vapor deposition, tungsten not only fills the via also covers the surface of the insulating layer. Following the elimination of the excess of tungsten, aluminum wiring is then formed on the dielectric layer and the via.

Previously, a RIE(reactive ion etching) process was employed in the tungsten-elimination step in conventional semiconductor processes. However, the RIE process has critical shortcomings in that it is apt to overetch the tungsten layer to partially etch even the tungsten in the via, resulting in poor contact with the aluminum wiring formed on the tungsten layer. Furthermore, any tungsten particles remaining on the wafer can cause fatal inferiority in the resulting semiconductor integrated circuit. It is the CMP(chemical mechanical polishing) process that has been developed to solve these problems with the RIE process.

The CMP process has come to be introduced in the art according to the increase of integrity and the number of layers of the semiconductor integrated circuits. In the CMP process, a semiconductor wafer is subjected to orbital movement combining rotation and translation while contacted with a polishing pad made of polyurethane and with a slurry composition comprising abrasives and

various other compounds, to planarize the surface of the wafer. Generally, slurry compositions used in such CMP process(hereinafter, referred to as 'CMP slurry') provides both chemical and mechanical polishing effects, while etchants, oxidants, acids, and dispersing agents being in charge of the chemical polishing function and abrasives, micro-particles of metal oxides being in charge of the mechanical polishing function. These two polishing functions allow any protrusion of the outer surface of the wafer to be selectively etched and polished, resulting in the best planarization of the wafer.

According to the polishing substrate, CMP slurry can be classified into oxide-polishing slurry for insulating layers such as $SiO_2$ layer and metal-polishing slurry for metal layers such as tungsten or aluminum layer. These two classes of CMP slurry are discriminated in the components exerting the chemical polishing function.

Meanwhile, the conventional metal-polishing CMP slurry has the typical problems represented by the oxide erosion due to the difference of polishing rate among a metal, a barrier metal and a dielectric layer, and the corrosion due to the excessive etch of metal layers by oxidant ingredients. If the erosion or the corrosion occurs during CMP process, contact with another metal layer deposited on the polished metal layer comes to be poor, so that the resulting semiconductor integrated circuit may not work normally. These problems are

considered to arise mainly from the excessive oxidizing power of the oxidants contained in the polishing slurry. Up to date, polishing rate required for the conventional semiconductor processes has been accomplished primarily by increasing either the amount or the strength of oxidants added to a CMP slurry. Consequently, oxide erosion, corrosion, pit, dishing and so on were inevitably caused. Such oxide erosion and corrosion are schematically illustrated in Figs. 1a and 1b, respectively.

Moreover, a metal CMP slurry is prepared in an acidic condition for the purpose of vigorous polishing of tungsten, and at such low pH usually decreases the dispersability of abrasive particles, which results in significant deterioration of the reproducibility of polishing performance of a slurry.

## Summary of the Invention

The present invention concerns the discovery that the addition of a propylenediaminetetraacetate-metal complex and carboxylic acid to a non-selective, metal CMP slurry containing a little amount of peroxide and inorganic acid as oxidants can considerably improve the polishing rate, the within-wafer nonuniformity, and the wafer-to-wafer nonuniformity, as well as the dispersion stability of the slurry.

The present invention features a slurry composition

for use in chemical mechanical polishing of metal, the composition essentially consisting of a peroxide, an inorganic acid, a propylenediaminetetraacetate-metal complex, a carboxylic acid, and a metal oxide powder.

In a preferred embodiment of the present invention, a CMP slurry composition is prepared by dispersing in de-ionized water (i) a peroxide and an inorganic acid that act as a mild oxidant in combination, (ii) a metal complex containing propylenediaminetetraacetate ligand that prevents abraded tungsten oxide particles from the re-adhesion to the polished surface and improves the dispersion stability, (iii) a carboxylic acid that is helpful in improving reproducibility of polishing performance and dispersion stability, and (iv) a metal oxide powder that acts as an abrasive.

All of the above features and other features of the present invention will be successfully achieved from the present invention described in the following.

## Brief Description of the Drawings

Figs. 1a and 1b are schematic representations illustrating the oxide erosion and the corrosion, respectively, in CMP process of a metal layer.

Fig. 2 is a schematic representation illustrating the working mechanism of PDTA-Fe in W-CMP process using a slurry composition according to the present invention.

Fig. 3 is a graph illustrating the dependence of polishing rate on the added amount of PDTA-Fe.

Fig. 4 is a graph illustrating the dependence of polishing reproducibility on the added amount of malic acid.

## Disclosure of the Invention

In the present invention, as an oxidant for oxidizing metal substrate to be polished are preferred peroxides such as hydrogen peroxide, benzoyl peroxide, calcium peroxide, barium peroxide and sodium peroxide, and most preferably is used hydrogen peroxide considering oxidizing power and dispersion stability of the resulting slurry. Hydrogen peroxide has a relatively high oxidation potential, but oxidation rate is so low as to avoid the various problems with a strong oxidant unless it is not used in an excessive amount. Preferably, the slurry composition of the present invention contains 0.5~5wt% of the peroxide.

To complement the oxidizing power of the slurry, at least one inorganic acid is used in addition to the peroxide. Preferable inorganic acid can be exemplified by nitric acid, sulfuric acid, hydrochloric acid and phosphoric acid. Regarding the surface contamination after polishing, nitric acid is most preferred. In the present invention, the inorganic acid also functions as a pH-controlling agent to facilitate the oxidation of

tungsten. The content of inorganic acid in a slurry composition of the present invention is preferably 0.001~5.0wt%, more preferably 0.001~3.0wt%.

In the case that these two types of oxidant, i.e., the peroxide and the inorganic acid, are added over the upper limits of the above mentioned ranges, respectively, the oxide erosion, corrosion, pit, dishing and so on are likely to occur, and in the opposite case, desired polishing rate can not be accomplished.

Typically, CMP slurry compositions comprising the small amount of mild oxidants such as peroxide and inorganic acid can polish a metal layer and a barrier layer(primarily, a Ti/TiN layer) at sufficiently similar rates to prevent oxide erosion, but they would be improper to the conventional semiconductor processes due to the excessively low polishing rate. Though the addition of excessive oxidants could improve the polishing rate, it would cause various problems including the oxide erosion and the corrosion and further make the handling of the slurry difficult because of the strong acidity. Alternative to this approach, we employ specific metal complexes to efficiently achieve the polishing rate required for semiconductor processes. The metal complexes consists of a propylenediaminetetraacetate(PDTA) ligand and a metal(M) atom, wherein bond energy of O-M is lower than that of O-W. Hereinafter, such metal complexes are referred to as 'PDTA-M complex', or shortly 'PDTA-M'.

The probable mechanism by which the PDTA-M complex enhances the polishing rate could be explained as follows: the PDTA ligand forms a complex with tungsten oxide, WxOy, which was abraded from an oxidized tungsten layer during CMP process, and removes them from the reaction system, facilitating the oxidation reaction of the tungsten layer. Usually, however powerful oxidant may be used, it cannot overcome the decrease of polishing rate resulted from the accumulation of abraded metal oxide according to the progress of polishing, because the metal oxide inhibits the polishing by re-adhering onto the surface of the metal layer to be polished. The present invention aims to solve this re-adhesion problem. The PDTA ligand is a multidentate ligand, which has four ligand atoms and thus easily forms a chelate, PDTA-M. Advantageously, by selecting the metal atom so that the bond energy of O-M is lower than that of O-W, the PDTA-M complex can be spontaneously converted into PDTA-W complex during polishing process. For example, in the case of PDTA-Fe complex, the bond energy of O-Fe is 93.3kcal/mol while that of O-W being 160kcal/mol, and therefore the Fe atom coordinated to the PDTA ligand can be easily replaced with a W atom, that is, the PDTA-Fe complex is converted into a PDTA-W complex. Thus, by use of the PDTA-M complex, the re-adhesion of tungsten oxide is efficiently blocked, and therefore the reproducibility of polishing performance including polishing rate as well as selectivity are also improved.

While PDTA-Fe complex are most preferable in terms of the cost and the efficiency of absorption of the polished metal oxide, any metal atom can be substituted for Fe atom so long as it can form coordination bonds with the PDTA ligand and binds to oxygen atom more weakly than tungsten atom does. Non-limiting examples of such PDTA-metal complex include PDTA-Ni and PDTA-Co. Figure 2 schematically illustrates the working mechanism of PDTA-Fe complex during polishing of a tungsten layer using a slurry composition of the present invention.

Moreover, the PDTA-M complex improves the storage stability of a slurry composition of the present invention so that the polishing performance represented by scratch and polishing rate is reproducible after a long lapse of time. Where silica powder is added to a slurry composition as an abrasive, the dispersability of silica is certain to significantly decrease at an acidic pH required for usual metal polishing processes because the isoelectric point of silica has the smallest absolute value over pH 2~4. Therefore, as time lapses, re-coagulation of the silica particles progresses spontaneously to form macro-aggregates, resulting in precipitation and scratch. The PDTA-M complex prevents such coagulation of abrasive particles including silica so that the long-term storage stability of a slurry composition of the present invention is enhanced.

To a slurry composition of the present invention is preferably added the PDTA-M complex in an amount of

0.001~0.5wt%, more preferably 0.05~0.3wt%. If excessive PDTA-M complex is added, metallic impurities increase in a slurry composition and thus the reliability of the resulting semiconductor products would be deteriorated. On the other hand, if the PDTA-M complex is deficient, the efficiency of capturing tungsten oxide as well as of stabilizing dispersability of abrasives declines.

Where hydrogen peroxide is used as an oxidant as in the present invention, the oxidizing power of a slurry composition becomes lower depending on time due to the decomposition of hydrogen peroxide into $O_2$ and $H_2O$. Based on this observation, we use at least one carboxylic acid having one or more carboxylic groups to further enhance the reproducibility of polishing performance and the storage stability of a slurry composition of the present invention. Non-limiting examples of such carboxylic acid include acetic acid, citric acid, glutaric acid, glycolic acid, formic acid, lactic acid, malic acid, maleic acid, oxalic acid, phthalic acid, succinic acid, and tartaric acid, while malic acid being most preferred. The content of carboxylic acid in a slurry composition of the present invention is preferably 0.1~10wt%, more preferably 0.1~2wt%. Excessive carboxylic acid over 10wt% may rather reduce the dispersion stability of a slurry composition, while the desired effect cannot be obtained with an insufficient amount of carboxylic acid.

In the present invention, as an abrasive for polishing tungsten film oxidized by the oxidants as

described above can be used a powder of metal oxide such as silica, alumina, ceria and titania, and the silica is most preferred because it gives the excellent dispersability and the least possibility of scratches. Preferably, the metal oxide powder amounts to 0.1~10wt%, more preferably 1~7wt% in a slurry composition of the present invention. If it is over 10wt%, the dispersion stability of a slurry composition becomes poor and furthermore the scratches and the oxide erosion may occur, and if it is below 0.1wt%, the polishing rate appropriate to the usual semiconductor processes cannot be achieved.

The present invention can be more clearly understood with referring to the following examples. It should be understood that the following examples are not intended to restrict the scope of the present invention in any manner. The polishing performance of the respective slurry compositions obtained from each example was estimated as follows:

- Polisher: Model No. 6EC(STRASBAUGH, USA)
- Polishing Condition:
  - Pad type: IC1400/SubaIV Stacked(Rodel, USA)
  - Platen speed: 75rpm
  - Quill speed: 35rpm
  - Pressure: 4psi
  - Back pressure: 0psi
  - Temperature: 25°C
  - Slurry flow: 250ml/min

- Polishing Substrates: As test wafers were used W blanket wafers, each of which had been prepared by sequentially depositing 1,000Å HTO layer, 1,000Å TiN layer and 10,000Å W layer on a poly-Si wafer.

**Example 1: Dependence of polishing rate on the added amount of PDTA-Fe**

To a flask were added 50g of Aerosil 90G(Degussa AG, Germany), 917.5g of de-ionized water, 10.0g of malic acid, 0.3g of nitric acid, and 20.0g of hydrogen peroxide, and then stirred at 2,000rpm for 2 hours, followed by high-pressure dispersion under the pressure of 1,200psi. The resulting slurry was filtered through a 1μm filter, and 0.0g, 0.02g, 4.0g or 10.0g of PDTA-Fe was added thereto, to provide polishing slurry compositions. Polishing of the test wafers(W blanket wafers) was conducted using the respective slurry compositions for 2 minutes under the condition as described above. The results are set forth in Table 1 and Figure 3.

**Table 1**

| Slurry | PDTA-Fe | Polishing Rate for W* | Polishing Rate for P-TEOS** |
|---|---|---|---|
| I | 0.0g | 863 Å/min | 48 Å/min |
| II | 0.02g | 1,006 Å/min | 53 Å/min |
| III | 4.0g | 2,445 Å/min | 87 Å/min |
| IV | 10.0g | 2,718 Å/min | 105 Å/min |

* W: tungsten

** P-TEOS: poly-tetraorthosilicate

**Example 2: Effect of PDTA-Fe on the oxide erosion and the corrosion**

The slurry III of the above Example 1, and other slurry compositions having the same composition as the slurry III with the exception that $Fe(NO_3)_3$ or $KIO_3$ was substituted for PDTA-Fe were used, respectively, for polishing patterned wafers having the line width of 0.2μm under the condition as described above. The results are set forth in Table 2.

**Table 2**

| Sample | PDTA-Fe | $Fe(NO_3)_3$ | $KIO_3$ | Polishing Rate for W | Oxide Erosion | Corrosion Rate |
|---|---|---|---|---|---|---|
| 1 | 4.0g | 0.0g | 0.0g | 2,486 Å/min | 85 Å | 10 Å/min |
| 2 | 0.0g | 15.0g | 0.0g | 2,445 Å/min | 460 Å | 120 Å/min |
| 3 | 0.0g | 0.0g | 20.0g | 2,718 Å/min | 328 Å | 150 Å/min |

**Example 3: Dependence of reproducibility of polishing performance on the added amount of malic acid**

A series of slurry compositions was prepared according to the same manner as in the preparation of the slurry III of the above Example 1 with the exception of varying the amount of malic acid. Polishing of test wafers(W blanket wafers) was conducted using the respective slurry compositions for 2 minutes under the condition as described above. The results are shown in Figure 4.

**Example 4: Effect of PDTA-Fe on the dispersion stability**

**of a slurry composition**

The slurry III of the above Example 1, and a control slurry composition having the same composition as the slurry III with the exception of lack of PDTA-Fe were subjected to the polishing test as described above on day 0, 30, 60, and 120 after the preparation thereof. The results are set forth in Table 3 together with the mean particle size of the respective slurry compositions, which was measured by means of ELS 8000(Ostuka Co., Japan).

**Table 3**

| Sample | PDTA-Fe | Day after Preparation | Polishing Rate for W | Mean Particle Size |
|---|---|---|---|---|
| 1 | 0.0g | 0 | 863 Å/min | 185 nm |
| 2 | 4.0g | 0 | 2,445 Å/min | 185 nm |
| 3 | 0.0g | 30 | 425 Å/min | 210 nm |
| 4 | 4.0g | 30 | 2,375 Å/min | 186 nm |
| 5 | 0.0g | 60 | 388 Å/min | 248 nm |
| 6 | 4.0g | 60 | 2,485 Å/min | 188 nm |
| 7 | 0.0g | 120 | 376 Å/min | 447 nm |
| 8 | 4.0g | 120 | 2,418 Å/min | 188 nm |

**Example 5: Dependence of polishing performance on the added amount of hydrogen peroxide and nitric acid**

A series of slurry compositions was prepared according to the same manner as in the preparation of the slurry III of the above Example 1 with the exception of varying the amount of hydrogen peroxide or nitric acid. Polishing of patterned wafers having the line width of

0.2μm was conducted using the respective slurry compositions for 2 minutes under the condition as described above. The results are set forth in Table 4.

**Table 4**

| Sample | Hydrogen Peroxide | Nitric Acid | Polishing Rate for W | Corrosion Rate | Oxide Erosion |
|---|---|---|---|---|---|
| 1 | 20g | 0.3g | 2,486 Å/min | 10 Å/min | 85 Å |
| 2 | 60g | 0.3g | 3,253 Å/min | 130 Å/min | 684 Å |
| 3 | 2g | 0.3g | 637 Å/min | 4 Å/min | 62 Å |
| 4 | 20g | 0.005g | 1,204 Å/min | 5 Å/min | 47 Å |
| 5 | 20g | 0.8g | 2,765 Å/min | 8 Å/min | 116 Å |

As stated above, by virtue of the present invention, it has become possible to accomplish the optimum polishing rate in CMP processes without typical problems such as oxide erosion, corrosion, pit, dishing and so on. Further, the slurry compositions of the present invention have been so improved in the dispersion stability that they are suitable for long-term storage.

The simple modification and change of the present invention will be readily made by persons skilled in the art and it should be understood that all of such modification and change are encompassed within the scope of the present invention.

## Claims

1. A slurry composition for use in chemical mechanical polishing of metal, comprising a peroxide, an inorganic acid, a PDTA(propylenediaminetetraacetate)-metal complex, a carboxylic acid, a metal oxide powder, and de-ionized water, wherein bond energy between metal atom and oxygen atom in the PDTA-metal complex is lower than that of O-W.

2. The composition according to claim 1, wherein the composition comprises 0.5~5wt% of the peroxide, 0.001~5.0wt% of the inorganic acid, 0.001~0.5wt% of the PDTA-metal complex, 0.1~10wt% of the carboxylic acid, and 0.1~10wt% of the metal oxide powder.

3. The composition according to claim 1, wherein the peroxide is one or more selected from the group consisting of hydrogen peroxide, benzoyl peroxide, calcium peroxide, barium peroxide, and sodium peroxide.

4. The composition according to claim 1, wherein the inorganic acid is one or more selected from the group consisting of nitric acid, sulfuric acid, hydrochloric acid, and phosphoric acid.

5. The composition according to claim 1, wherein the PDTA-metal complex is PDTA-Fe, PDTA-Ni, or PDTA-Co.

6. The composition according to claim 1, wherein the carboxylic acid is one or more selected from the group consisting of acetic acid, citric acid, glutaric acid, glycolic acid, formic acid, lactic acid, malic acid,

maleic acid, oxalic acid, phthalic acid, succinic acid, and tartaric acid.

7. The composition according to claim 1, wherein the metal oxide is silica, alumina, ceria, titania, or mixtures thereof.

8. The composition according to claim 2, wherein PDTA-metal complex content of the composition is 0.05~0.3wt%.