

## TITLE OF THE INVENTION:

Chemical Additives for  
Chemical Mechanical Planarization (CMP) Polishing Compositions

## CROSS REFERENCE TO RELATED PATENT APPLICATIONS

**[0001]** The application claims the benefit of U.S. Application No. 63/607,266 filed on December 07, 2023. The disclosure of the application is hereby incorporated by reference.

## BACKGROUND OF THE INVENTION

**[0002]** This invention relates to chemical additives used in Chemical Mechanical Planarization (CMP) polishing compositions. More specifically, the invention relates to amino alcohol compounds used as chemical additives in copper Chemical Mechanical Planarization (CMP) polishing compositions. This invention also relates to the CMP polishing methods and systems using the copper CMP polishing composition.

**[0003]** In the semiconductor industry, semiconductor devices have structured layers, and multilevel interconnects comprised of stacked thin-films consisting of one or more of the following materials: copper (Cu), tantalum (Ta), titanium (Ti), titanium nitride (TiN), aluminum-copper (Al-Cu), aluminum-silicon (Al Si), tungsten (W), doped polysilicon (poly-Si), and various combinations thereof.

**[0004]** Typically, different materials are deposited on top of each other in complicated structures. The depositions of the semiconductor devices are done with variety of methods. However, a CMP process is needed after each deposition step to ensure that the deposited layer is flat and has a surface roughness in the low scale ready for the next deposition step.

**[0005]** In the advanced node Cu CMP process, the Cu line width on the advanced node patterned wafers has been significantly reduced which resulting in a notable increase in the Cu step height difference between the array and field areas after electroplating process. Therefore, achieving a high planarization efficiency becomes crucial to minimize these step height variations across difference feature sizes.

**[0006]** Thus, it is essential to enhance the dishing level to a desired level while maintaining planarization efficiency in the Cu CMP process. This allows for a reduction in the overall processing time while ensuring that the desired dishing level is achieved based on process requirements.

**[0007]** In addition, a rotating wafer holder brings the to-be-polished wafer in contact with a polishing pad in a typical CMP process step. The CMP polishing composition is usually applied between the to-be-polished wafer and the polishing pad.

**[0008]** So, it is the combination of a high removal rate of the to-be-planarized material and a low removal rate of the to-be-preserved material which defines the effectiveness of a CMP polishing composition.

**[0009]** There remains a need within the art since the known Cu CMP slurries in the field are not able to provide a performance meeting all the requirements.

#### BRIEF SUMMARY OF THE INVENTION

**[0010]** The present invention satisfies the need by using the chemical additives in Chemical Mechanical Planarization (CMP) polishing compositions; more specifically, by using amino alcohol compounds as chemical additives in copper Chemical Mechanical Planarization (CMP) polishing compositions.

**[0011]** In one aspect (Aspect 1), there is provided a CMP polishing composition comprising, consisting essentially of, or consisting of:

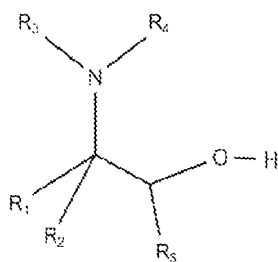
- a) an abrasive;
  - b) a chemical additive; and
  - c) a water-soluble solvent ; and
- optionally at least one of
- d) a chelator;
  - e) a corrosion inhibitor;
  - f) a biocide;
  - g) an organic quaternary ammonium salt;
  - h) an oxidizing agent;
- and

i) a pH adjusting agent;

the pH of the CMP polishing composition ranges from 3 to 11, 4 to 10, 5 to 9, or 6 to 8.

**[0012]** The abrasive can be any known abrasive particles, includes but is not limited to inorganic oxide particles, metal oxide-coated inorganic oxide particles, organic polymer particles, metal oxide-coated organic polymer particles, and combinations thereof.

**[0013]** The chemical additive includes but is not limited to amino alcohol compound having a structure A as shown below:



A

**[0014]** In structure A,  $R_1$  and  $R_2$  each independently includes but is not limited to: H; OH; C1 - C12, C1-C8, or C1-C4 alkyl; or C1 - C12, C1-C8, or C1-C4 alkyl alcohol; and  $R_3$ ,  $R_4$  and  $R_5$  each independently includes but is not limited to: H; C1-C12, C1-C8, or C1-C4 alkyl; or C1 - C12, C1-C8, or C1-C4 alkyl alcohol.

**[0015]** Some examples of the chemical additive include but are not limited to 2-(dimethylamino)-2-methyl-1-propanol, 2-amino-2-methyl-1-propanol, 2-amino-2-ethyl-1,3-propanediol, 3-amino-4-octanol, 2-amino-2-hydroxymethyl-1,3-propanediol, 2-amino-2-methyl-1,3-propanediol, and 2-amino-1-butanol.

**[0016]** The optional chelator includes but is not limited to amino acids and derivatives, and amines.

**[0017]** The amino acids and amino acid derivatives included, but not limited to, glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, valine, leucine, isoleucine, phenylamine, proline, serine, threonine, tyrosine, glutamine, asparagine, glutamic acid, aspartic acid, tryptophan, histidine, arginine, lysine, methionine, cysteine, iminodiacetic acid, and combinations thereof.

**[0018]** The optional corrosion inhibitors include but are not limited to family of hetero aromatic compounds containing nitrogen atom(s) in their aromatic rings, such as 1,2,4-

triazole, benzotriazole and benzotriazole derivatives, tetrazole and tetrazole derivatives, imidazole and imidazole derivatives, benzimidazole and benzimidazole derivatives, pyrazole and pyrazole derivatives, and tetrazole and tetrazole derivatives.

**[0019]** The optional biocide can be any biocide which provides active ingredients to prevent biological growth and thus provide more stable shelf time of the CMP polishing compositions.

**[0020]** Example of the biocide includes but is not limited to Kathon™, and Kathon™ CG/ICP II from Dow Chemical Co. ; which have 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one as the active ingredients; and Neolone™ M10 from CHEMPOINT, Bellevue, WA 98004 USA; which has methyl isothiazolinone as the active ingredient.

**[0021]** The optional organic quaternary ammonium salt includes but is not limited to choline salt, such as choline bicarbonate salt, or all other salts formed between choline and other anionic counter ions.

**[0022]** The optional oxidizer includes but is not limited to peroxy compound selected from the group consisting of hydrogen peroxide, urea peroxide, peroxyformic acid, peracetic acid, propaneperoxoic acid, substituted or unsubstituted butaneperoxoic acid, hydroperoxy-acetaldehyde, potassium periodate, ammonium peroxymonosulfate; and non-per-oxy compound selected from the group consisting of ferric nitrite, KClO<sub>4</sub>, KBrO<sub>4</sub>, KMnO<sub>4</sub>; and combinations thereof.

**[0023]** The optional pH adjusting agent includes but is not limited to (a)nitric acid, sulfuric acid, tartaric acid, succinic acid, citric acid, malic acid, malonic acid, various fatty acids, various polycarboxylic acids, and mixtures thereof to lower the pH; and (b) potassium hydroxide, sodium hydroxide, ammonia, tetraethylammonium hydroxide, ethylenediamine, piperazine, polyethyleneimine, modified polyethyleneimine, and mixtures thereof to raise the pH.

**[0024]** The water-soluble solvent is selected from the group consisting of deionized (DI) water, distilled water, and alcoholic organic solvents.

**[0025]** In another aspect (Aspect 2), there is provided a CMP polishing method for chemical mechanical planarization of a semiconductor substrate comprising at least one surface containing Cu, comprising, consisting essentially of, or consisting of the steps of: contacting the at least one surface with a polishing pad;

delivering the chemical mechanical planarization polishing composition of Aspect 1; polishing the at least one surface containing Cu with the chemical mechanical planarization composition.

**[0026]** In yet another aspect (Aspect 3), there is provided a CMP polishing system, comprising, consisting essentially of, or consisting of:

a semiconductor substrate comprising at least one surface containing Cu;

a polishing pad; and

the chemical mechanical planarization composition of Aspect 1;

wherein the at least one surface containing Cu is in contact with the polishing pad and the chemical mechanical planarization composition.

**[0027]** The at least one surface can further contain at least one second material which can be any materials used in the semiconductor substrate or pattern wafer together with Cu; includes but is not limited to Ta; Ti; TaN; TiN; Ta; TaN; Ti; TiN, Co, Ru; dielectric materials such as SiO<sub>2</sub>, SiN, SiC; and low-k and ultra-low-k materials; such as different Black Diamond™ films.

**[0028]** Other aspects, features and embodiments of the invention will be more fully apparent from the ensuing disclosure and appended claims.

**[0029]** The embodiments of the invention can be used alone or in combinations with each other.

#### DETAILED DESCRIPTION OF THE INVENTION

**[0030]** As industry standards trend toward smaller device features, there is a continuously developing need for new Cu CMP polishing compositions that enhance the dishing level to minimize the step height variations across different feature sizes while maintaining planarization efficiency in the Cu CMP process for the broad and advanced node applications.

**[0031]** The present invention satisfies the need by providing new Cu CMP polishing compositions using amino alcohol compounds as chemical additives, as well as providing methods and systems using the CMP polishing compositions.

**[0032]** In one aspect (Aspect 1), there is provided a CMP polishing composition comprising, consisting essentially of, or consisting of:

a) an abrasive;

- b) a chemical additive; and
- c) a water-soluble solvent ; and
- optionally at least one of
- d) a chelator;
- e) a corrosion inhibitor;
- f) a biocide;
- g) an organic quaternary ammonium salt;
- h) an oxidizing agent;
- and
- i) a pH adjusting agent;

pH of the CMP polishing composition ranges from 3 to 11, 4 to 10, 5 to 9, or 6 to 8.

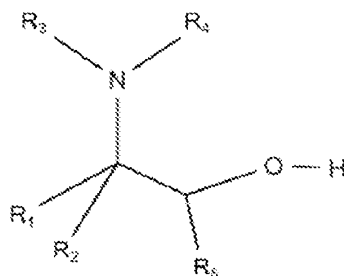
**[0033]** The abrasive includes but is not limited to inorganic oxide particles, metal oxide-coated inorganic oxide particles, organic polymer particles, metal oxide-coated organic polymer particles, and combinations thereof.

**[0034]** The abrasive particles used for the disclosed herein Cu bulk CMP polishing compositions include, but are not limited to, the following: colloidal silica or high purity colloidal silica; the colloidal silica particles doped by other metal oxide within lattice of the colloidal silica, such as alumina doped silica particles; silica sol of sodium silicates or/and potassium silicates; fumed silica; colloidal aluminum oxide including alpha-, beta-, and gamma-types of aluminum oxides; colloidal and photoactive titanium dioxide; cerium oxide; colloidal cerium oxide; nano-sized inorganic metal oxide particles, such as alumina, titania, zirconia, ceria etc.; nano-sized diamond particles; nano-sized silicon nitride particles; mono-modal, bi-modal, multi-modal colloidal abrasive particles; organic polymer-based soft abrasives; surface-coated or modified abrasives; or other composite particles, and mixtures thereof.

**[0035]** The CMP polishing composition contains 0.0025 wt.% to 25 wt.% abrasives; the preferred concentration of abrasives ranges from 0.0025 wt.% to 2.5 wt.%. The most preferred concentration of abrasives ranges from 0.005 wt.% to 1.0 wt.%.

[0036] The chemical additive includes but is not limited to amino alcohol compounds.

[0037] The amino alcohol compound includes but is not limited to have a general structure A as shown below:



A;

where,  $R_1$  and  $R_2$  in structure A each independently includes but is not limited to: H; OH; C1 - C12, C1-C8, or C1-C4 alkyl; or C1 - C12, C1-C8, or C1-C4 alkyl alcohol; and  $R_3$ ,  $R_4$  and  $R_5$  in structure A each independently includes but is not limited to: H; C1-C12, C1-C8, or C1-C4 alkyl; or C1 - C12, C1-C8, or C1-C4 alkyl alcohol.

[0038] Example of amino alcohol compound includes but is not limited to 2-(dimethylamino)-2-methyl-1-propanol, 2-amino-2-methyl-1-propanol, 2-amino-2-ethyl-1,3-propanediol, 3-amino-4-octanol, 2-amino-2-hydroxymethyl-1,3-propanediol, 2-amino-2-methyl-1,3-propanediol, and 2-amino-1-butanol.

[0039] The amino alcohol compound can be used alone or in combinations.

[0040] The amino alcohols feature distinct steric hindrance structures. Not to be bound by theory, in the case of these amino alcohols compounds it is believed that the steric hindrance structures exhibit the capacity for providing weak protection within the lower-lying regions of the pattern, thereby facilitating the enhancement of planarization efficiency (PE). PE can be evaluated by examining changes in film thickness at the bottom and top of the feature. It is determined by plotting the step height reduction of a specific feature (e.g., a 100nm line/space) against the removed thickness of the copper (Cu) film. The slope of this plot reflects the planarization efficiency achieved, taking into account the combination of chemicals and mechanical polish parameters used in the composition in the polishing process.

[0041] Simultaneously, owing to their relatively moderate chelation abilities, these compounds facilitate metal dissolution during the polishing process, consequently

adjusting the Cu line dishing level. This dual--functional characteristic allows the use of these amino alcohol compounds as effective chemical additives in Cu CMP polishing compositions for manipulating and tailoring dishing effects while maintaining the planarization efficiency.

**[0042]** The chemical additive ranges from 0.0001-0.5 wt. %, 0.0005-0.25wt. %, 0.00075-0.1 wt. %, 0.001-0.075 wt. %, 0.0015-0.06 wt. %, or 0.002-0.05wt. %,

**[0043]** The optional chelator includes but is not limited to amino acids and derivatives, amines as disclosed in US11401441BB; the disclosure of which is incorporated herein by reference.

**[0044]** The amino acids and amino acid derivatives included, but not limited to, glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, valine, leucine, isoleucine, phenylamine, proline, serine, threonine, tyrosine, glutamine, asparagine, glutamic acid, aspartic acid, tryptophan, histidine, arginine, lysine, methionine, cysteine, iminodiacetic acid, and combinations thereof.

**[0045]** The CMP polishing composition contains 0.1 wt.% to 18 wt.% , 0.5 wt.% to 10 wt.%; or 0.75 wt.% to 2.5 wt.% of chelator.

**[0046]** The optional corrosion inhibitors include but are not limited to the family of hetero aromatic compounds containing nitrogen atom(s) in their aromatic rings, such as 1,2,4-triazole, benzotriazole and benzotriazole derivatives, such as 5-methyl-benzotriazole; tetrazole and tetrazole derivatives; imidazole and imidazole derivatives; benzimidazole and benzimidazole derivatives; pyrazole and pyrazole derivatives; and tetrazole and tetrazole derivatives.

**[0047]** The CMP polishing composition contains 0.005 wt.% to 1.0 wt.% corrosion inhibitor; the preferred concentration ranges from 0.01 wt.% to 0.5 wt.%; and the most preferred concentration ranges from 0.02 wt.% to 0.2 wt.%.

**[0048]** An optional biocide can be any biocide which provides active ingredients to prevent biological growth and thus provide more stable shelf time of the CMP polishing compositions.

**[0049]** Example of the biocide includes but is not limited to Kathon™, Kathon™ CG/ICP II, from Dow Chemical Co.; which have active ingredients of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one; and Neolone™ M10 from

CHEMPOINT, Bellevue, WA 98004 USA; which has active ingredient of methyl isothiazolinone.

**[0050]** The CMP polishing composition contains 0.0001 wt.% to 0.05 wt.% biocide; the preferred concentration ranges from 0.0002 wt.% to 0.025 wt.%; and the most preferred concentration ranges from 0.002 wt.% to 0.01 wt.%

**[0051]** The optional organic quaternary ammonium salt includes but is not limited to choline salt, such as choline bicarbonate salt, or all other salts formed between choline and other anionic counter ions, as disclosed in US11401441; the disclosure of which is incorporated herein by reference.

**[0052]** The optional oxidizer includes but is not limited to peroxy compound selected from the group consisting of hydrogen peroxide, urea peroxide, peroxyformic acid, peracetic acid, propaneperoxoic acid, substituted or unsubstituted butaneperoxoic acid, hydroperoxy-acetaldehyde, potassium periodate, ammonium peroxymonosulfate; and non-per-oxy compound selected from the group consisting of ferric nitrite,  $\text{KClO}_4$ ,  $\text{KBrO}_4$ ,  $\text{KMnO}_4$ ; and combinations thereof.

**[0053]** The CMP polishing composition contains 0.1 wt.% to 10 wt.% oxidizing agents; the preferred concentration ranges from 0.25wt.% to 3wt.%; and the most preferred concentration ranges from 0.5wt.% to 2.0wt.%.

**[0054]** The optional pH adjusting agent includes but is not limited to (a)nitric acid, sulfuric acid, tartaric acid, succinic acid, citric acid, malic acid, malonic acid, various fatty acids, various polycarboxylic acids, and mixtures thereof to lower the pH; and (b) potassium hydroxide, sodium hydroxide, ammonia, tetraethylammonium hydroxide, ethylenediamine, piperazine, polyethyleneimine, modified polyethyleneimine, and mixtures thereof to raise the pH.

**[0055]** The CMP polishing composition contains 0 wt.% to 1 wt.% pH adjusting agent; the preferred concentration ranges from 0.01 wt.% to 0.5 wt.%; and the most preferred concentration ranges from 0.1 wt.% to 0.25 wt.%.

**[0056]** The water-soluble solvent is selected from the group consisting of deionized (DI) water, distilled water, and alcoholic organic solvents.

**[0057]** In another aspect (Aspect 2), there is provided a CMP polishing method for chemical mechanical planarization of a semiconductor substrate comprising at least one surface containing Cu, comprising, consisting essentially of, or consisting steps of:

contacting the at least one surface with a polishing pad;  
delivering the chemical mechanical planarization polishing composition of Aspect 1;  
polishing the at least one surface containing Cu with the chemical mechanical planarization composition.

**[0058]** In yet another aspect (Aspect 3), there is provided a CMP polishing system, comprising, consisting essentially of, or consisting of:

a semiconductor substrate comprising at least one surface containing Cu;

a polishing pad; and

the chemical mechanical planarization composition of Aspect 1;

wherein the at least one surface containing Cu is in contact with the polishing pad and the chemical mechanical planarization composition.

**[0059]** The at least one surface can further contain at least one second material which can be any materials used in the semiconductor substrate or pattern wafer together with Cu; includes but is not limited to Ta; Ti; TaN; TiN; Ta; TaN; Ti; TiN, Co, Ru; dielectric materials such as SiO<sub>2</sub>, SiN, SiC; and low-k and ultra-low-k materials; such as different Black Diamond™ films.

**[0060]** The following non-limiting examples are presented to further illustrate the present invention.

## GLOSSARY

## COMPONENTS

**[0061]** All raw Chemicals, such as glycine, alanine, benzotriazole, nitric acid et al were supplied by MilliporeSigma, St. Louis, MO.

**[0062]** Cu pattern MIT754 was supplied by SKORPIOS, Albuquerque, NM 87109-4358.

**[0063]** Colloidal silica (such as PL-1M) was supplied by Fuso Chemical Co., LTD, Japan,

## CMP Methodology

## PARAMETERS

## General

- [0064] Å or A: angstrom(s) – a unit of length
- [0065] BP: back pressure, in psi units
- [0066] CMP: chemical mechanical planarization = chemical mechanical polishing
- [0067] CS: carrier speed
- [0068] DF: Down force: pressure applied during CMP, unit: psi
- [0069] min: minute(s)
- [0070] ml: milliliter(s)
- [0071] mV: millivolt(s)
- [0072] mM: millimolar
- [0073] psi: pounds per square inch
- [0074] PS: platen rotational speed of polishing tool, in rpm (revolution(s) per minute)
- [0075] SF: composition flow, ml/min
- [0076] Wt. %: weight percentage (of a listed component)
- [0077] Cu: Ta Selectivity: (removal rate of Cu)/ (removal rate of Ta)
- [0078] Removal Rates: Measured removal rate at a given down pressure. The down pressure of the CMP tool was 2.0, 3.0, 4.0 or 4.8 psi in the examples.

## Metrology

- [0079] Films were measured with a ResMap CDE, model 168, manufactured by Creative Design Engineering, Inc, 20565 Alves Dr., Cupertino, CA, 95014. The ResMap tool is a four-point probe sheet resistance tool. Forty-nine-point diameter scan at 5mm edge exclusion for film was taken.

## CMP Tool

**[0080]** For Examples 1 and 2, TriboLab CMP polishing tool from Bruker was used to measure RR of blanket Cu film and RR of blanket Ta film, and thus the calculated polishing selectivity of Cu:Ta (removal rate of Cu/ removal rate of Ta); and Cu dishing on 300mm Cu pattern wafer MIT 754.

**[0081]** Polishing conditions were: DuPont DGK pad; Kinik 34J in-situ conditioning Disk; Downforce = 4.8psi; T/H RPM = 80/70 rpm, composition flow rate = 250ml/min; testing film size : 4 x 4 cm coupon; dishing data was collected at endpoint plus 20 seconds overpolish;

**[0082]** For Examples 3, 4 and 5 Ebara tool was also used for measuring Cu dishing on 300mm Cu pattern wafer MIT 754.

**[0083]** Polishing conditions were: DuPont DGK pad; Kinik 34J in-situ conditioning Disk; Downforce = 1.5 psi; T/H RPM = 80/70 rpm, composition flow rate = 350ml/min; dishing data was collected at endpoint plus 20 seconds overpolish;

## Polishing Experiments

**[0084]** The polishing experiments were performed to assess the RR of blanket Cu film and Ta film, as well as evaluating planarization efficiency (PE) and dishing levels on Cu patterned wafers. These tests were conducted using the reference Cu CMP polishing composition and were compared to samples incorporating different amino alcohols as chemical additives.

## Example 1

**[0085]** Polishing on the blanket Cu and Ta films were performed in Examples 1. The Cu:Ta selectivity was calculated.

**[0086]** The reference polishing composition (Ref.) contained 1.125 wt.% glycine, 0.125 wt.% alanine, 0.067 wt.% 1,2,4-triazole, 0.0025 wt.% 5-methyl-benzotriazole, and 0.003 wt.% methyl isothiazolinone . Colloidal silica (PL-1M, cocoon type, primary particle size 15 nm) was added at 0.1wt.%. 1.0 wt.% of H<sub>2</sub>O<sub>2</sub> was added at the point of use. The pH of the reference sample is adjusted to 6 to 8 using nitric acid or potassium hydroxide.

[0087] The working polishing compositions (WC) were obtained by adding 0.0025 wt.% to 0.01wt% different disclosed amino alcohol compounds having the disclosed general structure A into to the reference Ref.: 2-(dimethylamino)-2-methyl-1-propanol for WC 1, 2-amino-2-methyl-1-propanol for WC 2, 2-amino-2-ethyl-1,3-propanediol for WC 3, 3-amino-4-octanol for WC 4, and 2-amino-2-hydroxymethyl-1,3-propanediol for WC 5, respectively. The different amino alcohol compounds were supplied by Angus Chemicals, now Advanion Corporation.

[0088] The polishing results from adding the same amount of 0.005 wt.% different amino alcohol compounds into to the reference (Ref.) for the blanket Cu and Ta films, as well as the Cu:Ta selectivity, were listed in Table 1.

Table 1. Cu, Ta and TaN Film RR and Selectivity

| Composition | Cu RR<br>(Å/min.) | Ta RR<br>(Å/min.) | TaN RR<br>(Å/min.) | Cu: Ta<br>Selectivity | Cu: TaN<br>Selectivity |
|-------------|-------------------|-------------------|--------------------|-----------------------|------------------------|
| Ref.        | 7882              | 38                | 24                 | 207                   | 328                    |
| WC 1        | 7246              | 6                 | 6                  | 1208                  | 1208                   |
| WC 2        | 6941              | 20                | 12                 | 347                   | 578                    |
| WC 3        | 7501              | 22                | 18                 | 341                   | 417                    |
| WC 4        | 7369              | 7                 | 17                 | 1053                  | 433                    |
| WC 5        | 6974              | 5                 | 20                 | 1395                  | 349                    |

[0089] As the results shown, adding the disclosed amino alcohol compounds reduced Cu, Ta, and TaN film removal rates due to the weak passivation effects during Cu CMP process.

[0090] Such passivation effects were stronger for Ta and TaN films than for Cu film resulting in increased Cu: Ta/TaN selectivity.

[0091] The Cu: Ta selectivity was increased from 207:1 to the range of 234:1 to 1395:1 by using different disclosed amino alcohol compounds.

Example 2

[0092] Polishing on Cu patterned wafers was performed on the Mini polisher to see the planarization efficiency (PE%) and the Cu line dishing on smaller Cu line features.

[0093] PE% was determined by measuring step height reduction of a 100mm line/space feature against the removed thickness of the copper (Cu) film after 30 seconds polishing.

[0094] The same Ref. and working compositions WC 1 to WC 5 used in Example 1 were used in Example 2.

[0095] Results were listed in Table 2.

Table 2. PE% and Line Dishing on Cu pattern wafers

| Composition | PE%<br>On 100mm<br>Line | Dishing (Å)<br>on 2μm<br>Line | Dishing (Å)<br>on 0.18μm<br>Line |
|-------------|-------------------------|-------------------------------|----------------------------------|
| Ref.        | 74.5                    | 450                           | 242                              |
| WC 1        | 76.9                    | 632                           | 279                              |
| WC 2        | 79.4                    | 787                           | 380                              |
| WC 3        | 73.5                    | 602                           | 300                              |
| WC 4        | 73.0                    | 464                           | 249                              |
| WC 5        | 80.0                    | 524                           | 263                              |

[0096] As the results shown in Table 2, the use of the disclosed amino alcohol compounds at least maintained and mostly increased PE% from the reference sample.

[0097] Importantly, the use of disclosed amino alcohol compounds did promote the Cu dishing to the different levels.

[0098] Please note that Cu line dishing levels are purposely increased with the use of chemical additives of disclosed amino alcohol compounds to meet the critical requirements for advanced node Cu CMP processes.

Example 3

[0099] Polishing on Cu patterned wafers was performed using Ebara tool to see the planarization efficiency (PE%) and the Cu line dishing on smaller Cu line features.

[00100] PE% was determined by measuring step height reduction of a 100mm line/space feature against the removed thickness of the copper (Cu) film after 30 seconds polishing.

[00101] The same Ref. and working compositions WC 1 to WC 5 used in Example 1 were used in Example3.

[00102] The new working compositions WC 6 to WC 8 were obtained by adding the same amount (0.005 wt.%) of disclosed amino alcohols having the disclosed general structure A into Ref. : amino-2-propanol for WC 6, 2-(Isopropylamino)ethanol for WC 7, and 2-(Methylamino)ethanol for WC 8, respectively.

[00103] The comparative compositions(CC) were obtained by adding the same amount (0.005 wt.%) of amino alcohols which do not have the disclosed general structure A into Ref. : 2-(2-Aminoethoxy)ethanol for CC 1 and 3-Morpholinepropanamine for CC 2; respectively.

[00104] Results were listed in Table 3.

Table 3. PE% and Line Dishing on Cu pattern wafers

| Composition | PE% on 100um line | Dishing (Å) on 2μm Line | Change relative to Ref. | Dishing (Å) on 0.18μm Line | Change relative to Ref. |
|-------------|-------------------|-------------------------|-------------------------|----------------------------|-------------------------|
| Ref.        | 140               | 394                     |                         | 255                        |                         |
| WC 1        | 149               | 446                     | 13%                     | 280                        | 10%                     |
| WC 2        | 145               | 430                     | 9%                      | 272                        | 7%                      |
| WC 3        | 147               | 440                     | 12%                     | 278                        | 9%                      |
| WC 4        | 153               | 414                     | 5%                      | 266                        | 4%                      |
| WC 5        | 154               | 457                     | 16%                     | 289                        | 13%                     |
| WC 6        | 143               | 448                     | 14%                     | 279                        | 9%                      |
| WC 7        | 153               | 438                     | 11%                     | 271                        | 6%                      |
| WC 8        | 153               | 419                     | 6%                      | 272                        | 7%                      |
| CC 1        | 148               | 404                     | 2%                      | 251                        | -2%                     |
| CC 2        | 143               | 403                     | 2%                      | 251                        | -2%                     |

[00105] The results from Ebara tool shown in Table 3 were consistent with the results from the Mini Polisher shown in Table 2, the use of the disclosed amino alcohol compounds having the structure A clearly increased PE% from the reference sample and promoted the Cu dishing to the different levels.

[00106] As a comparison, the amino alcohol compounds (used in CC 1 and CC2) which do not have the sterically hindered groups as shown the structure A did not provide the same performance.

Example 4

- [00107] Polishing on Cu patterned wafers was performed using Ebara tool to see the planarization efficiency (PE%) and the Cu line dishing on smaller Cu line features.
- [00108] PE% was determined by measuring step height reduction of a 100mm line/space feature against the removed thickness of the copper (Cu) film after 30 seconds polishing.
- [00109] The same Ref. and working composition WC 1 used in Example 1 were used in Example 4.
- [00110] Working compositions WC 9 and WC 10 were obtained by adding 0.0075 wt.% and 0.01W% of 2-(dimethylamino)-2-methyl-1-propanol into to the Ref. respectively.
- [00111] The results were shown in Table 4.

Table 4. PE% and Line Dishing on Cu pattern wafers

| Composition | PE% on 100um line | Dishing (Å) on 2μm Line | Dishing (Å) on 0.18μm Line |
|-------------|-------------------|-------------------------|----------------------------|
| Ref.        | 140               | 394                     | 255                        |
| WC 1        | 149               | 446                     | 280                        |
| WC 9        | 142               | 417                     | 244                        |
| WC 10       | 142               | 419                     | 232                        |

- [00112] The results from Table 4 showed that the use of 2-(dimethylamino)-2-methyl-1-propanol at different concentrations increased PE% and promoted the Cu dishing for 2μm Line from the reference sample. The increased amount of the amino alcohol did not promote the Cu dishing for 0.18μm Line.

Example 5

- [00113] Polishing on Cu patterned wafers was performed using Ebara tool to see the planarization efficiency (PE%) and the Cu line dishing on smaller Cu line features.
- [00114] PE% was determined by measuring step height reduction of a 100mm line/space feature against the removed thickness of the copper (Cu) film after 30 seconds polishing.
- [00115] The new reference polishing composition (Ref. 1) contained 1.125 wt.% glycine, 0.125 wt.% alanine, 0.050 wt.% 1,2,4-triazole, 0.0025 wt.% 5-methyl-

benzotriazole, and 0.003 wt.% methyl isothiazolinone. Colloidal silica (PL-1M, cocoon type, primary particle size 15 nm) was added at 0.1wt.%. 0.9 wt.% of H<sub>2</sub>O<sub>2</sub> was added at the point of use. The pH of the reference sample is adjusted to 6 to 8 using nitric acid or potassium hydroxide.

[00116] The working composition WC 11 to WC 14 were obtained by adding 0.0025 wt.%, 0.005 wt.%, 0.0075 wt.% and 0.01W% 2-(dimethylamino)-2-methyl-1-propanol into to Ref. 1 respectively.

[00117] The results were shown in Table 5.

Table 5. PE% and Line Dishing on Cu pattern wafers

| Composition | PE% on 100um line | Dishing (Å) on 2μm Line | Dishing (Å) on 0.18μm Line |
|-------------|-------------------|-------------------------|----------------------------|
| Ref. 1      | 140.0             | 410                     | 280                        |
| WC 11       | 140.0             | 435                     | 296                        |
| WC 12       | 142.0             | 506                     | 343                        |
| WC 13       | 139.0             | 497                     | 311                        |
| WC 14       | 134.0             | 485                     | 282                        |

[00118] The results from Table 4 showed that the use of the disclosed amino alcohol compound increased PE% from the reference sample Ref.1.

[00119] Importantly, the use of the disclosed amino alcohol compound in the tested amount range clearly promoted the dishing.

[00120] In this invention, specific amino alcohol compounds with sterically hindered groups at the R1 and R2 positions as shown in the general structure A are used. These amino alcohol compounds have demonstrated a weak suppression effect on Cu, Ta and Ta/N removal rates (RR). The weak suppression serves as an indicator for protecting low-lying areas during the removal of protruded features, thereby maintaining planarization efficiency.

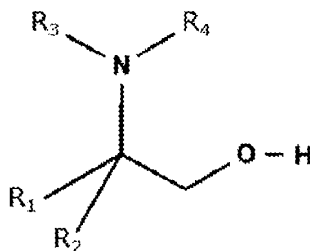
[00121] Furthermore, the reduction in Ta and TaN RR enhances the Cu to Ta/TaN selectivity, leading to improved control over dishing levels during the overpolishing step.

[00122] Please note that Cu line dishing levels are purposely increased with the use of chemical additives of disclosed amino alcohol compounds to meet the critical requirements for advanced node Cu CMP processes.

**[00123]** The embodiments of this invention listed above, including the working example, are exemplary of numerous embodiments that may be made of this invention. It is contemplated that numerous other configurations of the process may be used, and the materials used in the process may be elected from numerous materials other than those specifically disclosed.

## Claims

1. A Chemical Mechanical Planarization polishing composition comprising, consisting essentially of, or consisting of:
  - a) an abrasive;
  - b) a chemical additive; and
  - c) a water-soluble solvent ;optionally at least one of
  - d) a chelator;
  - e) a corrosion inhibitor;
  - f) a biocide;
  - g) an organic quaternary ammonium salt;
  - h) an oxidizing agent; and
  - i) a pH adjusting agent;wherein the chemical additive comprises amino alcohol compound, the water-soluble solvent is selected from the group consisting of deionized (DI) water, distilled water, and alcoholic organic solvents; and pH of the CMP polishing composition ranges from 3 to 11, 4 to 10, 5 to 9, or 6 to 8.
2. The Chemical Mechanical Planarization polishing composition of Claim 1, wherein the amino alcohol compound has a general structure A as shown below:



A;

wherein  $R_1$  and  $R_2$  each independently selected from the group consisting of H; OH; C1 - C12, C1-C8, or C1-C4 alkyl; or C1 - C12, C1-C8, or C1-C4 alkyl alcohol; and  $R_3$ ,  $R_4$  and  $R_5$  each independently selected from the group consisting of H; C1-C12, C1-C8, or C1-C4 alkyl; or C1 - C12, C1-C8, or C1-C4 alkyl alcohol.

3. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 2, wherein the chemical additive is selected from the group consisting of 2-(dimethylamino)-2-methyl-1-propanol, 2-amino-2-methyl-1-propanol, 2-amino-2-ethyl-1,3-propanediol, 3-amino-4-octanol, 2-amino-2-hydroxymethyl-1,3-propanediol, 2-amino-2-methyl-1,3-propanediol, 2-amino-1-butanol, and combinations thereof.
4. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 3, wherein the chemical additive is selected from the group consisting of 2-(dimethylamino)-2-methyl-1-propanol, 2-amino-2-methyl-1-propanol, 2-amino-2-ethyl-1,3-propanediol, 3-amino-4-octanol, 2-amino-2-hydroxymethyl-1,3-propanediol, and combinations thereof.
5. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 4, wherein concentration of the chemical additive ranges from 0.0001-0.1 wt. %, 0.0005-0.08 wt. %, 0.001-0.06 wt. %, 0.0015-0.04 wt. %, 0.002-0.03 wt. %, 0.0025-0.02 wt. %, 0.003-0.01 wt. %, or 0.0035-0.008 wt. %.
6. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 5, wherein the abrasive is selected from the group consisting of colloidal silica; colloidal silica particles doped by other metal oxide within lattice of the colloidal silica; silica sol selected from the group consisting of sodium silicates, potassium silicates, and combinations thereof; fumed silica; colloidal aluminum oxide selected from the group consisting of alpha-, beta-, and gamma-types of aluminum oxides; colloidal and photoactive titanium dioxide, cerium oxide, colloidal cerium oxide; nano-sized diamond particles; nano-sized silicon nitride particles; organic polymer-based soft abrasives; surface-coated or modified abrasives; and combinations thereof.

7. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 6, wherein the abrasive is selected from the group consisting of colloidal silica; colloidal silica particles doped by other metal oxide within lattice of the colloidal silica; surface-coated or modified colloidal silica; and combinations thereof.
8. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 7, wherein the abrasive is selected from the group consisting of colloidal silica; surface-coated or modified colloidal silica; and combinations thereof.
9. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 8, wherein concentration of the abrasive ranges from 0.0001-0.5 wt. %, 0.0005-0.25wt. %, 0.00075-0.1 wt. %, 0.001-0.075 wt. %, 0.0015-0.06 wt. %, or 0.002-0.05wt. %.
10. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 9, where the chelator is selected from the group consisting of amino acid and derivatives, amines, and combinations thereof.
11. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 10, where the chelator is amino acid or its derivatives selected from the group consisting of glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, valine, leucine, isoleucine, phenylamine, proline, serine, threonine, tyrosine, glutamine, asparagine, glutamic acid, aspartic acid, tryptophan, histidine, arginine, lysine, methionine, cysteine, iminodiacetic acid, and combinations thereof.
12. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 11, where the chelator is a combination of at least two amino acids or their derivatives, wherein the amino acid or its derivatives is selected from the group consisting of glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, valine, leucine, isoleucine, phenylamine, proline, serine, threonine, tyrosine, glutamine, asparagine, glutamic acid, aspartic acid, tryptophan,

histidine, arginine, lysine, methionine, cysteine, iminodiacetic acid, and combinations thereof.

13. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 12, where the chelator is a combination of at least two amino acids or their derivatives selected glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, their derivatives, and combinations thereof.
14. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 13, where concentration of the chelator ranges from 0.1 wt.% to 18 wt.% , 0.5 wt.% to 10 wt.%; or 0.75 wt.% to 2.5 wt.%.
15. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 14, wherein the corrosion inhibitor is a hetero aromatic compound containing nitrogen atom(s) in the aromatic rings.
16. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 15, wherein the corrosion inhibitor is selected from the group consisting of 1,2,4-triazole, benzotriazole and benzotriazole derivatives, tetrazole and tetrazole derivatives, imidazole and imidazole derivatives, benzimidazole and benzimidazole derivatives, pyrazole and pyrazole derivatives, tetrazole and tetrazole derivatives, and combinations thereof.
17. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 16, wherein the corrosion inhibitor is selected from the group consisting of 1,2,4-triazole, benzotriazole and benzotriazole derivatives, and combinations thereof.
18. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 17, wherein concentration of the corrosion inhibitor ranges from 0.005 wt.% to 1.0 wt.%, 0.01 wt.% to 0.5 wt.%, or 0.02 wt.% to 0.2 wt.%.
19. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 18, wherein the biocide comprises ingredient selected from the group consisting of 5-chloro-2-methyl-4-isothiazolin-3-one, 2-methyl-4-isothiazolin-3-one and combinations thereof.

20. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 19, wherein concentration of the biocide ranges from 0.0001 wt.% to 0.05 wt.%, 0.0002 wt.% to 0.025 wt.%, or 0.002 wt.% to 0.01 wt.%.
21. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 20, wherein the oxidizer is a peroxy compound selected from the group consisting of hydrogen peroxide, urea peroxide, peroxyformic acid, peracetic acid, propaneperoxoic acid, substituted or unsubstituted butaneperoxoic acid, hydroperoxy-acetaldehyde, potassium periodate, ammonium peroxymonosulfate; and non-per-oxy compound selected from the group consisting of ferric nitrite,  $\text{KClO}_4$ ,  $\text{KBrO}_4$ ,  $\text{KMnO}_4$ ; and combinations thereof.
22. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 21, wherein the oxidizer is hydrogen peroxide.
23. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 22, wherein concentration of the oxidizer ranges from 0.10 wt.% to 10.00 wt.%, 0.25wt.% to 3.00 wt.%; or 0.50 wt.% to 2.00 wt.%.
24. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 23, wherein the pH adjusting agent is selected from the group consisting of (a) nitric acid, sulfuric acid, tartaric acid, succinic acid, citric acid, malic acid, malonic acid, various fatty acids, various polycarboxylic acids, and mixtures thereof to lower the pH; and (b) potassium hydroxide, sodium hydroxide, ammonia, tetraethylammonium hydroxide, ethylenediamine, piperazine, polyethyleneimine, modified polyethyleneimine, and mixtures thereof to raise the pH.
25. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 24, wherein concentration of the pH adjusting agent ranges from 0.00 wt.% to 1.00 wt.%, 0.01 wt.% to 0.50 wt.%, or 0.10 wt.% to 0.25 wt.%.
26. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 25, wherein the Chemical Mechanical Planarization polishing composition comprises at least one selected from the group consisting of colloidal

silica, fumed silica, silica sol of sodium silicates or potassium silicates; at least one selected from the group consisting of glycine and alanine; at least one selected from the group consisting of 2-(dimethylamino)-2-methyl-1-propanol, 2-amino-2-methyl-1-propanol, 2-amino-2-ethyl-1,3-propanediol, 3-amino-4-octanol, 2-amino-2-hydroxymethyl-1,3-propanediol, 2-amino-2-methyl-1,3-propanediol, 2-amino-1-butanol, and combinations thereof; and has a pH of 5 to 9, or 6 to 8.

27. A Chemical Mechanical Planarization polishing method for polishing a semiconductor substrate comprising at least one surface containing Cu, comprising, consisting essentially of, or consisting of:  
contacting the at least one surface with a polishing pad;  
delivering the chemical mechanical planarization polishing composition according to any one of Claims 1 - 26;  
polishing the at least one surface containing Cu with the chemical mechanical planarization composition.
28. The Chemical Mechanical Planarization polishing method according to claim 27, wherein the semiconductor substrate comprising at least another surface containing a second material; removal selectivity of Cu vs the second material is  $> 1$ ,  $> 5$ , or  $> 6$ ; and the second material is selected from the group consisting of Ta; Ti; TaN; TiN; Ta; TaN; Ti; TiN; SiO<sub>2</sub>, SiN, SiC; and low-k and ultra-low-k material.
29. A Chemical Mechanical Planarization polishing system, comprising:  
a semiconductor substrate comprising at least one surface containing Cu;  
a polishing pad; and  
the chemical mechanical planarization polishing composition according to any one of claims 1 to 26;  
wherein the at least one surface containing Cu is in contact with the polishing pad and the chemical mechanical planarization composition.

30. The Chemical Mechanical Planarization polishing system according to claim 29; wherein the semiconductor substrate comprising at least another surface containing a second material; removal selectivity of Cu vs the second material is  $> 1$ ,  $> 5$ , or  $> 6$ ; and the second material is selected from the group consisting of Ta; Ti; TaN; TiN; Ta; TaN; Ti; TiN; SiO<sub>2</sub>; SiN; SiC; and low-k and ultra-low-k material.