

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
31 March 2011 (31.03.2011)

PCT

(10) International Publication Number
WO 2011/036158 A2

(51) International Patent Classification:
C25D 7/12 (2006.01)

(21) International Application Number:
PCT/EP2010/063929

(22) International Filing Date:
22 September 2010 (22.09.2010)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/246,161 28 September 2009 (28.09.2009) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report (Rule 48.2(g))

(54) Title: **WAFER PRETREATMENT FOR COPPER ELECTROPLATING**

(57) Abstract: The present invention is directed to a pretreatment process for copper electroplating of via or trench features on a wafer, comprising filling the via or trench feature with a pretreatment solution, wherein the pretreatment solution comprises copper ions.



WO 2011/036158 A2

Wafer Pretreatment for Copper Electroplating

Field of the Invention

[0001] The present invention relates to a pretreatment process for copper electroplating of via and trench features on a semiconductor wafer. The process of the invention is particularly suited for plating deep vias (including through silicon vias (TSV)) or trenches, or those with high aspect ratios.

Background of the Invention

[0002] Copper electroplating is one of the key processes for fabricating semiconductor interconnections. During copper electroplating, it is sometimes difficult to achieve ideal fill results for vias, trenches and other connecting structures on a wafer.

[0003] In addition to the processes of chemical formulation and bath composition, the pretreatment process is of critical importance in achieving desired fill yield. The objective of pretreatment is preventing air bubbles from remaining at the bottom of vias.

[0004] It is well understood that it is difficult to remove air from the bottom of a via using an electrolyte solution. US 6,562,222 teaches that acidic copper sulfate electrolytes can easily dissolve the copper seed layers due to the sulfuric acid

contained in the electroplating solution. Thus, current industrial pretreatment practice is to soak the wafer in a surfactant solution or in deionized water prior to copper plating. For example, JP2008001963 discloses a pretreatment solution containing ammonium and surfactants. US 6,491,806 uses deionized water in the wafer pretreatment, eliminating bubbles from the fill water in the vias. During electroplating, copper ions must diffuse from the top of the via or trench to plate the bottom of the via or trench. However, some copper will deposit on the top side wall of the via or trench, due to a higher copper ion concentration near the side walls than at the bottom. This leads to pinching off, causing formation of voids or seams. Additives such as accelerators, suppressors and levelers can inhibit the rate of top and top side wall deposit to achieve void free results. However, with vias of higher aspect ratios, the side wall constricts the copper ion channel, reducing diffusion of copper ions, and increasing the difficulty of preventing voids or seams in the via or trench. Hence, a more robust solution is required.

[0005] US 2007/235343 A1 discloses the pretreatment with a solution comprising a sulfur containing organic compound. Optionally also copper ions may be present in the pretreatment solution in a range of 0.01 to about 5.0 g/l.

3

Summary Of the Invention

[0006] In view of the problems described, the present invention provides a pretreatment process for copper electroplating of via and trench features on a wafer to reduce voids and defects, including filling the via or trench feature with a pretreatment solution, wherein the pretreatment solution comprises copper ions from 10 g/L to 300 g/L.

[0007] The present invention also provides a process for copper plating, a copper electroplating pretreatment solution comprising copper ions and the use of solutions comprising copper ions from 10 g/L to 300 g/L for pretreatment before copper electroplating.

Detailed Description of the Invention

[0008] Due to the above-mentioned concerns and teachings in the prior art, copper electrolytes and copper ions had not previously been considered for use in pretreatment processes for plating vias or trenches. Surprisingly, however, it is found that using a pretreatment solution comprising copper ions in sufficient concentration can effectively eliminate the occurrence of voids or seams when plating copper in vias or trenches of a wafer. After the pretreatment step, the vias and trenches are full of the pretreatment solution. During electroplating, the copper ions left at the bottom of a via

compensate for limited diffusion of copper ions from the electroplating solution to the bottom of the via, and are immediately available as a copper source for plating on the surface of the bottom of the via. Thus, an ideal and desired fill result can be more easily achieved, especially for vias or trenches of greater aspect ratio or depth.

[0009] Because of the copper ions left in vias or trenches, the present invention can reduce the time required for electroplating. Less over-plating and enhanced uniformity can also be achieved. Common step-up current densities for plating are unnecessary and a higher current density can be used from the onset of the plating process. Additionally, a larger range in the quantity of additives in the electroplating solution can be controlled during the electroplating process without causing undesired results.

[0010] The copper electroplating pretreatment solution used in the process of the present invention contains 10 g/L to 300 g/L of copper ions, preferably, 10 g/L to 136 g/L of copper ions, more preferably, 20 g/L to 200 g/L, even more preferably, 30 g/L to 136 g/L. And preferably, the pretreatment solution has a higher copper concentration than the electrolyte used in a copper electroplating process. The electrolyte currently used in a copper electroplating process typically contains copper ions from 30 g/L to 100 g/L.

[0011] Copper ions can be obtained by any source commonly used in the semiconductor field, including but not limited to copper sulfate, copper alkanesulfonate, copper phosphate, copper fluoroborate, and copper cyanide or similar copper salts. Preferably, copper ions may be provided by copper sulfate or copper methanesulfonate.

[0012] Additives such as accelerators (brighteners), suppressors, and levelers are typically included in a copper electroplating solution to improve electroplating behavior by improving surface deposition and thickness uniformity and enhancing chemical reactions and filling of high aspect ratio features.

[0013] Such additives can also be optionally added to the pretreatment solution used in the process of the present invention.

[0014] Accelerators (or brighteners) are used for accelerating size reduction of deposited particles. The accelerator typically is sulfur-containing organic compounds and relatively increases rate of copper deposition in a pattern on which a trench with a narrow width is formed. Examples of suitable accelerators are set forth in US 6,679,983 including n,n-dimethyl-dithiocarbamic acid-(3-sulfopropyl)ester; 3-mercapto-propylsulfonic acid-(3-sulfopropyl)ester; 3-mercaptopropylsulfonic acid (sodium salt); carbonic acid-dithio-

o-ethylester-s-ester with 3-mercapto-1-propane sulfonic acid (potassium salt); bissulfopropyl disulfide; 3-(benzthiazolyl-s-thio)propyl sulfonic acid (sodium salt); pyridinium propyl sulfobetaine; 1-sodium-3-mercaptopropane-1-sulfonate; disodium bis-(3-sulfopropyl) disulfide; or mixtures thereof. Preferably, the accelerator comprises disodium bis-(3-sulfopropyl) disulfide. The concentration of the accelerator in the pretreatment solution of the present invention is preferably from 0 mL/L to about 50 mL/L, more preferably from 0 mL/L to 35 mL/L. The concentration of the active compound of the accelerator in the pretreatment solution of the present invention is preferably from 0 ppm to 400 ppm.

[0015] Suppressors are used for increasing an over voltage for depositing a plating copper at more uniform electrodeposition. Suppressors for copper electroplating are generally oxygen-containing high molecular weight compounds. Suitable suppressors include, but are not limited to, carboxymethylcellulose, nonylphenolpolyglycol ether, octandiolbis-(polyalkylene glycolether), octanolpolyalkylene glycolether, oleic acidpolyglycol ester, polyethylenepropylene glycol, polyethylene glycol, polyethylene glycoldimethylether, polyoxypropylene glycol, polypropylene glycol, polyvinylalcohol, stearic acidpolyglycol ester, polyethylene oxide, stearyl alcoholpolyglycol ether, and the like. Preferably, the

suppressor comprises poly(ethylene oxide-propylene oxide). The concentration of the suppressor in the pretreatment solution of the present invention is preferably from 0 mL/L to about 40 mL/L, more preferably from 0 mL/L to about 30 mL/L. The concentration of the active compound of the suppressor in the pretreatment solution of the present invention is preferably from 0 ppm to 600 ppm.

[0016] Preferably, the pretreatment solution is essentially free of any accelerator, i.e. any sulfur-containing organic compound. "Essentially free of any sulfur containing organic compound" means that the solution comprises less than 0.1 mg/L, preferably less than 0.01 mg/L, most preferably less than 0.001 mg/l of a sulfur containing organic compound.

[0017] Levelers are used for reducing surface roughness. They are similar to suppressors in that they reduce deposition rate. Levelers for copper electroplating generally comprise nitrogen-containing organic compounds. Compounds with an amino group or substituted amino groups are commonly used. Such compounds are disclosed in US 4,376,685, US 4,555,315, and US 3,770,598.

Examples include 1-(2-hydroxyethyl)-2-imidazolidinethione; 4-mercaptopyridine; 2-mercaptothiazoline; ethylene thiourea; thiourea; alkylated polyalkyleneimine. Preferably, the leveler is 1-(2-hydroxyethyl)-2-imidazolidinethione. The concentration of the leveler in the pretreatment solution of the present

invention is preferably from 0 mL/L to about 50 mL/L, more preferably from 0 to about 40 mL/L. The concentration of the active compound of the leveler in the pretreatment solution of the present invention is from 0 ppm to 500 ppm.

[0018] The pretreatment solution of the present invention may also comprise a surfactant. The surfactant is used to lower the surface tension of the solution. Useful surfactants include high molecular weight polymers, modified polyacrylic polymer, modified polysiloxane, preferably polyglycol type polymers and co-polymers. The concentration of surfactant in the pretreatment solution may range from 0 wt% to 3 wt%.

[0019] The pretreatment solution of the present invention may also comprise an acid. The acid can be selected from the group consisting of sulfuric acid, alkanesulfonic acids (such as methanesulfonic acid, ethanesulfonic acid, propanesulfonic acid and trifluoro-methanesulfonic acid), sulfamic acid; hydrochloric acid; hydrobromic acid; and fluoroboric acid and mixture thereof. Preferably, the acid is sulfuric acid, methanesulfonic acids or hydrochloric acid. The concentration of the acid is from 0 mL/L to about 40 mL/L.

[0020] According to one aspect of the present invention, the via or trench feature being plated has an aspect ratio greater than 2:1, preferably 3:1 to 40:1. According to another aspect, the

via or trench feature has a depth of more than 10 micrometers, preferably 10 micrometers to 300 micrometers.

[0021] According to a further aspect of the present invention, the process of the subject invention can further comprise a water rinse step or spin dry step to remove the pretreatment solution from the surface of the wafer.

EXAMPLES AND COMPARATIVE EXAMPLES

[0022] Examples of the present invention and comparative examples will be described. These examples illustrate only preferable embodiments of the present invention, and the present invention is not limited to these examples.

[0023] The examples show the pretreatment solutions, electroplating solutions, and via patterns. In each example, the test wafer was pretreated with the pretreatment solution and then immersed in deionized water (DI water) for about 2 seconds. The "pretreated" here means, for example, contacted, wetted or rinsed. For comparative examples 1 and 3, the step of immersing in DI water was omitted because the pretreatment solutions in both cases were ultra pure water. The wafer was then immersed in the electroplating solution for plating. The anode was a copper anode. Except for Examples 15 and 16 and Comparative Examples 5 and 6, the power supply supplied an average current density of 0.3 ASD (Ampere per square decimeter). Plating was continued for about 40 minutes. For Example 15 and Comparative

10

Example 5 the power supply supplied an average current density of 0.1 ASD. Plating was continued for about 30 minutes. For Example 16 and Comparative Examples 6 the power supply supplied an average current density of 0.8 ASD. Plating was continued for about 30 minutes.

Comparative Example 1

[0024] Pretreatment solution: ultra pure water.

[0025] Electroplating solution: CuPurTM T 1000 (copper sulfate, copper ion concentration 40 g/L), CuPurTM T 2000 additive 15 mL/L (as an accelerator available from BASF), CuPurTM T 3000 additive 5 mL/L (as a suppressor available from BASF), CuPurTM T 4000 additive 5 mL/L (as a leveler available from BASF).

[0026] The vias had an aspect ratio of 8:1 (depth:opening diameter), resulting from an opening having a diameter of 6 micrometers and a depth of 50 micrometers. The plating result showed voids in the bottom.

Example 1

[0027] Pretreatment solution: copper sulfate with copper ion concentration 10 g/L.

[0028] Electroplating solution: CuPurTM T 1000 (copper sulfate, copper ion concentration 40 g/L), CuPurTM T 2000 additive 15 mL/L (as an accelerator available from BASF), CuPurTM T 3000 additive 5 mL/L (as a suppressor available from BASF), CuPurTM T 4000 additive 5 mL/L (as a leveler available from BASF).

11

[0029] The vias had an aspect ratio of 8:1 (depth:opening diameter), resulting from an opening having a diameter of 6 micrometers and a depth of 50 micrometers. The plating result was void-free and seam-free.

Example 2

[0030] Pretreatment solution: copper sulfate with copper ion concentration 40 g/L.

[0031] Electroplating solution: CuPurTM T 1000 (copper sulfate, copper ion concentration 40 g/L), CuPurTM T 2000 additive 15 mL/L (as an accelerator available from BASF), CuPurTM T 3000 additive 5 mL/L (as a suppressor available from BASF), CuPurTM T 4000 additive 5 mL/L (as a leveler available from BASF).

[0032] The vias had an aspect ratio of 8:1 (depth:opening diameter), resulting from an opening having a diameter of 6 micrometers and a depth of 50 micrometers. The plating result was void-free and seam-free.

Example 3

[0033] Pretreatment Solution: copper sulfate with copper ion concentration 80 g/L.

[0034] Electroplating solution: CuPurTM T 1000 (copper sulfate, copper ion concentration 40 g/L), CuPurTM T 2000 additive 15 mL/L (as an accelerator available from BASF), CuPurTM T 3000 additive 5 mL/L (as a suppressor available from BASF), CuPurTM T 4000 additive 5 mL/L (as a leveler available from BASF).

12

[0035] The vias had an aspect ratio of 8:1 (depth:opening diameter), resulting from an opening having a diameter of 6 micrometers and a depth of 50 micrometers. The plating result was void-free and seam-free.

Example 4

[0036] Pretreatment solution: copper methanesulfonate with copper ion concentration 90 g/L.

[0037] Electroplating solution: CuPurTM T 1000 (copper sulfate, copper ion concentration 40 g/L), CuPurTM T 2000 additive 15 mL/L (as an accelerator available from BASF), CuPurTM T 3000 additive 5 mL/L (as a suppressor available from BASF), CuPurTM T 4000 additive 5 mL/L (as a leveler available from BASF).

[0038] The vias had an aspect ratio of 8:1 (depth:opening diameter), resulting from an opening having a diameter of 6 micrometers and a depth of 50 micrometers. The plating result was void-free and seam-free.

Example 5

[0039] Pretreatment Solution: copper methanesulfonate with copper ion concentration 120 g/L.

[0040] Electroplating solution: CuPurTM T 1000 (copper sulfate, copper ion concentration 40 g/L), CuPurTM T 2000 additive 15 mL/L (as an accelerator available from BASF), CuPurTM T 3000 additive 5 mL/L (as a suppressor available from BASF), CuPurTM T 4000 additive 5 mL/L (as a leveler available from BASF).

13

[0041] The vias had an aspect ratio of 8:1 (depth:opening diameter), resulting from an opening having a diameter of 6 micrometers and a depth of 50 micrometers. The plating result was void-free and seam-free.

Example 6

[0042] Pretreatment solution: copper methanesulfonate with copper ion concentration 136 g/L.

[0043] Electroplating solution: CuPurTM T 1000 (copper sulfate, copper ion concentration 40 g/L), CuPurTM T 2000 additive 15 mL/L (as an accelerator available from BASF), CuPurTM T 3000 additive 5 mL/L (as a suppressor available from BASF), CuPurTM T 4000 additive 5 mL/L (as a leveler available from BASF).

[0044] The vias had an aspect ratio of 8:1 (depth:opening diameter), resulting from an opening having a diameter of 6 micrometers and a depth of 50 micrometers. The plating result was void-free and seam-free.

Comparative Example 2

[0045] Pretreatment solution: CuPurTM T5000 (0.3% surfactant; available from BASF).

[0046] Electroplating solution: CuPurTM T 1000 (copper sulfate, copper ion concentration 40 g/L), CuPurTM T 2000 additive 15 mL/L (as an accelerator available from BASF), CuPurTM T 3000 additive 5 mL/L (as a suppressor available from BASF), CuPurTM T 4000 additive 5 mL/L (as a leveler available from BASF).

14

[0047] The vias had an aspect ratio of 10:1 (depth:opening diameter), resulting from an opening having a diameter of 6 micrometers and a depth of 60 micrometers. The plating result showed voids in the bottom.

Comparative Example 3

[0048] Pretreatment solution: ultra pure water.

[0049] Electroplating solution: CuPurTM T 1010 (copper methanesulfonate, copper ion concentration 90 g/L), CuPurTM T 2000 additive 12 mL/L (as an accelerator available from BASF), CuPurTM T 3000 additive 6 mL/L (as a suppressor available from BASF), CuPurTM T 4000 additive 16 mL/L (as a leveler available from BASF).

[0050] The vias had an aspect ratio of 8:1 (depth:opening diameter), resulting from an opening having a diameter of 6 micrometers and a depth of 50 micrometers. The plating result showed voids in the bottom.

Comparative Example 4

[0051] Pretreatment Solution: CuPurTM T5000 (0.3% surfactant; available from BASF).

[0052] Electroplating solution: CuPurTM T 1010 (copper methanesulfonate, copper ion concentration 90 g/L), CuPurTM T 2000 additive 12 mL/L (as an accelerator available from BASF), CuPurTM T 3000 additive 6 mL/L (as a suppressor available from

15

BASF), CuPurTM T 4000 additive 16 mL/L (as a leveler available from BASF).

[0053] The vias had an aspect ratio of 10:1 (depth:opening diameter), resulting from an opening having a diameter of 6 micrometers and a depth of 60 micrometers. The plating result showed voids in the bottom.

Example 7

[0054] Pretreatment solution: copper sulfate with copper ion concentration 40 g/L, sulfuric acid 10 g/L, and chloride ion 50 ppm.

[0055] Electroplating solution: CuPurTM T 1000 (copper sulfate, copper ion concentration 40 g/L), CuPurTM T 2000 additive 15 mL/L (as an accelerator available from BASF), CuPurTM T 3000 additive 5 mL/L (as a suppressor available from BASF), CuPurTM T 4000 additive 5 mL/L (as a leveler available from BASF).

[0056] The vias had an aspect ratio of 8:1 (depth:opening diameter), resulting from an opening having a diameter of 6 micrometers and a depth of 50 micrometers. The plating result was void-free and seam-free.

Example 8

[0057] Pretreatment solution: copper sulfate with copper ion concentration 40 g/L, CuPurTM T 2000 additive 15 mL/L (as an accelerator available from BASF), CuPurTM T 3000 additive 5 mL/L

16

(as a suppressor available from BASF), CuPur™ T 4000 additive 5 mL/L (as a leveler available from BASF).

[0058] Electroplating solution: CuPur™ T 1000 (copper sulfate, copper ion concentration 40 g/L), CuPur™ T 2000 additive 15 mL/L (as an accelerator available from BASF), CuPur™ T 3000 additive 5 mL/L (as a suppressor available from BASF), CuPur™ T 4000 additive 5 mL/L (as a leveler available from BASF).

[0059] The vias had an aspect ratio of 8:1 (depth:opening diameter), resulting from an opening having a diameter of 6 micrometers and a depth of 50 micrometers. The plating result was void-free and seam-free.

Example 9

[0060] Pretreatment solution: copper methanesulfonate with copper ion concentration 90 g/L, methanesulfonic acid 5 mL/L.

[0061] Electroplating solution: CuPur™ T 1000 (copper sulfate, copper ion concentration 40 g/L), CuPur™ T 2000 additive 15 mL/L (as an accelerator available from BASF), CuPur™ T 3000 additive 5 mL/L (as a suppressor available from BASF), CuPur™ T 4000 additive 5 mL/L (as a leveler available from BASF).

[0062] The vias had an aspect ratio of 8:1 (depth:opening diameter), resulting from an opening having a diameter of 6 micrometers and a depth of 50 micrometers. The plating result was void-free and seam-free.

Example 10

17

[0063] Pretreatment solution: copper methanesulfonate with copper ion concentration 90 g/L, CuPur™ T 2000 additive 15 mL/L (as an accelerator available from BASF), CuPur™ T 3000 additive 2 mL/L (as a suppressor available from BASF).

[0064] Electroplating solution: CuPur™ T 1000 (copper sulfate, copper ion concentration 40 g/L), CuPur™ T 2000 additive 15 mL/L (as an accelerator available from BASF), CuPur™ T 3000 additive 5 mL/L (as a suppressor available from BASF), CuPur™ T 4000 additive 5 mL/L (as a leveler available from BASF).

[0065] The vias had an aspect ratio of 8:1 (depth:opening diameter), resulting from an opening having a diameter of 6 micrometers and a depth of 50 micrometers. The plating result was void-free and seam-free.

Example 11

[0066] Pretreatment solution: copper methanesulfonate with copper ion concentration 90 g/L, CuPur™ T 2000 additive 12 mL/L (as an accelerator available from BASF), CuPur™ T 3000 additive 2 mL/L (as a suppressor available from BASF), and surfactant (0.2 w%).

[0067] Electroplating solution: copper methanesulfonate (copper ion concentration 90 g/L), CuPur™ T 2000 additive 12 mL/L (as an accelerator available from BASF), CuPur™ T 3000 additive 6 mL/L (as a suppressor available from BASF), CuPur™ T 4000 additive 16 mL/L (as a leveler available from BASF).

18

[0068] The vias had an aspect ratio of 10:1 (depth:opening diameter), resulting from an opening having a diameter of 6 micrometers and a depth of 60 micrometers. The plating result was void-free and seam-free.

Example 12

[0069] Pretreatment solution: copper methanesulfonate with copper ion concentration 120 g/L, CuPurTM T 2000 additive 15 mL/L (as an accelerator available from BASF), CuPurTM T 3000 additive 2 mL/L (as a suppressor available from BASF), and surfactant (0.2 w%).

[0070] Electroplating solution: CuPurTM T 1000 (copper sulfate, copper ion concentration 40 g/L), CuPurTM T 2000 additive 15 mL/L (as an accelerator available from BASF), CuPurTM T 3000 additive 5 mL/L (as a suppressor available from BASF), CuPurTM T 4000 additive 5 mL/L (as a leveler available from BASF).

[0071] The vias had an aspect ratio of 10:1 (depth:opening diameter), resulting from an opening having a diameter of 6 micrometers and a depth of 60 micrometers. The plating result was void-free and seam-free.

Example 13

[0072] Pretreatment Solution: copper methanesulfonate with copper ion concentration 120 g/L, CuPurTM T 2000 additive 15 mL/L (as an accelerator available from BASF), CuPurTM T 3000 additive

19

2 mL/L (as a suppressor available from BASF), and surfactant (0.2 w%).

[0073] Electroplating solution: copper methanesulfonate (copper ion concentration 90 g/L), CuPur™ T 2000 additive 12 mL/L (as an accelerator available from BASF), CuPur™ T 3000 additive 6 mL/L (as a suppressor available from BASF), CuPur™ T 4000 additive 16 mL/L (as a leveler available from BASF).

[0074] The vias had an aspect ratio of 4:1 (depth:opening diameter), resulting from an opening having a diameter of 30 micrometers and a depth of 150 micrometers. The plating result was void-free and seam-free.

Example 14

[0075] Pretreatment Solution: copper methanesulfonate with copper ion concentration 180 g/L, CuPur™ T 2000 additive 15 mL/L (as an accelerator available from BASF), CuPur™ T 3000 additive 2 mL/L (as an suppressor available from BASF), CuPur™ T 4000 additive 2 mL/L (as a leveler available from BASF), and surfactant (0.2 w%).

[0076] Electroplating solution: copper methanesulfonate (copper ion concentration 90 g/L), CuPur™ T 2000 additive 12 mL/L (as an accelerator available from BASF), CuPur™ T 3000 additive 6 mL/L (as a suppressor available from BASF), CuPur™ T 4000 additive 16 mL/L (as a leveler available from BASF).

20

[0077] The vias had an aspect ratio of 10:1 (depth:opening diameter), resulting from an opening having a diameter of 6 micrometers and a depth of 60 micrometers. The plating result was void-free and seam-free.

Comparative Example 5

[0078] Pretreatment Solution: copper sulfate with copper ion concentration 0.67 g/L (10.6 mmol/L), CuPur™ T 2000 additive 1.06 g/L (3 mmol/L) (as an accelerator available from BASF).

[0079] Electroplating solution: copper methanesulfonate (copper ion concentration 90 g/L), CuPur™ T 2000 additive 12 mL/L (as an accelerator available from BASF), CuPur™ T 3000 additive 6 mL/L (as a suppressor available from BASF), CuPur™ T 4000 additive 16 mL/L (as a leveler available from BASF).

[0080] The vias had an aspect ratio of 6:1 (depth:opening diameter), resulting from an opening having a diameter of 10 micrometers and a depth of 60 micrometers. The cross section of the features showed bottom voids.

Example 15

[0081] Pretreatment Solution: copper sulfate with copper ion concentration 60 g/L.

[0082] Electroplating solution: copper methanesulfonate (copper ion concentration 90 g/L), CuPur™ T 2000 additive 12 mL/L (as an accelerator available from BASF), CuPur™ T 3000 additive 6 mL/L

21

(as a suppressor available from BASF), CuPur™ T 4000 additive 16 mL/L (as a leveler available from BASF).

[0083] The vias had an aspect ratio of 6:1 (depth:opening diameter), resulting from an opening having a diameter of 10 micrometers and a depth of 60 micrometers. The cross section of the features was void-free and seam free.

Comparative Example 6

[0084] Pretreatment Solution: copper sulfate with copper ion concentration 0.67 g/L (10.6 mmol/L), CuPur™ T 2000 additive 1.06 g/L (3 mmol/L) (as an accelerator available from BASF).

[0085] Electroplating solution: copper sulfate (copper ion concentration 40 g/L), CuPur™ T 2000 additive 15 mL/L (as an accelerator available from BASF), CuPur™ T 3000 additive 5 mL/L (as a suppressor available from BASF), CuPur™ T 4000 additive 10 mL/L (as a leveler available from BASF).

[0086] Two trenches were tested. A 10 micrometer trench had an aspect ratio of 11:2 (depth:width), resulting from a width of 10 micrometers and a depth of 55 micrometers. A 20 micrometer trench had an aspect ratio of 13:2 (depth:width), resulting from a width of 20 micrometers and a depth of 65 micrometers. The cross section of the features showed bottom defects.

Example 16

[0087] Pretreatment Solution: copper sulfate with copper ion concentration 60 g/L.

22

[0088] Electroplating solution: copper sulfate (copper ion concentration 40 g/L), CuPurTM T 2000 additive 15 mL/L (as an accelerator available from BASF), CuPurTM T 3000 additive 5 mL/L (as a suppressor available from BASF), CuPurTM T 4000 additive 10 mL/L (as a leveler available from BASF).

[0089] Two trenches were tested. The 10 micrometer trench had an aspect ratio of 11:2 (depth:width), resulting from a width having 10 micrometers and a depth of 55 micrometers. The 20 micrometer trench had an aspect ratio of 13:2 (depth: width), resulting from a width having 20 micrometers and a depth of 65 micrometers. The cross section of the features was defect-free and seam-free.

[0090] The final filling features of the examples and comparative examples were checked by cleavage cross-sectional optical microscope or scanning electron microscope (SEM) and in some case by using focused ion beam (FIB) for double confirmation of the observation, and the results are shown in TABLE 1. The results show that the present invention has an excellent effect in eliminating occurrence of voids and seams in the filling result.

TABLE 1

No.	Aspect ratio	Filling result
Comparative Example 1	8:1	Voids occurred

Comparative Example 2	10:1	Voids occurred
Comparative Example 3	8:1	Voids occurred
Comparative Example 4	10:1	Voids occurred
Example 1	8:1	Void-free and seam-free
Example 2	8:1	Void-free and seam-free
Example 3	8:1	Void-free and seam-free
Example 4	8:1	Void-free and seam-free
Example 5	8:1	Void-free and seam-free
Example 6	8:1	Void-free and seam-free
Example 7	8:1	Void-free and seam-free
Example 8	8:1	Void-free and seam-free
Example 9	8:1	Void-free and seam-free
Example 10	8:1	Void-free and seam-free
Example 11	10:1	Void-free and seam-free
Example 12	10:1	Void-free and seam-free
Example 13	4:1	Void-free and seam-free
Example 14	10:1	Void-free and seam-free
Comparative Example 5	6:1	Voids occurred
Comparative Example 6	13:2	Defects occurred
Example 15	6:1	Void-free and seam-free
Example 16	13:2	Defect-free and seam-free

[0091] Holding other parameters constant, Table 2 shows the filling results for different concentrations of copper ions in the pretreatment solution. The results clearly show that a pretreatment solution of the present invention comprising any of the tested concentrations of copper ions will eliminate occurrence of voids or seams. In Comparative Examples 5 and 6 the same concentrations of copper ions and accelerator as used in Example 1 of US 2007/235343 were used. The experiments were repeated in examples 15 and 16, respectively, however, without accelerator and higher copper concentrations.

TABLE 2

No.	[Cu ²⁺] g/L	Copper source	Filling Result
Comparative 1	0	--	Voids occurred
Comparative 5	0.67	Copper sulfate	Voids occurred
Comparative 6	0.67	Copper sulfate	Defects occurred
Example 1	10	Copper sulfate	Void-free and seam-free
Example 2	40	Copper sulfate	Void-free and seam-free
Example 3	80	Copper sulfate	Void-free and seam-free

Example 4	90	Copper	25	Void-free and seam-free
			methanesulfonate	
Example 5	120	Copper		Void-free and seam-free
			methanesulfonate	
Example 6	136	Copper		Void-free and seam-free
			methanesulfonate	
Example 15	90	Copper sulfate		Void-free and seam-free
Example 16	40	Copper sulfate		Defect-free and seam-
				free

[0092] The invention is not limited by the embodiments described above, which are presented as examples only, and can be modified in various ways within the scope of protection defined by the appended patent claims.

What is claimed is:

1. A pretreatment process for copper electroplating of a via or trench feature on a wafer comprising:

filling the via or trench feature with a pretreatment solution, wherein the pretreatment solution comprises copper ions from 10 g/L to 300 g/L.

2. The process of Claim 1 wherein the pretreatment solution has a copper concentration higher than that of the electroplating solution used in a copper electroplating process.

3. The process according to anyone of the preceding Claims wherein the pretreatment solution is essentially free of any sulfur-containing organic compound.

4. The process according to Claim 3 wherein the concentration of copper ions ranges from 30 g/L to 136 g/L.

5. The process according to anyone of the preceding Claims wherein the pretreatment solution further comprises an additive.

6. The process of Claim 5 wherein the additive is an accelerator, a suppressor, a leveler, a surfactant, an acid or mixtures thereof.

7. The process of Claim 6, wherein the concentration of the accelerator is from 0 mL/L to about 50 mL/L.

8. The process of Claim 6, wherein the concentration of the active compound of the accelerator is from 0 ppm to 400 ppm.

9. The process of Claim 6, wherein the concentration of the suppressor is from 0 mL/L to about 40 mL/L.

10. The process of Claim 6, wherein the concentration of the active compound of the suppressor is from 0 ppm to 600 ppm.

11. The process of Claim 6, wherein the concentration of the leveler is from 0 mL/L to about 50 mL/L.

12. The process of Claim 6, wherein the concentration of the active compound of the leveler is from about 0 ppm to 500 ppm.

13. The process of Claim 6, wherein the concentration of the surfactant is from 0 wt% to about 3 wt%.

14. The process of Claim 6, wherein the acid is selected from the group consisting of sulfuric acid, alkanesulfonic acids, sulfamic acid, hydrochloric acid, hydrobromic acid, fluoroboric acid, and mixtures thereof.

15. The process of Claim 14, wherein the acid is sulfuric acid, methanesulfonic acid or hydrochloric acid.

16. The process of Claim 6, wherein the concentration of the acid is from 0 mL/L to about 40 mL/L.

17. The process according to anyone of the preceding Claims wherein the via or trench feature has an aspect ratio greater than 2:1.

18. The process according to anyone of the preceding Claims wherein the via or trench feature has a depth of more than 10 microns.

19. The process according to anyone of the preceding Claims, further comprising a water rinse step or spin dry step to remove the pretreatment solution from the surface of the wafer.

20. A process for copper electroplating of a via or trench feature on a wafer comprising:

pretreating the via or trench feature according to anyone of the preceding claims,

contacting the via or trench feature with a copper electroplating solution, and

applying a current density to the wafer for a time sufficient to deposit a copper layer onto the substrate.

21. A copper electroplating pretreatment solution for a via or trench feature on a wafer, comprising copper ions from 10 g/L to 300 g/L.

22. Use of a solution comprising copper ions from 10 g/L to 300 g/L for pretreatment of a via or trench feature on a wafer before electrodeposition of copper into the feature.