TITLE OF THE INVENTION:

Chemical Mechanical Planarization Polishing for Interconnects Diffusion Barrier Materials

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. provisional applications 63/633,249 filed on April 12, 2024, the entire contents of which is incorporated herein by reference thereto for all allowable purposes.

BACKGROUND OF THE INVENTION

[0002] This invention relates to chemical mechanical planarization (CMP) polishing of diffusion barrier materials (such as ruthenium) for metal interconnects (such as copper) in semiconductor manufacture. The CMP compositions, formulations, or slurries (they are used interchangeably), the method and the system of using the compositions have been disclosed.

[0003] Chemical mechanical planarization (CMP) is an important step in the manufacturing process of transistors.

[0004] These are different types of layers and/or materials that need to be polished. The interlayer dielectrics (ILD) comprise dielectric materials such as silicon oxide, silicon nitride, etc. The metal interconnects comprise metals such as tungsten, copper, aluminum, etc.. The diffusion barrier materials such as ruthenium, cobalt, Ta, etc..

[0005] The polishing process enables the creation of smooth, defects free layers that are later being covered with other layers to produce the stack. The polishing of the layers is done in a chemical mechanical process using a water-based composition that contains several components such as abrasive particles, oxidant, catalyst, stabilizers, ligands, and other additives as described in International journal of precision engineering and manufacturing, 2016, 17(12), 1751.

[0006] During the polishing process of metal layer, the metal surface is oxidized resulting in more brittle layer that can be removed by friction with the abrasive material. Then, a second layer is oxidized and removed in a repeating cycle.

[0007] In the field of electronic interconnects, aluminum was replaced by copper to meet the size reduction according to Moore's law as described in Journal of The Electrochemical Society, 2019, 166 (1), D3219-D3225. Copper's advantages over aluminum are lower resistivity (which implies less power dissipation and lower RC delays) and an improved resistance to electromigration.

[0008] Introduction of copper on low-K dielectrics like Si poses a new problem: interdiffusion of Cu atoms into Si. Thus, a diffusion barrier layer is required to prevent dielectric leakage. Ruthenium (Ru) is one of the most desirable metals for barrier layer due to its hardness (provides wear protection of electrical contacts), high melting point, low resistivity in comparison to Tantalum(Ta), and its good adhesion to Cu as described in RSC Adv., 2022, 12, 228.

[0009] Ru removal rate (RR) is usually very low due to the hardness of the oxidized layer as described in ECS Journal of Solid-State Science and Technology, 2017, 6 (8) P521-P525. To increase the RR, it is custom to add a chelator which will increase the dissolution of the oxide layer into the solution and increase the corrosion of Ru. Several chelators were mentioned in the literature such as ethylene diamine, 5-methylbenzotriazole, dodecyl benzene sulfonate, FA/O chelator (Ethylenediaminetetraacetic Acid) and guanidine carbonate as described in the literatures listed above and in Journal of Semiconductors, 2015, 36 (7), 076002-1 and US2023052829. However, these chelators have disadvantage such as insufficient removal rate (RR) and/or toxicity.

[0010] There is a significant need for barrier metal CMP compositions that can afford high removal rates of ruthenium or other barrier metals and the removal rates are tunable relative to the removal rates of other materials (e.g., copper, dielectric, et al). This is especially significant since barrier layer polishing is increasingly used in semiconductor manufacture as this industry continues to move towards smaller and smaller feature sizes.

SUMMARY OF THE INVENTION

[0011] The present invention satisfies the need by providing a new family of chelators to increase the removal rate of barrier metals such as Ru. These chelators are cyclic molecules containing at least one N-C-C-N bond where the bond between N and C can be either single or double bond. Those chelators can complex the Ru

ion and stabilize it in solution. All chelators in this family are less toxic than what have been taught in the literature.

[0012] In one aspect (Aspect 1), there is provided a CMP polishing composition comprising, consisting essentially of, or consisting of:

a) abrasive;

b) cyclic chelator comprising at least one N-C-C-N group and at least one cyclic ring wherein the bond between N and C can be either single or double bond;

c) oxidizer; and

d) water-soluble solvent ;

optionally at least one of

e) corrosion inhibitor;

f) chemical additive;

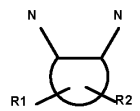
g) biocide;

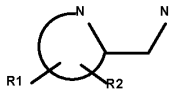
h) and

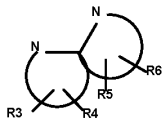
i) pH adjusting agent.

[0013] 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. Abrasive particles comprise silica are preferred.

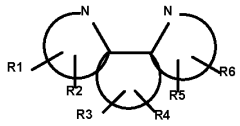
[0014] The cyclic chelator comprising at least one N-C-C-N group and at least one cyclic ring is selected from the group consisting of cyclopentane, cyclohexane, cyclohexadiene, cyclopentadiene, phenanthroline, benzene, pyridine, pyrimidine, pyrazine, terpyridine, azepine, diazepine, indazole, pyrazole, triazole, tetrazole ring, and combinations thereof; and the cyclic chelator has a structure selected from the group consisting of:

a. 

, b. 

, c. 

,

d. 

, and combinations thereof;

wherein each cyclic ring structure contains at least two R groups and each of the R: R_1, R_2, R_3, R_4, R_5 and R_6 independently includes but is not limited to H; OH; CH_3; NH_2; secondary or tertiary amine; NO; NO_2; acid includes but is not limited to COOH, SO_3H, PO_3H and their salt; CN; SCN; NCS; amide; ketone; aldehyde; ester; ether; thiol; alkyl chains having 2-6 carbons; alkyl alcohols; cyclic group includes but is not limited to cyclopentane, cyclohexane, cyclohexadiene, cyclopentadiene, phenanthroline, benzene, pyridine, pyrimidine, pyrazine, terpyridine, azepine, diazepine, indazole, pyrazole, triazole, tetrazole ring, or combination of those rings; the bond between N and C in the N-C-C-N group can be either single or double bond; and the cyclic rings in structures c. and d. can be bonded in any way, including but not limited to through conjugation, at least one single bond, at least one double bond, or combinations of single and double bonds.

[0015] Preferably, R groups are polar groups to improve solubility.

[0016] The 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, $KClO_4$, $KBrO_4$, $KMnO_4$; and combinations thereof.

[0017] The corrosion inhibitor includes but is 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.

[0018] The chemical additive includes but is not limited to a chelator which is not a cyclic chelator comprising at least one N-C-C-N group and at least one cyclic ring, such as an inorganic silicate, examples are potassium silicate, sodium silicate, and ammonium silicate; ammonium hydroxide; and combinations thereof; a dispersing agent includes but is not limited to polyacrylic acid and its salts, an example is polyacrylic acid ammonium salt.

[0019] A 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] The corrosion inhibitor can be any corrosion inhibitor which prevents corrosion and attain global flatness on the wafer surface. The corrosion inhibitor includes but is not limited to hetero aromatic compounds containing nitrogen atom(s) in their aromatic rings. The corrosion inhibitor can be triazole or/and non-triazole corrosion inhibitor. The corrosion inhibitor includes but is not limited to 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; and non-triazole corrosion inhibitor disclosed in US 63/554,451, which is incorporated herein by reference in its entirety.

[0021] A biocide includes but is not limited to Neolone™ M10, a methyl isothiazolinone-based biocide from DuPont; Kathon™, Kathon™ CG/ICP II, from Dow Chemical Co. They have active ingredients of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one.

[0022] The pH adjusting agent includes but is not limited to nitric acid, sulfuric acid, tartaric acid, succinic acid, citric acid, malic acid, malonic acid, various fatty acids, various polycarboxylic acids, potassium hydroxide, sodium hydroxide, ammonia, tetraethylammonium hydroxide, piperazine, polyethyleneimine, modified polyethyleneimine, and mixtures thereof to adjust the pH.

[0023] pH of the CMP polishing composition is ≥ 5, ≥ 6, ≥ 7, or ≥ 8; such as 5 to 12, 6 to 12, 7 to 12, 8 to 12, 5 to 11, 6 to 11, 7 to 11 or 8 to 11.

[0024] The water-soluble solvent includes but is not limited to deionized (DI) water, distilled water, organic alcohols, and combinations thereof. DI water is preferred.

[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 Ru or other diffusion barrier metals; comprising, consisting essentially of, or consisting of the steps of:

providing the chemical mechanical planarization polishing composition of Aspect 1;

providing a polishing pad;

contacting the at least one surface containing Ru or other diffusion barrier metals with the polishing pad and the chemical mechanical planarization polishing composition;

polishing the at least one surface containing Ru or other diffusion barrier metals.

[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 Ru or other diffusion barrier metals.
a polishing pad; and
the chemical mechanical planarization composition of Aspect 1;
wherein the at least one surface containing Ru or other diffusion barrier metals 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 patten wafer together with Ru; includes but is not limited to Cu, Ta; Ti; TaN; TiN; Ta; TaN; Ti; TiN; dielectric materials such as SiO_2, SiN, SiC; and low-k and ultra-low-k materials; such as different Black Diamon™ films.

[0028] Other aspects, features and embodiments of the invention will be more fully apparent from the ensuing disclosure and appended claims. The embodiments of the invention can be used alone or in combinations with each other.

BRIEF DESCRIPTION OF THE DRAWING

[0029] Fig. 1 depicts the Tafel plot for Ru with the presence of Ru chelator (dashed lines) and without the presence of Ru chelator (solid line).

DETAILED DESCRIPTION OF THE INVENTION

[0030] In the field of CMP, smooth polishing of different layers is required to produce the semiconductor stack. Ru is used as diffusion barrier layer metal to prevent interdiffusion of Cu atoms into Si. It is known in the art that the CMP removal rate(RR) of Ru is low due to the hardness of its oxide layer.

[0031] The present invention discloses a family of new chelators used in the CMP polishing compositions, to increase the dissolution of RuO_x into the solution, and thus ultimately to increase the RR of Ru.

[0032] Specifically, the chelators are cyclic molecules containing at least one N-C-C-N group and at least one cyclic ring where the bond between N and C can be either single or double bond which can complex the Ru ion and stabilize it in solution. The chelators contain at least 2 N atoms to improve chelation.

[0033] Without wishing to be bound by theory, it has been hypothesized that the chelators containing at least one cyclic ring in combination with at least N-C-C-N group increase the Ru chelation ability, the corrosion of the Ru layer and the dissolution of Ru ions into the solution; and thus increases the RR of Ru.

[0034] According to the Material Safety Data Sheet(SDS) from the manufactures, all disclosed chelators in this family are less toxic than what have been taught in the literature.

[0035] In one aspect (Aspect 1), there is provided a CMP polishing composition comprising, consisting essentially of, or consisting of:

a) abrasive;

b) cyclic chelator comprising at least one N-C-C-N group and at least one cyclic ring;

c) oxidizer; and

d) water-soluble solvent ;

optionally at least one of

e) corrosion inhibitor;

f) chemical additive;

g) biocide;

h) and

i) pH adjusting agent;

wherein the bond between N and C can be single or double bond.

[0036] 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. Abrasive particles comprise silica are preferred.

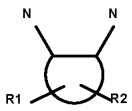
[0037] The abrasive particles used for the disclosed CMP polishing compositions include, but are not limited to, the following: colloidal silica or high purity colloidal silica; the colloidal silica particles doped by other metal oxide within lattice of the colloidal silica, such as alumina doped silica 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

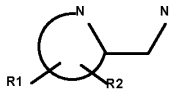
particles, such as alumina, titania, zirconia, ceria etc.; nano-sized diamond particles; nano-sized silicon nitride particles; mono-modal, bi-modal, multi-modal colloidal abrasive particles; organic polymer-based soft abrasives; metal oxide-coated inorganic oxide particles including surface-coated or modified abrasives, such as silica particles having surfaces coated with ceria particles (ceria coated silica particles); or other composite particles, and mixtures thereof. Abrasive particles comprise silica such as colloidal silica or high purity colloidal silica are preferred.

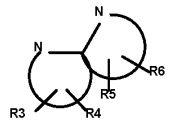
[0038] The CMP polishing composition contains 0.0025 wt.% to 25 wt.%; 0.0025 wt.% to 20 wt.%; 0.005 wt.% to 10.0 wt.% or 0.01 wt.% to 5 wt.% abrasives.

[0039] The cyclic chelator comprising at least one N-C-C-N group and at least one cyclic ring is selected from the group consisting of cyclopentane, cyclohexane, cyclohexadiene, cyclopentadiene, phenanthroline, benzene, pyridine, pyrimidine, pyrazine, terpyridine, azepine, diazepine, indazole, pyrazole, triazole, tetrazole ring, and combinations thereof.

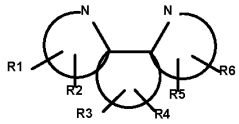
[0040] The cyclic chelator has a structure selected from the group consisting of:

a. 

, b. 

, c. 

,

d. 

, and combinations thereof;

wherein each cyclic ring structure contains at least two R groups and each of R_1, R_2, R_3, R_4, R_5 and R_6 independently includes but is not limited to H; OH; CH_3; NH_2; secondary or tertiary amine; NO; NO_2; acid includes but is not limited to COOH, SO_3H, PO_3H and their salt; CN; SCN; NCS; amide; ketone; aldehyde; ester; ether; thiol; alkyl chains having 2-6 carbons; alkyl alcohols; cyclic group includes but is not limited to cyclopentane, cyclohexane, cyclohexadiene, cyclopentadiene, phenanthroline, benzene, pyridine, pyrimidine, pyrazine, terpyridine, azepine, diazepine, indazole, pyrazole, triazole, tetrazole ring, or combination of those rings; the bond between N and C can be either single or double bond; and the cyclic rings in structures c. and d. can be bonded in any way, including but not limited to through

conjugation, at least one single bond, at least one double bond, or combinations of single and double bonds.

[0041] Preferably, R groups are polar groups to improve solubility.

[0042] The chelator contains at least one N-C-C-N group and at least one cyclic ring. The ring(s) may be attached to any bonds of the N-C-C-N group or be part of the N-C-C-N structure as depicted in the structures above. Most of the cyclic ring contains at least one N atom .

[0043] The chelator should be water soluble (>0.1 wt.%) at pH=8-11, odorless, compatible with hydrogen peroxide (the oxidant) and non-toxic. The complex formed with the chelator should also be water soluble (≥0.005g/100g) at pH=8-11.

[0044] Some of the disclosed chelators can be adsorbed on the Cu layer and thus inhibiting the removal of Cu. Those chelators will act as a chelator to Ru and an inhibitor to Cu at the same time, and thus advantageously increase the selectivity between the two metals. Example of chelators that do both are 2,6-Di(2H-1,2,3-triazol-4-yl)pyridine, 2,6-Di(1H-pyrazol-3-yl)pyridine, and 8-Aminoquinoline.

[0045] Example of the chelator includes but is not limited to 1,4,8,12-Tetraazacyclopentadecane, 2-(1H-Pyrazol-3-yl)pyridine, 2-(1H-Imidazol-2-yl)pyridine, 4,5-Diazafluoren-9-one, [2,2'-Bipyridin]-4-amine, 4,4'-Diamino-2,2'-bipyridyl, 6,6'-Diamino-2,2'-bipyridyl, 6,6'-Dicyano-2,2'-bipyridyl, 2,2'-Bipyridine-3,3'-diol, 2,2'-Bipyridine-5,5'-diol, 2,2'-Bipyridine-6,6'-diol, 2-(2-Pyridyl)benzimidazole, 2,6-Di(2H-1,2,3-triazol-4-yl)pyridine, 3,5-Di(2-pyridyl)pyrazole, 6-(1H-pyrazol-1-yl)-2,2'-bipyridine, 3,6-Di(2-pyridyl)-1,2,4,5-tetrazine, 2,2'-Bipyridine-3,3'-dicarboxylic Acid, 2,2'-Bipyridine-6,6'-dicarboxylic Acid, 2,2'-Bipyridine-4,4'-dicarboxylic Acid, 2,6-Bis(2-pyridyl)-4(1H)-pyridone, 2,2':6',2''-Terpyridine-4'-carboxylic Acid, [2,2':6',2''-Terpyridine]-4,4',4''-tricarboxylic acid, 4-[2-(2-methoxyethoxy)ethoxy]-6-(pyridin-2-yl)-2,2'-bipyridine (and other similar materials with longer ethoxy chains), [2,2':6',2''-Terpyridine]-3',4'-dicarboxylic acid, 4'-(4-Carboxyphenyl)-[2,2':6',2''-terpyridine]-5,5''-dicarboxylic acid, 2,2'-Bicinchoninic Acid, 1,2-Cyclohexanediamine, 2-(Pyridin-2-yl)-1H-pyrrolo[2,3-b]pyridine, 2,6-Di(1H-pyrazol-3-yl)pyridine, 2,6-Di(1H-pyrazol-1-yl)isonicotinic acid, [2,2':6',2''-Terpyridine]-4,4',4''-triyltrimethanol, 2-(1H-Imidazol-2-yl)pyridine-4-carboxylic acid, 2,6-Di(1H-pyrazol-1-yl)isonicotinic acid, Di-(2-picolyl)amine, 2,2'-Bipyrazine, purine, 2,2'-Bipyrimidine, 7-Amino-1H-indazole, Thiopicolinamide, Picolinimidamide Hydrochloride, Pyridine-2,6-dicarboximidamide Dihydrochloride, 2-(1H-Tetrazol-5-yl)pyridine, 2-(1H-1,2,4-Triazol-3-yl)pyridine, 4,7-Dihydroxy-1,10-phenanthroline, Pyrazino[2,3-f][1,10]phenanthroline,

Bathophenanthrolinedisulfonic Acid Disodium Salt Hydrate, 1,10-Phenanthroline-2,9-Dicarboxylic Acid, 1,10-Phenanthroline-4,7-dicarboxylic acid, 2,6-bis(4,5-dihydrooxazol-2-yl)pyridine, 2-(4,5-dihydro-2-oxazolyl)pyridine, bis[(1H-pyrazol-5-yl)methyl]amine, bis[(1H-pyrrol-2-yl)methyl]amine, Pyridine-2,6-diyldimethanamine, N1-(2-Pyridinylmethyl)-1,2-ethanediamine, 2-(1H-Pyrazol-1-ylmethyl)pyridine, and 8-Aminoquinoline.

[0046] The CMP polishing composition contains 0.0005 wt.% to 5 wt.%; 0.005 wt.% to 0.5 wt.%; or 0.0025 wt.% to 0.05wt.% of cyclic chelator comprising at least one N-C-C-N group and at least one cyclic ring .

[0047] The 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, $KClO_4$, $KBrO_4$, $KMnO_4$; and combinations thereof.

[0048] The CMP polishing composition contains 0.1 wt.% to 10 wt.%; 0.25 wt.% to 3 wt.%; or 0.5 wt.% to 2.0 wt.% oxidizer.

[0049] The corrosion inhibitor can be corrosion inhibitor which prevents corrosion and attain global flatness on the wafer surface. The corrosion inhibitor includes but is not limited to hetero aromatic compounds containing nitrogen atom(s) in their aromatic rings.

[0050] The corrosion inhibitor can be triazole or/and non-triazole corrosion inhibitor. The corrosion inhibitor includes but is not limited to 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; and non-triazole corrosion inhibitor disclosed in US 63/554,451, which is incorporated herein by reference in its entirety.

[0051] The CMP polishing composition contains 0.005 wt.% to 1.0 wt.%, 0.01 wt.% to 0.5 wt.%; or 0.02 wt.% to 0.2 wt.% corrosion inhibitor.

[0052] The chemical additive includes but is not limited to a chelator which is not a cyclic chelator comprising at least one N-C-C-N group and at least one cyclic ring, such as an inorganic silicate, examples are potassium silicate, sodium silicate, and ammonium silicate; ammonium hydroxide; and combinations thereof; a dispersing

agent includes but is not limited to polyacrylic acid and its salts, an example is polyacrylic acid ammonium salt

[0053] The CMP polishing composition contains 0.005 wt.% to 5.0 wt.%, 0.01 wt.% to 0.5 wt.%; or 0.02 wt.% to 0.2 wt.% chemical additive.

[0054] A 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.

[0055] A biocide includes but is not limited to Neolone™ M10, a methyl isothiazolinone-based biocide from DuPont; Kathon™, Kathon™ CG/ICP II, from Dow Chemical Co. They have active ingredients of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one.

[0056] The CMP polishing composition contains 0.0001 wt.% to 0.05 wt.%; 0.0002 wt.% to 0.025 wt.%; or 0.002 wt.% to 0.01 wt.% biocide.

[0057] The pH adjusting agent includes but is not limited to nitric acid, sulfuric acid, tartaric acid, succinic acid, citric acid, malic acid, malonic acid, various fatty acids, various polycarboxylic acids, potassium hydroxide, sodium hydroxide, ammonia, tetraethylammonium hydroxide, piperazine, polyethyleneimine, modified polyethyleneimine, and mixtures thereof to adjust the pH.

[0058] The CMP polishing composition contains 0 wt.% to 1 wt.%; 0.01 wt.% to 0.5 wt.%; or 0.1 wt.% to 0.25 wt.% pH adjusting agent.

[0059] pH of the CMP polishing composition is ≥ 5, ≥ 6, ≥ 7, or ≥ 8; such as 5 to 12, 6 to 12, 7 to 12, 8 to 12, 5 to 11, 6 to 11, 7 to 11 or 8 to 11.

[0060] The water-soluble solvent includes but is not limited to deionized (DI) water, distilled water, organic alcohols, and combinations thereof. DI water is preferred.

[0061] 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 Ru or other diffusion barrier metals; comprising, consisting essentially of, or consisting of the steps of:

providing the chemical mechanical planarization polishing composition of Aspect 1;

providing a polishing pad;

contacting the at least one surface containing Ru or other diffusion barrier metals with the polishing pad and the chemical mechanical planarization polishing composition;

polishing the at least one surface containing Ru or other diffusion barrier metals

[0062] 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 Ru or other diffusion barrier metals
a polishing pad; and
the chemical mechanical planarization composition of Aspect 1;
wherein the at least one surface containing Ru or other diffusion barrier metals is in contact with the polishing pad and the chemical mechanical planarization composition.

[0063] The at least one surface can further contain at least one second material which can be any materials used in the semiconductor substrate or patten wafer together with Ru; includes but is not limited to Cu, Ta; Ti; TaN; TiN; Ta; TaN; Ti; TiN; dielectric materials such as SiO_2, SiN, SiC; and low-k and ultra-low-k materials; such as different Black Diamon™ films.

[0064] The polishing composition, method and system described herein will be illustrated in more detail with reference to the following examples, but it should be understood that it is not deemed to be limited thereto.

GLOSSARY

COMPONENTS

[0065] Raw chemicals, RuO_2 powder (99% metal purity), were purchased from American Elements 10884 Weyburn Avenue, Los Angeles, CA, 90024

[0066] Colloidal silica (SH3) having a Mean Particle Size (MPS) about 65-70 nm was supplied by Fuso Chemical Co., LTD, Japan.

[0067] 200mm CVD Ruthenium blanket wafers were supplied by Advantiv Technologies 46781 Fremont Blvd Fremont, CA 94538.

Polishing Experiments

CMP Methodology

PARAMETERS

General

[0068] Å or A: angstrom(s) – a unit of length

[0069] BP: back pressure, in psi units

[0070] CMP: chemical mechanical planarization = chemical mechanical polishing

[0071] CS: carrier speed

[0072] DF: Down force: pressure applied during CMP, unit: psi

[0073] min: minute(s)

[0074] ml: milliliter(s)

[0075] mV: millivolt(s)

[0076] mM: *millimolar*

[0077] psi: pounds per square inch

[0078] PS: platen rotational speed of polishing tool, in rpm (revolution(s) per minute)

[0079] SF: composition flow, ml/min

[0080] wt. %: weight percentage (of a listed component relative to the composition)

[0081] Removal Rates: Measured removal rate at a given down pressure. The down pressure of the CMP tool was 2.0 psi in working example 3 (1). The down pressure of the CMP tool was 1.0 psi in working example 3 (2).

General Experimental Procedure

[0082] All percentages are weight percentages unless otherwise indicated.

[0083] In the examples presented below, CMP experiments were run using the procedures and experimental conditions given below.

Working Example 1: Screening the chelator using RuO_2 powder

[0084] The candidates for the chelator should have the ability to dissolve Ru ions into the solution. All chelators were purchased from Bet Dekel located at 16 Hatidhar St., Raanana, 43655, Israel, POB 2094.

[0085] In a typical procedure, 15mg of RuO_2 (99% metal purity) powder was weighted into a plastic vial equipped with magnetic stirrer. One or mixture of the chelators was added, and the mixture was suspended in KOH solution at a pH around 11.

[0086] After mixing the suspensions for 24 hours, the solids were filtered twice. The amount of Ru dissolved in the filtrate was determined by inductively coupled plasma mass spectrometry (ICP-MS).

[0087] The data was summarized in Table 1.

Table 1: ICP-MS values for different chelators

Chelator name	Ru concentration in filtrate (ppb, ICP-MS)
2,2'-Bipyridine-3,3'-diol	750
1,2-Cyclohexanediamine (cis- and trans-mixture)	290
2,6-Di(2H-1,2,3-triazol-4-yl)pyridine	250
Di-(2-picolyl)amine	1155
3,6-Di(2-pyridyl)-1,2,4,5-tetrazine	1990
2-(1H-1,2,4-Triazol-3-yl)pyridine	1050
2-(1H-Pyrazol-3-yl)pyridine	260

[0088] Table 1 indicated that the tested chelators dissolved the Ru ions into the KOH solution.

Working Example 2: Electrochemistry measurements

[0089] A 99.9% purity Ru rod has 3 mm diameter, was supplied by American Elements, located at10884 Weyburn Avenue, Los Angeles, CA USA) was cut into 0.5 cm slices using a diamond saw and fit into hollow Teflon sleeves of appropriate diameter. To facilitate electrical connection to potentiostat leads, the electrodes were fit with brass connections that were screwed into the upper part of the Teflon sleeves and graphite powder was used to fill the gap between Ru and the brass rod. The electrodes were checked with a multimeter and adjusted until continuity was verified. The active area of the working electrode exposed to the surface was therefore a flat disc with an area of 7.1 mm^2. Following fabrication, electrodes were polished on a bench-mounted rotating grinder-polisher using a series of SiC papers (all polishing

supplies were purchased from Buehler, located at 41 Waukegan Road Lake Bluff, IL USA): 240 grit until planar, 400 grit until smooth, and 600 grit to a near-mirror finish. This was followed by polishing with 6 and 1 mm diamond suspension on MicroCloth, degreasing with ethanol, and rinsing with ultrapure water. Electrodes were stored in ultrapure water between experiments.

[0090] Electrochemical experiments were carried out using a Biologic (4 rue Vaucanson, 38170 Seyssinet-Pariset, France) VSP potentiostat in a 3-electrode cell using a Hg/HgO reference electrode with 1 M NaOH (ALS Japan, Tokyo) and a coiled Pt wire as counter electrode (Holland Moran, Avraham Giron St. 15, Yehud, Israel). The cell was contained in a 25 mL vial and contained approximately 15 mL of solution. Each solution contained 0.15% hydrogen peroxide, 20 mM chelator, and was adjusted to the desired pH using potassium hydroxide.

[0091] Measurements were replicated in triplicate. Electrochemical experiments were conducted according to the following four-part program: First, 30 seconds open-circuit potential (OCV) measurement; second, 10 cycles cyclic voltammetry (CV) ± 250 mV around OCV at a scan rate of 20 mV/s; third, 10 minutes OCV measurement; fourth, potentiodynamic polarization scan ± 450 mV around OCV at a scan rate of 5 mV/s. Prior to each experiment, electrodes were polished with 600 grit SiC paper to remove pitting or scratches, followed by 6 and 1 mm diamond suspension as described above.

[0092] Fig. 1 depicted the Tafel plot for Ru with (dashed lines) and without (baseline, solid line) the presence of Ru chelator.

[0093] Table 2 listed the open OCV, E_{corr} and J_{corr}, for each one of the measured chelators at 20 millimolar (mM).

Chelator	Concentration of Chelator	Average OCV (mV)	Average Ecorr (mV)	Average Jcorr (uA/cm^2)
Baseline (no chelator)	0	277±5	224±1	27.5±0.9
1,2 cyclohexanediamine (cis and trans)	0.2%	166±10	167±13	36.6±0.8
Di-(2-picolyl)amine	0.4%	232±2	203±8	53.2±0.5
8-aminoquinoline	0.3%	238±3	197±13	29±2
2,6-Di(2H-1,2,3-triazol-4-yl)pyridine	0.4%	250±6	192±7	157±3

[0094] A downshift in open-circuit potential (OCV) and corrosion potential was observed for all compounds. A downshift in these potentials can be caused by

cathodic inhibition, or, conversely, a preferential increase in anodic activity, for example complexation or dissolution of the electrode material. In Fig. 1, all Tafel plots are shifted towards higher currents in the presence of a chelator, evidencing that cathodic inhibition is not taking place and that the shift in potential indicates a more anodically active surface.

[0095] In addition to a downshift in potential, the four Tafel plots in the presence of a chelator (Fig. 1) showed a shift towards higher currents, which indicates accelerated oxidation of ruthenium. The largest shift was 2,6-Di(2H-1,2,3-triazol-4-yl)pyridine, which showed an order-of-magnitude increase in corrosion current density, while the smallest shift for 8-aminoquinoline showed only a negligible increase in corrosion current density. The other two additives tested showed small to medium increases in corrosion current density.

[0096] The anodic (upper) arm of the Tafel plot for 1,2-cyclohexadiamine did not show any “bend” indicating the generation of a passive region, an indication that in the presence of this additive ruthenium corrosion proceeds with the formation of soluble species. Notably, the anodic arm of the Tafel plot for 2,6-Di(2H-1,2,3-triazol-4-yl)pyridine showed a bend indicating passivation at a lower potential than the baseline (onset of passivation at ~0.3 V vs. ~0.5 V for baseline), another indication of increased anodic activity.

Working Example 3: CMP on CVD deposited Ru wafers

(1) 200mm Blanket Wafers Polishing

[0097] 200mm blanket wafers including CVD Ruthenium, Copper, TEOS, and TaN were pre-measured for film thickness via 49-point diameter scan recipe to determine the average pre polish thickness of the wafer in angstroms.

[0098] The polishing tool used was Applied Materials Mirra. The pad type was a soft pad, Fujibo H800. The conditioner was a diamond disk, 3M A82.

[0099] The polishing tests were done with the following process conditions:

Downforce: 2psi

Platen speed: 90 RPM

Head speed: 84 RPM

Slurry flow rate: 200mL/min

Conditioner downforce: 3lbs, 50% in-situ

[00100] Two wafers per formulation were pre-measured.

[00101] The pre-measured wafers were polished for 1 minute. Upon completion of the polishing, the wafers were post measured with the same 49pt diameter scan recipe to determine the post thickness (in angstroms) of the film. To determine the removal rate performance of a given formulation, the post wafer thickness measurement is subtracted from the pre wafer thickness measurement to give a removal rate value in (Å/min).

[00102] A control formulation was made using colloidal silica (3.88 wt.%); potassium silicate (0.95 wt.%); benzotriazole (0.009 wt.%); nitric acid(0.048 wt.%); Poly(Acrylic acid) ammonium salt (0.008 wt.%); hydrogen peroxide (0.25 wt.%); and pH of the control slurry was about 10-11.

[00103] Different chelators having the same concentration 0.0125 wt.% were added to the control formulation to form different working polishing formulations as shown in Table 3.

[00104] The formulations were allowed to be thoroughly mixed.

[00105] Removal rates (RR) and Removal rates Selectivity were also shown in Table 3.

Table 3 Removal Rate RR (Å /min.) and RR Selectivity

Chelator	CVD Ru	Cu	Cu: CVD Ru	TEOS	TaN	Cu:TEOS
Control	18	271	15.26	727	601	0.37
Di-(2-picolyl) amine	30	331	11.02	714	590	0.46
2,6-Di(1H-pyrazol-3-yl) pyridine	31	236	7.75	679	508	0.35
8-Aminoquinoline	21	221	10.76	876	683	0.25
2-(1H-1,2,4-Triazol-3-yl) pyridine	24	305	12.61	707	582	0.43

3,6-Di(2-pyridyl)-1,2,4,5-tetrazine	22	296	13.44	677	597	0.44
2,6-Di(2H-1,2,3-triazol-4-yl) pyridine	28	256	9.15	677	724	0.38

[00106] The results demonstrated the impact of the disclosed chelators in boosting CVD Ru removal rates; and reducing the selectivity of Cu RR: Ru RR; which indicating that each chelator added to the control formulation complexing with Ru. Some of the chelators also inhibited the RR of Cu as it is adsorbed on the Cu layer during the polish process and thus further reduced the selectivity of Cu RR: Ru RR .

[00107] The results also showed that the working formulations provided tunable RR for TEOS and TaN.

[00108] Table 4 listed removal rates (RR) and removal rates selectivity from working polishing formulations using different chelators having different concentrations added to the control formulation.

Table 4 Removal rate RR (Å/min) and RR selectivity

Chelator	Conc. (wt.%)	CVD Ru	Cu	Cu:CVD Ru	TEOS	TaN	Cu:TEOS
Control	0.000	18	271	15.26	727	601	0.37
2,6-Di(2H-1,2,3-triazol-4-yl)pyridine	0.0025	18	259	14.79	666	586	0.39
	0.0075	21	269	12.8	679	630	0.4
	0.0125	28	256	9.15	677	724	0.38
	0.01313	28	266	9.65	727	548	0.37
Di-(2-picolyl)amine	0.0125	30	331	11.02	714	590	0.46
	0.025	32	523	16.33	712	513	0.73
2,6-Di(1H-pyrazol-3-yl)pyridine	0.0125	31	236	7.75	679	507.5	0.35

	0.025	31	184	5.94	752	568	0.24
2-(1H-1,2,4-Triazol-3-yl)pyridine	0.0025	17	230	13.91	707	641	0.32
	0.0125	24	305	12.61	707	582	0.43
	0.025	26	252	9.69	692	578	0.36

[00109] Within the most test ranges of concentrations for the chelators, RR of CVD Ru was boosted; the Cu/ CVD Ru selectivity was decreased while tunable RR for TEOS and TaN was provided.

[00110] Table 5 listed the working formulations having a chelator and an additive: ammonium hydroxide (NH_4OH) added to the control formulation. Removal rates (RR) and Removal rates Selectivity were also shown in Table 5.

Table 5 Removal rate RR (Å/min) and RR selectivity

Chelator	**Conc. (wt.%)**	**NH_4OH (wt.%)**	**CVD Ru**	**Cu**	**Cu:CVD Ru**	**TEOS**	**TaN**	**Cu:TEOS**
none	0.0	0.0335	28	474	17.01	723	547	0.66
2,6-Di(2H-1,2,3-triazol-4-yl)pyridine	0.01313		28	266	9.65	727	548	0.37
	0.01313	0.0335	35	423	12.27	783	638	0.54
2,6-Di(1H-pyrazol-3-yl)pyridine	0.025		31	184	5.94	752	568	0.24
	0.025	0.0335	44	393	9.04	840	641	0.47
2-(1H-1,2,4-Triazol-3-yl)pyridine	0.0125		24	305	12.61	707	582	0.43
	0.0125	0.0335	36	454	12.77	757	729	0.6

[00111] As the results shown in Table 5, the synergistic effect of ammonium hydroxide (NH_4OH) and chelators on CVD Ru RR was observed. The combination of a chelator with NH_4OH synergistically enhanced CVD Ru removal rate.

(2) 300mm Blanket Wafers Polishing

[00112] The polishing tool used was Applied Materials Reflexion. The pad type was a soft pad, Fujibo LMED-13. The conditioner was a brush disk, 3M PB32A-1.

[00113] 300mm blanket wafers including CVD Ruthenium, Copper, TEOS, and TaN or Ta were pre-measured for film thickness via 49-point diameter scan recipe to determine the average pre polish thickness of the wafer in angstroms.

[00114] Two wafers per formulation were pre-measured. The polishing tests were done with the following process conditions:

Downforce: 1.0 psi

Platen speed: 70 RPM

Head speed: 64 RPM

Slurry flow rate: 200 mL/min

Conditioner downforce: 2 bs, 100 % in-situ

[00115] The pre-measured wafers were polished for 1 minute. Upon completion of the polishing, the wafers were post measured with the same 49pt diameter scan recipe to determine the post thickness (in angstroms) of the film. To determine the removal rate performance of a given formulation, the post wafer thickness measurement is subtracted from the pre wafer thickness measurement to give a removal rate value in (Å/min).

[00116] A control formulation was made using colloidal silica (3.88 wt.%); potassium silicate (0.95 wt.%); benzotriazole (0.009 wt.%); nitric acid(0.048 wt.%); Poly(Acrylic acid) ammonium salt (0.008 wt.%); hydrogen peroxide (0.25 wt.%); and pH of the control slurry was about 10-11.

[00117] Removal rates (RR) and Removal rates Selectivity were also shown in Table 6.

Table 6 Removal Rate RR (Å /min.) and RR Selectivity

Chelator	Conc. (wt.%)	CVD Ru	Cu	Cu:CVD Ru	TEOS	TaN	Ta	Cu: TEOS
None (Control)	0	7	154	23.47	266	636	248	0.59
2,6-Di(2H-1,2,3-triazol-4-yl)pyridine	0.0131	13	212	16.74	300	597		0.71
	0.0263	12	181	14.68	290	561		0.62
1,2 - Cyclohexanediamine	0.0125	9	198	23.55	283	587		0.70
	0.0250	14	230	16.92	271	427		0.85
	0.0500	15	317	21.55	269		335	1.18
Di-(2-picolyl)amine	0.0250	11	251	23.45	294		305	0.85
	0.0125	11	195	17.06	299		363	0.65
2-(1H-1,2,4-Triazol-3-yl)pyridine	0.0125	13	159	12.16	188		200	0.84
	0.0250	15	188	12.58	193		183	0.97
	0.0500	15	141	9.70	196		185	0.72

[00118] As shown in Table 6, similar to the polishing test on 200 nm wafer, within the test ranges of concentrations for the chelators, RR of CVD Ru for 300 nm wafer was boosted which again indicating that each chelator added to the control formulation complexing with Ru. The Cu/ CVD Ru selectivity was decreased while tunable RR for TEOS, TaN and Ta was provided.

Working Example 4: Direct Injection to Atmospheric Pressure Chemical Ionization Mass Spectrometry (APCI-MS method)

[00119] In this example, direct injection to APCI-MS was performed.

[00120] FIA-MS-Conditions:

[00121] Eluent: Water (300 µL/min only for APCI measurement)

[00122] Column: none

[00123] Injection-volume: Syringe pump 5 µL/min (APCI) Syringe pump 10 µL/min (ESI)

[00124] Weight in quantity: Solution as received

[00125] MS: Bruker Impact II

[00126] Ion mode: positive

[00127] Ion source: Atmospheric pressure chemical ionisation/Electrospray ionization

[00128] In a typical procedure, 15mg of RuO_2 (99% metal purity) powder was weighted into a plastic vial equipped with magnetic stirrer. One of the tested chelators 2-(1H-Pyrazol-3-yl)pyridine and 2-(1H-1,2,4-Triazol-3-yl)pyridine was added, and the mixture was suspended in KOH solution at a pH around 11.

[00129] After mixing the suspensions for 24 hours, the solids were filtered twice.

[00130] The spectra from the solids has shown a new complex. That is, each tested chelator formed a complex with Ru in the solution.

[00131] All CMP polishing working data has demonstrated that using the disclosed chelators in the CMP polishing composition provided boosted RR of CVD Ru, decreased Cu/ CVD Ru selectivity, and desirable tunable RR for other materials.

[00132] Since RuO_2 is not soluble in basic water, without being bound by theory, it is believed that the dissolution of Ru into the solution through complexation with the chelator contributes to the removal rate increase of Ru.

[00133] 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 (CMP) polishing composition comprising, consisting essentially of, or consisting of:

   a) abrasive;

   b) cyclic chelator comprising at least one N-C-C-N group and at least one cyclic ring;

   c) oxidizer; and

   d) water-soluble solvent ;

   optionally at least one of

   e) corrosion inhibitor;

   f) chemical additive;

   g) biocide;

   and

   h) pH adjusting agent.

   wherein the bond between N and C can be either single or double bond.

2. The Chemical Mechanical Planarization (CMP) polishing composition according to Claim 1, wherein the composition comprises 0.0025 wt.% to 25 wt.%, 0.0025 wt.% to 20 wt.%, 0.005 wt.% to 10.0 wt.% , or 0.01 wt.% to 5 wt.% of the abrasive selected from the group consisting of inorganic oxide particles, metal oxide-coated inorganic oxide particles, organic polymer particles, metal oxide-coated organic polymer particles, and combinations thereof.

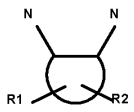
3. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 2, wherein the abrasive is selected from the group consisting of colloidal silica; colloidal silica particles doped by other metal oxide within lattice of the colloidal silica; silica sol selected from the 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

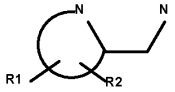
nitride particles; organic polymer-based soft abrasives; surface-coated or modified abrasives; and combinations thereof.

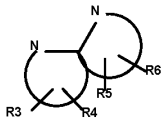
4. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 3, wherein the abrasive is selected from the group consisting of colloidal silica, cerium oxide, ceria coated silica particles, and combinations thereof.

5. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 4, wherein the composition comprises 0.0005 wt.% to 5 wt.%; 0.005 wt.% to 0.5 wt.%; or 0.0025 wt.% to 0.05wt.% of the cyclic chelator comprising at least one N-C-C-N group and at least one cyclic ring selected from the group consisting of cyclopentane, cyclohexane, cyclohexadiene, cyclopentadiene, phenanthroline, benzene, pyridine, terpyridine, azepine, diazepine, indazole, pyrazole, triazole, tetrazole ring, and combinations thereof.

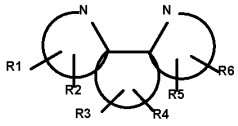
6. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 5, wherein the cyclic chelator comprising at least one N-C-C-N group and at least one cyclic ring has a structure selected from the group consisting of:

a. 

, b. 

, c. 

,

d. 

, and combinations thereof;

wherein each ring structure contains at least two R groups and each of R_1, R_2, R_3, R_4, R_5 and R_6 group independently is selected from the group consisting of H; OH; CH_3; NH_2; secondary or tertiary amine; NO; NO_2; acid includes but is not limited to COOH, SO_3H, PO_3H and their salt; CN; SCN; NCS; amide; ketone; aldehyde; ester; ether; thiol; alkyl chains having 1-6 carbons; alkyl alcohol; cyclic group selected from the group consisting of cyclopentane, cyclohexane, cyclohexadiene, cyclopentadiene, phenanthroline, benzene,

pyridine, pyrimidine, pyrazine, terpyridine, azepine, diazepine, indazole, pyrazole, triazole, tetrazole ring, and combinations thereof; and combinations thereof;

the bond between N and C can be single or double bond; and the cyclic rings in structures c. and d. can be bonded through conjugation, at least one single bond, at least one double bond, or combinations of single and double bonds.

7. The Chemical Mechanical Planarization polishing composition according to Claim 6, wherein at least one of the R groups in the cyclic chelator is a polar group.

8. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 – 7, wherein the cyclic chelator comprising at least one N-C-C-N group and at least one cyclic ring is selected from the group consisting of 1,4,8,12-Tetraazacyclopentadecane, 2-(1H-Pyrazol-3-yl)pyridine, 2-(1H-Imidazol-2-yl)pyridine, 4,5-Diazafluoren-9-one, [2,2'-Bipyridin]-4-amine, 4,4'-Diamino-2,2'-bipyridyl, 6,6'-Diamino-2,2'-bipyridyl, 6,6'-Dicyano-2,2'-bipyridyl, 2,2'-Bipyridine-3,3'-diol, 2,2'-Bipyridine-5,5'-diol, 2,2'-Bipyridine-6,6'-diol, 2-(2-Pyridyl)benzimidazole, 2,6-Di(2H-1,2,3-triazol-4-yl)pyridine, 3,5-Di(2-pyridyl)pyrazole, 6-(1H-pyrazol-1-yl)-2,2'-bipyridine, 3,6-Di(2-pyridyl)-1,2,4,5-tetrazine, 2,2'-Bipyridine-3,3'-dicarboxylic Acid, 2,2'-Bipyridine-6,6'-dicarboxylic Acid, 2,2'-Bipyridine-4,4'-dicarboxylic Acid, 2,6-Bis(2-pyridyl)-4(1H)-pyridone, 2,2':6',2''-Terpyridine-4'-carboxylic Acid, [2,2':6',2''-Terpyridine]-4,4',4''-tricarboxylic acid, 4-[2-(2-methoxyethoxy)ethoxy]-6-(pyridin-2-yl)-2,2'-bipyridine (and other similar materials with longer ethoxy chains), [2,2':6',2''-Terpyridine]-3',4'-dicarboxylic acid, 4'-(4-Carboxyphenyl)-[2,2':6',2''-terpyridine]-5,5''-dicarboxylic acid, 2,2'-Bicinchoninic Acid, 1,2-Cyclohexanediamine, 2-(Pyridin-2-yl)-1H-pyrrolo[2,3-b]pyridine, 2,6-Di(1H-pyrazol-3-yl)pyridine, 2,6-Di(1H-pyrazol-1-yl)isonicotinic acid, [2,2':6',2''-Terpyridine]-4,4',4''-triyltrimethanol, 2-(1H-Imidazol-2-yl)pyridine-4-carboxylic acid, 2,6-Di(1H-pyrazol-1-yl)isonicotinic acid, Di-(2-picolyl)amine, 2,2'-Bipyrazine, purine, 2,2'-Bipyrimidine, 7-Amino-1H-indazole, Thiopicolinamide, Picolinimidamide Hydrochloride, Pyridine-2,6-dicarboximidamide Dihydrochloride, 2-(1H-Tetrazol-5-yl)pyridine, 2-(1H-1,2,4-Triazol-3-yl)pyridine, 4,7-Dihydroxy-1,10-phenanthroline, Pyrazino[2,3-f][1,10]phenanthroline, Bathophenanthrolinedisulfonic Acid Disodium Salt Hydrate, 1,10-Phenanthroline-2,9-Dicarboxylic Acid, 1,10-Phenanthroline-4,7-dicarboxylic acid, 2,6-bis(4,5-dihydrooxazol-2-yl)pyridine, 2-(4,5-dihydro-2-

oxazolyl)pyridine, bis[(1H-pyrazol-5-yl)methyl]amine, bis[(1H-pyrrol-2-yl)methyl]amine, Pyridine-2,6-diyldimethanamine, N1-(2-Pyridinylmethyl)-1,2-ethanediamine, 2-(1H-Pyrazol-1-ylmethyl)pyridine, 8-Aminoquinoline, and combinations thereof.

9. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 8, wherein the cyclic chelator comprising at least one N-C-C-N group and at least one cyclic ring is selected from the group consisting of 1,2 - Cyclohexanediamine, 2,6-Di(2H-1,2,3-triazol-4-yl)pyridine, 2,6-Di(1H-pyrazol-3-yl)pyridine, Di-(2-picolyl)amine, 2-(1H-1,2,4-Triazol-3-yl)pyridine, 8-Aminoquinoline, 1,2 -Cyclohexanediamine, 3,6-Di(2-pyridyl)-1,2,4,5-tetrazine, and combinations thereof.

10. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 9, wherein the cyclic chelator comprising at least one N-C-C-N group and at least one cyclic ring is selected from the group consisting of 1,2 - Cyclohexanediamine, 2,6-Di(2H-1,2,3-triazol-4-yl)pyridine, 2,6-Di(1H-pyrazol-3-yl)pyridine, Di-(2-picolyl)amine, 2-(1H-1,2,4-Triazol-3-yl)pyridine, and combinations thereof.

11. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 10, wherein the composition comprises 0.1 wt.% to 10 wt.%; 0.25 wt.% to 3 wt.%; or 0.5 wt.% to 2.0 wt.% oxidizer of the oxidizer 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, $KClO_4$, $KBrO_4$, $KMnO_4$; and combinations thereof.

12. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 11, wherein the composition comprises 0.005 wt.% to 1.0 wt.%, 0.01 wt.% to 0.5 wt.%; or 0.02 wt.% to 0.2 wt.% of the corrosion inhibitor selected from the group consisting of 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 non-triazole corrosion inhibitor.

13. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 12, wherein the composition comprises 0.005 wt.% to 5.0 wt.%, 0.01 wt.% to 0.5 wt.%; or 0.02 wt.% to 0.2 wt.% of the chemical additive selected from the group consisting of inorganic silicate, polyacrylic acid and its salts, ammonium hydroxide, and a chelator which is not a cyclic chelator comprising at least one N-C-C-N group and at least one cyclic ring, and combinations thereof.

14. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 13, wherein the composition comprises 0.0001 wt.% to 0.05 wt.%; 0.0002 wt.% to 0.025 wt.%; or 0.002 wt.% to 0.01 wt.% of a biocide having an active ingredient of 5-chloro-2-methyl-4-isothiazolin-3-one, 2-methyl-4-isothiazolin-3-one, or combinations thereof.

15. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 14, wherein the water-soluble solvent is selected from the group consisting of deionized (DI) water, distilled water, organic alcohol, and combinations thereof; DI water is preferred. T

16. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 15, wherein the pH adjusting agent is selected from the group consisting of nitric acid, sulfuric acid, tartaric acid, succinic acid, citric acid, malic acid, malonic acid, various fatty acids, various polycarboxylic acids, potassium hydroxide, sodium hydroxide, ammonia, tetraethylammonium hydroxide, piperazine, polyethyleneimine, modified polyethyleneimine, and mixtures thereof.

17. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 16,
wherein the composition has a pH of ≥ 5, ≥ 6, ≥ 7, or ≥ 8; or 5 to 12, 6 to 12, 7 to 12, 8 to 12, 5 to 11, 6 to 11, 7 to 11 or 8 to 11.

18. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 17, wherein the composition comprises colloidal silica; the cyclic chelator comprising at least one N-C-C-N group and at least one cyclic ring

is selected from the group consisting of 1,2 -Cyclohexanediamine, 2,6-Di(2H-1,2,3-triazol-4-yl)pyridine, 2,6-Di(1H-pyrazol-3-yl)pyridine, Di-(2-picolyl)amine, 2-(1H-1,2,4-Triazol-3-yl)pyridine, 8-Aminoquinoline, 1,2 -Cyclohexanediamine, 3,6-Di(2-pyridyl)-1,2,4,5-tetrazine, and combinations thereof; hydrogen peroxide; water and the composition has a pH of 7 to 12 or 8 to 12.

19. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 18, wherein the composition comprises colloidal silica; the cyclic chelator comprising at least one N-C-C-N group and at least one cyclic ring is selected from the group consisting of 1,2 -Cyclohexanediamine, 2,6-Di(2H-1,2,3-triazol-4-yl)pyridine, 2,6-Di(1H-pyrazol-3-yl)pyridine, Di-(2-picolyl)amine, and 2-(1H-1,2,4-Triazol-3-yl)pyridine, hydrogen peroxide; water and the composition has a pH of 7 to 12 or 8 to 12

20. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 - 19, wherein the composition comprises colloidal silica; the cyclic chelator comprising at least one N-C-C-N group and at least one cyclic ring is selected from the group consisting of 1,2 -Cyclohexanediamine, 2,6-Di(2H-1,2,3-triazol-4-yl)pyridine, 2,6-Di(1H-pyrazol-3-yl)pyridine, Di-(2-picolyl)amine, and 2-(1H-1,2,4-Triazol-3-yl)pyridine; hydrogen peroxide; ammonium hydroxide; water and the composition has a pH of 7 to 11 or 8 to 11.

21. A Chemical Mechanical Planarization polishing method for chemical mechanical planarization of a semiconductor substrate comprising at least one surface containing Ru comprising, consisting essentially of, or consisting of the steps of:
providing the chemical mechanical planarization polishing composition according to any one of Claims 1 - 20;
providing a polishing pad;
contacting the at least one surface containing Ru with the polishing pad and the chemical mechanical planarization polishing composition;
polishing the at least one surface containing Ru.

22. The Chemical Mechanical Planarization polishing method of Claim 21, wherein the cyclic chelator comprising at least one N-C-C-N group and at least one cyclic ring in the chemical mechanical planarization polishing composition inhibits removal of Cu.

23. A Chemical Mechanical Planarization polishing system, comprising, consisting essentially of, or consisting of:
a semiconductor substrate comprising at least one surface containing Ru;
a polishing pad; and
the chemical mechanical planarization polishing composition according to any one of Claims 1 - 20;
wherein the at least one surface containing Ru is in contact with the polishing pad and the chemical mechanical planarization composition.

24. The Chemical Mechanical Planarization polishing system of Claim 23, wherein the cyclic chelator comprising at least one N-C-C-N group and at least one cyclic ring in the chemical mechanical planarization polishing composition inhibits removal of Cu.