TITLE OF THE INVENTION:

Corrosion Inhibitors for Metal Chemical Mechanical Planarization (CMP) Polishing Compositions

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. provisional applications 63/554,451 filed on February 16, 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 compositions, more specifically, metal such as copper Chemical Mechanical Planarization (CMP) polishing compositions (formulations or slurries; they are used interchangeably) using corrosion inhibitors. The invention also relates to the CMP polishing methods and systems using the copper CMP polishing composition.

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

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

[0005] Copper has emerged as the ultimate choice for the interconnect metal in integrated electronic device fabrication, owing to its outstanding combination of low resistivity, high reliability, and scalability. However, copper poses challenges in terms

of etching and spreading, rendering traditional etching technologies inadequate. The dual damascene process was introduced to address the challenges, wherein copper is deposited within pre-formed trenches and vias to create the desired interconnect structure. In this process, excess copper is typically removed through chemical mechanical planarization (CMP), ensuring global planarization while minimizing metal loss.

[0006] To meet the evolving demands of advanced technology nodes, the optimization of the CMP process has become increasingly crucial. As technology nodes continue to advance, striking a balance between high removal rates and minimal metal loss has become an ever more pressing concern. Therefore, any new polishing formulations must maintain high removal rates, exhibit high selectivity towards the barrier material, and maintain low defectivity levels.

[0007] Copper CMP slurries, in general, are composed of water, abrasive particles, oxidizers, complexing agents, and corrosion inhibitors. The selection and performance of corrosion inhibitors play a vital role in achieving optimal planarization and minimizing defectivity as taught by Lee, D.; Lee, H.; Jeong, H. Slurry components in metal chemical mechanical planarization (CMP) process: A review. *International Journal of Precision Engineering and Manufacturing* 2016, *17* (12), 1751.

[0008] Benzotriazole (BTA) is a commonly used corrosion inhibitor in copper CMP processes. It functions by forming a compact Cu(I)-BTA passivating film that protects the copper surface. Additionally, the BTA molecules can react with cupric ions to form a Cu(II)-BTA complex, which further adsorbs onto the surface and complements the passivating film as taught by Kokalj, A.; Peljhan, S.; Finšgar, M.; Milošev, I. What Determines the Inhibition Effectiveness of ATA, BTAH, and BTAOH Corrosion Inhibitors on Copper. *Journal of the American Chemical Society* 2010, *132* (46), 16657.

[0009] However, the presence of these strong passivating films can lead to increased defectivity when high material removal rates are achieved through the application of high mechanical forces as taught by Jiang, L.; Li, Q.; Chen, Y.; Wu, Y.; Sun, M.; Qian, L. Polyacrylic Acid as a Lubricant and a Complement to 1,2,4-Triazole for Copper Chemical Mechanical Polishing. *Tribology Letters* 2023, *71* (2), 62.

[0010] Studies on corrosion inhibitors have been done. For example, US10519116 deals with water-soluble pyrazole derivatives as corrosion inhibitors for inhibiting the

corrosion of metal surfaces in an aqueous system, demonstrating the broader scope of corrosion inhibition research.

[0011] Patents such as US10607853 describe CMP slurry compositions specifically designed for polishing copper interconnects, involving corrosion inhibitors like benzotriazole, methylbenzotriazole, 1,2,3- triazole, a triazole derivative, a benzotriazole derivative, or a methylbenzotriazole derivative. Similarly, in US10988635, a composition and method for copper barrier CMP utilizes triazoles other than benzotriazole, offering new possibilities for the optimization of copper CMP. An additional example of a polishing composition, suitable for objects with a metal wiring layer, is described in US9486892. This patent claims the effectiveness of various specific compounds, including 4-amino- pyrazolo[3,4-*d*]-pyrimidine, allopurinol, 3,4-dihydroxy-6-methylpyrazolo(3,4-*b*)-pyridine, and 6- methyl-1*H*-pyrazolo[3,4-*b*]-pyridine-3-amine, among others, as corrosion inhibitors for metals.

[0012] Furthermore, publications have explored the role of special additives in CMP compositions, particularly their impact on copper removal rate and defectivity. While some mention the presence of metal corrosion inhibitors, they do not specifically address their performance or performance differences. For instance, US9305806 describes a CMP slurry composition that utilizes a choline salt as a booster for copper removal rate, resulting in significant defect reduction. Similarly, US9978609 emphasizes the benefits of using at least two amino acid-based chelators to minimize dishing in copper CMP, while US11401441 reports on the use of tris chelating systems in CMP compositions. Additionally, US20200277514 provides detailed information on Copper CMP compositions that offer highly effective and adjustable copper removal rates for various applications. These compositions incorporate at least two chelators, including one organic amine and one selected from a group comprising amino acids, amino acid derivatives, and combinations thereof.

[0013] Thus, there remains a need within the art to explore new avenues for optimizing copper CMP slurries, addressing challenges such as defectivity and metal loss since the known Cu CMP slurries in the field are not able to provide a performance meeting all the requirements.

BRIEF SUMMARY OF THE INVENTION

[0014] The present invention satisfies the need by providing bulk copper CMP polishing formulations designed to meet the demanding requirements of advanced technology node Cu CMP applications; more specifically, to achieve high copper removal rates while effectively controlling copper corrosion.

[0015] In one aspect (Aspect 1), there is provided a CMP polishing composition comprising, consisting essentially of, or consisting of:

a) abrasive;

b) oxidizer;

c) non-triazole corrosion inhibitor; and

d) water-soluble solvent ;

optionally at least one of

e) chemical additive;

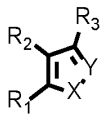
f) biocide;

g) and

h) pH adjusting agent;

wherein

the non-triazole corrosion inhibitor corrosion inhibitor has a general structure selected from the group consisting of (1), (2), (3), (4), and combinations thereof:



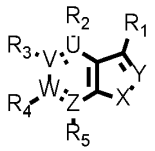
(1)

wherein:

X = NH, S or O and Y = N,

R_1 = H, CH_3, NH_2 or NH_2NH_2,

R_2 = substituted or unsubstituted pyridinyl or pyrimidyl group and R_3 = H, CH_3 or NH_2, or R_2 = H, CH_3 or NH_2 and R_3 = substituted or unsubstituted pyridinyl or pyrimidyl group;



(2)

wherein:

X = NH, S or O and Y = N,

U = C or N, V = C or N, W = C or N and Z = C or N with 3 ≥N ≥ 1 or 2 ≥N ≥ 1,

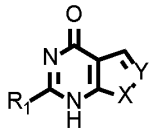
R_1 = H, CH_3 or NH_2,

R_2 = H, CH_3, OH or NH_2 when U = C,

R_3 = H, CH_3, OH or NH_2 when V = C,

R_4 = H, CH_3, OH or NH_2 when W = C,

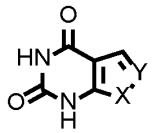
R_5 = H, CH_3, OH or NH_2 when Z = C;



(3)

wherein:

X = NH, S or O and Y = N or C and R_1 = H, CH_3 or NH_2; and



(4)

wherein:

X = NH, S or O and Y = N or C;

the chemical additive is selected from the group consisting of complexing agents, metal chelators, topography reducing additives, removal rate boosters, and combinations thereof;
and
pH of the CMP polishing composition ranges from 3 to 11, 4 to 10, 5 to 9, or 6 to 8.

[0016] 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. Silica particles are preferred abrasives.

[0017] 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.

[0018] The non-triazole corrosion inhibitor includes but is not limited to oxypurinol, allopurinol, pyrazolo[3,4-*b*]pyridine, 1*H*-pyrazolo[3,4-*b*]pyridine, 2-(1*H*-pyrazol-3-yl)pyridine, 2-(1*H*-pyrazol-3-yl)pyrazine, 2-(5-methyl-1*H*-pyrazol-3-yl)pyridine, 2-(1*H*-pyrazol-4-yl)pyrazine, 2-(1*H*-pyrazol-4-yl)pyridine, 6-methyl-1*H*-pyrazolo[3,4-*b*]pyridine, 1*H*-pyrazolo[3,4-*d*]pyrimidine-4-amine, 3-methyl-1*H*-pyrazolo[3,4-*b*]pyridine, 1*H*-pyrazolo[3,4-*b*]pyridine-5-amine, 4-(1*H*-pyrazol-4-yl)pyrimidine, 1*H*-pyrazolo[3,4-*b*]pyrazine, 1*H*-pyrazolo[3,4-*b*]pyridine-6-amine, tisopurine, and combinations thereof.

[0019] The chemical additive may include but is not limited to amino acids and derivatives, organic amines; and choline salt.

[0020] The amino acids and amino acid derivatives includes, but not limited to, glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, valine, leucine, isoleucine, phenylamine, proline, serine, threonine, tyrosine, glutamine, asparagine, glutamic acid, aspartic acid, tryptophan, histidine, arginine, lysine, methionine, cysteine, iminodiacetic acid, and combinations thereof.

[0021] The organic amine includes but is not limited to ethylenediamine, propylenediamine, and butylenediamine.

[0022] 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.

[0023] 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.

[0024] The pH adjusting agent includes but is not limited to (a) nitric acid, sulfuric acid, tartaric acid, succinic acid, citric acid, malic acid, malonic acid, various fatty acids, various polycarboxylic acids, and mixtures thereof to lower the pH; and (b) potassium hydroxide, sodium hydroxide, ammonia, tetraethylammonium hydroxide, piperazine, polyethyleneimine, modified polyethyleneimine, and mixtures thereof to raise the pH.

[0025] The water-soluble solvent is selected from the group consisting of deionized (DI) water, distilled water, and alcoholic organic solvents. DI water is preferred.

[0026] In another aspect (Aspect 2), there is provided a CMP polishing method for chemical mechanical planarization of a semiconductor substrate comprising at least one surface containing Cu, comprising, consisting essentially of, or consisting of the steps of:

contacting the at least one surface with a polishing pad;

delivering the chemical mechanical planarization polishing composition of Aspect 1;

polishing the at least one surface containing Cu with the chemical mechanical planarization composition.

[0027] In yet another aspect (Aspect 3), there is provided a CMP polishing system, comprising, consisting essentially of, or consisting of:

a semiconductor substrate comprising at least one surface containing Cu;

a polishing pad; and

the chemical mechanical planarization composition of Aspect 1;

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

[0028] 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 Cu; includes but is not limited to 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.

[0029] Other aspects, features and embodiments of the invention will be more fully apparent from the ensuing disclosure and appended claims.

[0030] The embodiments of the invention can be used alone or in combinations with each other.

DETAILED DESCRIPTION OF THE INVENTION

[0031] As industry standards trend toward smaller device features, there is a continuously developing need for new metal (such as Cu) CMP polishing compositions that can enhance copper removal rates while effectively controlling metal (such as Cu) corrosion in the metal CMP process for the broad and advanced node applications.

[0032] However, it should be noted that the prior-art references do not specifically address the performance differences of corrosion inhibitors or distinguish their efficacy. Instead, they may claim various classes of molecules, such as nitrogen-containing cyclic compounds, without providing detailed information on their individual performance characteristics.

[0033] The use of nitrogen-containing compounds, such as azoles, is widely recognized for their corrosion inhibition properties on metal such as copper. These compounds are believed to form a protective organic film on the copper surface by coordinating with the metal through their nitrogen lone pair electrons. Additionally, nitrogen-containing compounds, including azoles, have the ability to precipitate copper (II) from aqueous solutions, thus minimizing corrosion potentials arising from galvanic reactions between copper and other metals.

[0034] The present invention has revealed significant variations among different nitrogen-containing compounds in terms of their static etch rate (SER) and performance in copper removal rate using a same CMP composition. Surprisingly, working with other chemicals in the disclosed CMP polishing compositions, certain compounds have demonstrated both exceptionally high removal rates and strong copper corrosion protection simultaneously.

[0035] Thus, the present invention has provided enhance copper removal rates while effectively controlling copper corrosion through the use of a specific selected non-triazole corrosion inhibitor containing pyrazole or its derivatives. The specific selected non-triazole corrosion inhibitor surpasses the benchmark 1,2,4-triazole which is a commonly used corrosion inhibitor in the field of metal polishing. By maintaining the general formulation unchanged, specific pyrazole compounds demonstrate exceptional copper corrosion protection while enabling high or even higher metal removal rates.

[0036] In one aspect (Aspect 1), there is provided a CMP polishing composition comprising, consisting essentially of, or consisting of:

a. abrasive;

b. oxidizer;

c. non-triazole corrosion inhibitor; and

d. water-soluble solvent ;

optionally at least one of

e. chemical additive;

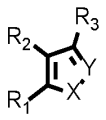
f. biocide;

g. and

h. pH adjusting agent;

wherein

the non-triazole corrosion inhibitor corrosion inhibitor has a general structure selected from the group consisting of (1), (2), (3), (4), and combinations thereof:



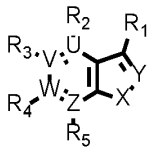
(1)

wherein:

X = NH, S or O and Y = N,

R_1 = H, CH_3, NH_2 or NH_2NH_2,

R_2 = substituted or unsubstituted pyridinyl or pyrimidyl group and R_3 = H, CH_3 or NH_2, or R_2 = H, CH_3 or NH_2 and R_3 = substituted or unsubstituted pyridinyl or pyrimidyl group;



(2)

wherein:

X = NH, S or O and Y = N,

U = C or N, V = C or N, W = C or N and Z = C or N with 3 ≥N ≥ 1 or 2 ≥N ≥ 1,

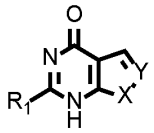
R_1 = H, CH_3 or NH_2,

R_2 = H, CH_3, OH or NH_2 when U = C,

R_3 = H, CH_3, OH or NH_2 when V = C,

R_4 = H, CH_3, OH or NH_2 when W = C,

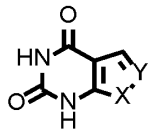
R_5 = H, CH_3, OH or NH_2 when Z = C;



(3)

wherein:

X = NH, S or O and Y = N or C and R_1 = H, CH_3 or NH_2; and



(4)

wherein:

X = NH, S or O and Y = N or C;

the chemical additive is selected from the group consisting of complexing agents, metal chelators, topography reducing additives, removal rate boosters, and combinations thereof;
and
pH of the CMP polishing composition ranges from 3 to 11, 4 to 10, 5 to 9, or 6 to 8.

[0037] 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.

[0038] The abrasive particles used for the disclosed herein Cu bulk CMP polishing compositions include, but are not limited to, the following: colloidal silica or high purity colloidal silica; the colloidal silica particles doped by other metal oxide within lattice of the colloidal silica, such as alumina doped silica particles; silica sol of sodium silicates or/and potassium silicates; fumed silica; colloidal aluminum oxide including alpha-, beta-, and gamma-types of aluminum oxides; colloidal and photoactive titanium dioxide; cerium oxide; colloidal cerium oxide; nano-sized inorganic metal oxide particles, such as alumina, titania, zirconia, ceria etc.; nano-sized diamond particles; nano-sized silicon nitride particles; mono-modal, bi-modal, multi-modal colloidal abrasive particles; organic polymer-based soft abrasives; metal oxide-coated inorganic oxide particles including but not limited to ceria coated inorganic metal oxide particles, such as ceria-coated silica particles; or other composite particles, and mixtures thereof. Colloidal silica or high purity colloidal silica are preferred.

[0039] The CMP polishing composition contains 0.0025 wt.% to 25 wt.%; 0.0025 wt.% to 2.5 wt.%; or 0.005 wt.% to 1.0 wt.% abrasives.

[0040] 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.

[0041] 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.

[0042] The non-triazole corrosion inhibitor corrosions having a general structure (1) include but are not limited to 2-(1*H*-pyrazol-3-yl)pyridine, 2-(1*H*-pyrazol-3-yl)pyrazine, 2-(5-methyl-1*H*-pyrazol-3-yl)pyridine, 2-(1*H*-pyrazol-4-yl)pyrazine, 2-(1*H*-pyrazol-4-yl)pyridine, 5-(Pyridin-2-yl)-1*H*-pyrazol-4-amine, 4-(1*H*-pyrazol-4-yl)pyrimidine.

[0043] The non-triazole corrosion inhibitor corrosions having a general structure (2) include but are not limited to 1*H*-pyrazolo[3,4-*b*]pyridine, 1*H*-pyrazolo[3,4-*d*]pyrimidine, 6-methyl-1*H*-pyrazolo[3,4-*b*]pyridine, 1*H*-pyrazolo[3,4-*d*]pyrimidine-4-amine, 3-methyl-1*H*-pyrazolo[3,4-*b*]pyridine, 1*H*-pyrazolo[3,4-*b*]pyridine-5-amine, 1*H*-pyrazolo[3,4-*b*]pyrazine, 1*H*-pyrazolo[3,4-*b*]pyridine-6-amine, 6-methyl-1*H*-pyrazolo[3,4-*b*]pyridine.

[0044] The non-triazole corrosion inhibitor corrosion having a general structure (3) includes but is not limited to allopurinol and tisopurine.

[0045] The non-triazole corrosion inhibitor corrosion having a general structure (4) includes but is not limited to oxypurinol.

[0046] 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.% non-triazole corrosion inhibitor.

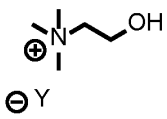
[0047] The optional chemical additive includes but is not limited to amino acids and derivatives, organic amines; and choline salt as disclosed in US11401441BB; the disclosure of which is incorporated herein by reference.

[0048] The amino acids and amino acid derivatives includes, but not limited to, glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, valine, leucine, isoleucine, phenylamine, proline, serine, threonine, tyrosine, glutamine, asparagine, glutamic acid, aspartic acid, tryptophan, histidine, arginine, lysine, methionine, cysteine, iminodiacetic acid, and combinations thereof.

[0049] The organic amine includes, but not limited to ethylenediamine, propylenediamine, and butylenediamine.

[0050] The choline salt includes but is not limited to choline bicarbonate salt, or all other salts formed between choline and other anionic counter ions.

[0051] The choline salts can have the general molecular structures shown below:



wherein anion Y^- can be bicarbonate, hydroxide, p-toluene-sulfonate, bitartrate, and other suitable anionic counter ions.

[0052] The CMP polishing composition optionally contains 0.1 wt.% to 18 wt.% , 0.5 wt.% to 10 wt.%; or 0.75 wt.% to 2.5 wt.% of the chemical additive.

[0053] The optional biocide can be any biocide which provides active ingredients to prevent biological growth and thus provide more stable shelf time of the CMP polishing compositions.

[0054] The 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.

[0055] The CMP polishing composition optionally contains 0.0001 wt.% to 0.05 wt.%; 0.0002 wt.% to 0.025 wt.%; or 0.002 wt.% to 0.01 wt.% biocide.

[0056] The optional pH adjusting agent includes but is not limited to (a)nitric acid, sulfuric acid, tartaric acid, succinic acid, citric acid, malic acid, malonic acid, various fatty acids, various polycarboxylic acids, and mixtures thereof to lower the pH; and (b) potassium hydroxide, sodium hydroxide, ammonia, tetraethylammonium hydroxide, piperazine, polyethyleneimine, modified polyethyleneimine, and mixtures thereof to raise the pH.

[0057] The CMP polishing composition optionally contains 0 wt.% to 1 wt.%; 0.01 wt.% to 0.5 wt.%; or 0.1 wt.% to 0.25 wt.% pH adjusting agent.

[0058] The water-soluble solvent is selected from the group consisting of deionized (DI) water, distilled water, and alcoholic organic solvents.

[0059] In another aspect (Aspect 2), there is provided a CMP polishing method for chemical mechanical planarization of a semiconductor substrate comprising at least one surface containing Cu, comprising, consisting essentially of, or consisting steps of:

contacting the at least one surface with a polishing pad;

delivering the chemical mechanical planarization polishing composition of Aspect 1;

polishing the at least one surface containing Cu with the chemical mechanical planarization composition.

[0060] In yet another aspect (Aspect 3), there is provided a CMP polishing system, comprising, consisting essentially of, or consisting of:
a semiconductor substrate comprising at least one surface containing Cu;
a polishing pad; and
the chemical mechanical planarization composition of Aspect 1;
wherein the at least one surface containing Cu is in contact with the polishing pad and the chemical mechanical planarization composition.

[0061] 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 Cu; includes but is not limited to 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.

[0062] The following non-limiting examples are presented to further illustrate the present invention.

GLOSSARY

COMPONENTS

[0063] 1*H*-pyrazolo[3,4-*d*]pyrimidine (CAS: 271-80-7), 1*H*-pyrazolo[3,4-*b*]pyridine (CAS: 271-73-8), 2-(1*H*-pyrazol-3-yl)pyridine, 1*H*-Indazol-5-ol (CAS: 15579-15-4), 2-(1*H*-pyrazol-4-yl)pyridine (CAS: 439106-75-9), 4-(1*H*-pyrazol-4-yl)pyrimidine (CAS: 28648-87-5), 1*H*-pyrazolo[3,4-*b*]pyridine-5-amine (CAS: 942185-01-5), 1*H*-pyrazolo[3,4-*b*]pyridine-6-amine (CAS: 63725-49-5), 3-amino-1*H*-pyrazole-4-carboxamide (CAS: 5334-31-6) and 3-(1*H*-pyrazol-3-yl)pyridine (CAS: 45887-08-9) were supplied by Ambeed, Arlington Hts, USA, 2-(1H-pyrazol-4-yl)pyrazine (CAS: 849924-97-6) was supplied by Combi-Blocks, Inc. San Diego, USA, 1*H*-pyrazolo[3,4-*d*]pyrimidine-4-amine (CAS: 2380-63-4), 2-(1*H*-pyrazol-3-yl)pyrazine (CAS: 111781-54-5) and tisopurine (CAS: 5334-23-6) were supplied by abcr GmbH, Karlsruhe, Germany, 1*H*-pyrazolo[3,4-*b*]pyrazine (CAS: 272-60-6) and 1*H*-pyrazolo[3,4-*b*]pyridine-5-carboxylic acid (CAS: 952182-02-4) were supplied by Advanced ChemBlock Inc, Hayward, USA. All other raw chemicals were sourced from Merck KGaA, Darmstadt, Germany.

[0064] Static etch rate tests were conducted using blanket copper wafers with 8K – 12K Angstroms in thickness which are diced to 1” x 1” copper coupons. The copper

blanket wafers were purchased from Silicon Valley Microelectronics, 1150 Campbell Ave, Calif., 95126.

[0065] Colloidal silica (PL-2C) was supplied by Fuso Chemical Co., LTD, Japan.

Evaluation of the Static Etch Rate

[0066] This static etch rate of copper in CMP composition was measured using a four-point probe technique.

[0067] Before the measurements, copper coupons (1" x 1") were prepared by surface cleaning in a 0.6% citric acid solution for 5 minutes to remove native oxide and contamination,

followed by rinsing in DI water and drying.

[0068] Pre- measurements of the copper thickness were taken across the coupons at multiple sites and the results were used as pre-thickness. The copper coupons were then immersed in a CMP composition for 5 minutes at a controlled temperature of 50 °C in a water bath. Post-measurements of the copper thickness were then conducted using the same four-point probe technique as used in the pre-measurements and the results were used as post-thickness..

[0069] The CMP compositions comprised: 0.46 wt.% glycine, 0.8 wt.% DL-alanine, 0.01 wt.% Fuso PL-2 abrasives, 1 wt.% H_2O_2, and different corrosion inhibitors as shown in Table 1. The CMP compositions had a pH of 7.2 – 7.4 adjusted with KOH as needed.

[0070] The static etch rate (SER) of copper was calculated by subtracting the post-thickness from the pre-thickness and dividing by the dipping time.

[0071] The results were shown in Table 1.

TABLE 1

Compound	Conc [wt.%]	SER [A/min]
1,2,4-triazole (comparative)	0.1	285
oxypurinol	0.1	140
allopurinol	0.1	5
1*H*-pyrazolo[3,4-*d*]pyrimidine	0.1	2
1*H*-pyrazolo[3,4-*b*]pyridine	0.1	75
2-(1*H*-pyrazol-3-yl)pyridine	0.1	75
2-(1*H*-pyrazol-4-yl)pyrazine	0.1	4

2-(1*H*-pyrazol-4-yl)pyridine	0.1	5
4-(1*H*-pyrazol-4-yl)pyrimidine	0.1	30
1*H*-pyrazolo[3,4-*b*]pyridine-5-amine	0.1	45
1*H*-pyrazolo[3,4-*d*]pyrimidine-4-amine	0.05	20
1*H*-pyrazolo[3,4-*b*]pyrazine	0.06	70
1*H*-pyrazolo[3,4-*b*]pyridine-6-amine	0.09	120
tisopurine	0.05	60

[0072] Table 1 listed a compilation of corrosion inhibitors disclosed in the present invention, demonstrating their comparable or superior efficacy in terms of copper corrosion protection compared to triazole compound, such as 1,2,4-triazole which is commonly used in the field.

[0073] Table 2 listed pyrazoles or derivatives that are similar to the compounds in Table 1 but not disclosed in the present invention. Table 2 has shown that those pyrazoles or derivatives exhibited lower activity in terms of copper corrosion protection. In some cases, some pyrazoles or derivatives completely lost their ability to effectively protect copper against corrosion in the used slurry composition.

TABLE 2

Compound	**Conc [wt.%]**	**SER [A/min]**
1*H*-indazol-5-ol	0.1	425
3-amino-7-azaindole	0.1	925
1*H*-indazole	0.1	920
3-phenyl-1*H*-pyrazole	0.1	885
3-methylpyrazole	0.1	1440
2-(1*H*-pyrazole-3-yl)phenol	0.1	2225
(1*H*-pyrazol-1-yl)methanol	0.1	1010
3,5-dimethylpyrazole	0.1	1890
3,5-diisopropylpyrazole	0.1	1965
2-(1*H*-pyrazol-3-yl)pyrazine	0.1	970
3-amino-1*H*-pyrazole-4-carboxamide	0.1	780
3-(1*H*-pyrazol-3-yl)pyridine	0.1	1275
N-(5-methyl-1*H*-pyrazol-3-yl)acetamide	0.1	1790
1*H*-indazol-4-amine	0.1	880
1*H*-indazol-7-amine	0.075	805
1*H*-pyrazolo[3,4-*b*]pyridine-5-carboxylic acid	0.05	1080
none	-	2321

[0074] As demonstrated here, even nitrogen-containing cyclic compounds or pyrazoles having structures closely related to the general structures (1) to (4) of the non-triazole corrosion inhibitors did not exhibit close performance. The tables highlighted the performance disparities, emphasized the unexpected superior efficacy of the compounds listed in Table 1 for copper corrosion protection in the context of the present invention.

Polishing Experiments

CMP Methodology

PARAMETERS

General

[0075] Å or A: angstrom(s) – a unit of length

[0076] BP: back pressure, in psi units

[0077] CMP: chemical mechanical planarization = chemical mechanical polishing

[0078] CS: carrier speed

[0079] DF: Down force: pressure applied during CMP, unit: psi

[0080] min: minute(s)

[0081] ml: milliliter(s)

[0082] mV: millivolt(s)

[0083] mM: millimolar

[0084] psi: pounds per square inch

[0085] PS: platen rotational speed of polishing tool, in rpm (revolution(s) per minute)

[0086] SF: composition flow, ml/min

[0087] Wt. %: weight percentage (of a listed component)

[0088] Removal Rates: Measured removal rate at a given down pressure. The down pressure of the CMP tool was 2.5 psi in the examples.

[0089] In the conducted mini polisher test, the CMP tool utilized was the Tribolab CMP, manufactured by Bruker. During the CMP process for Cu blanket coupon studies, an IC1010 polishing pad was employed. Prior to the test, the IC1010 pad was subjected to a break-in procedure by polishing 25 coupons with a copper CMP composition. Subsequently, the pad was conditioned for 14 minutes using the 4DNS80AMC1 conditioner, manufactured by Saesol.

[0090] For the experiments, PVD Cu coupons with a diameter of 50.8 mm were cut from 300mm wafers manufactured by Silicon Valley Microelectronics, 1150 Campbell Ave, Calif., 95126. The polishing step was carried out with the following conditions: table speed of 90 rpm, head speed of 87 rpm, downforce of 2.5 psi, composition flow rate of 14.3 mL/min, and ex-situ conditioning.

[0091] The CMP compositions comprised: 0.46 wt.% glycine, 0.8 wt.% DL-alanine, 0.01 wt.% Fuso PL-2 abrasives and 1 wt.% H_2O_2 and different corrosion inhibitors at different concentrations as shown in Table 3. 1,2,4-triazole was used as a reference.

[0092] The CMP compositions had a pH of 7.2 – 7.4 adjusted with KOH as needed.

[0093] To measure the removal rates (RR) of the Cu films, a four-point probe (model R50-100 4PP) manufactured by Filmetrics was employed. The removal rates were determined in units of Angstroms per minute (Å/min).

TABLE 3 Cu RR and SER

Compound	Conc [wt.%]	SER [Å/min]	Cu RR [Å/min]
1,2,4-triazole (Comparative)	0.067	346	1987
allopurinol	0.05	15	427
allopurinol	0.03	87	882
allopurinol	0.02	349	2222
1*H*-pyrazolo[3,4-*b*]pyridine	0.1	91	927
1*H*-pyrazolo[3,4-*b*]pyridine	0.05	221	1390
1*H*-pyrazolo[3,4-*b*]pyridine	0.04	227	1978
1*H*-pyrazolo[3,4-*b*]pyridine	0.03	355	2623
1*H*-pyrazolo[3,4-*b*]pyridine	0.02	664	2823

[0094] Table 3 presented a comprehensive overview of Cu removal rates (Cu RR) for various disclosed non-triazole corrosion inhibitors. Additionally, the corresponding static etch rate (SER) results were also provided.

[0095] Table 3 provides valuable insights into the relationship between concentrations, Cu RR, and SER for each tested corrosion inhibitor, aiding in the evaluation and comparison of their performance characteristics.

[0096] Importantly, the disclosed non-triazole corrosion inhibitor have demonstrated exceptional copper corrosion protection while enabling high or even higher copper removal rates.

[0097] 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. oxidizer;

c. non-triazole corrosion inhibitor; and

d. water-soluble solvent ;

optionally at least one of

e. chemical additive;

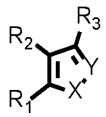
f. biocide;

g. and

h. pH adjusting agent;

wherein

the non-triazole corrosion inhibitor corrosion inhibitor has a general structure selected from the group consisting of (1), (2), (3), (4), and combinations thereof:



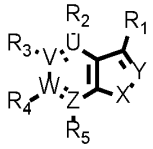
(1)

wherein:

X = NH, S or O and Y = N,

R_1 = H, CH_3, NH_2 or NH_2NH_2,

R_2 = substituted or unsubstituted pyridinyl or pyrimidyl group and R_3 = H, CH_3 or NH_2, or R_2 = H, CH_3 or NH_2 and R_3 = substituted or unsubstituted pyridinyl or pyrimidyl group;



(2)

wherein:

X = NH, S or O and Y = N,

U = C or N, V = C or N, W = C or N and Z = C or N with 3 ≥N ≥ 1 or 2 ≥N ≥ 1,

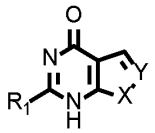
R_1 = H, CH_3 or NH_2,

R_2 = H, CH_3, OH or NH_2 when U = C,

R_3 = H, CH_3, OH or NH_2 when V = C,

R_4 = H, CH_3, OH or NH_2 when W = C,

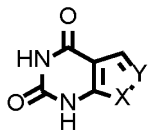
R_5 = H, CH_3, OH or NH_2 when Z = C;



(3)

wherein:

X = NH, S or O and Y = N or C and R_1 = H, CH_3 or NH_2.



(4)

wherein:

X = NH, S or O and Y = N or C;

the chemical additive is selected from the group consisting of complexing agents, metal chelators, topography reducing additives, removal rate boosters, and combinations thereof;

and

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

2. The Chemical Mechanical Planarization (CMP) polishing composition according to Claim 1, 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; metal oxide-coated inorganic oxide particles; and combinations thereof .

3. The Chemical Mechanical Planarization (CMP) polishing composition according to any one of Claims 1 - 2, wherein the abrasive is selected from the group consisting of colloidal silica; ceria, metal oxide-coated inorganic oxide particles, and combinations thereof.

4. The Chemical Mechanical Planarization (CMP) polishing composition according to any one of Claims 1 - 3, wherein the CMP polishing composition contains 0.0025 wt.% to 25 wt.%, 0.0025 wt.% to 2.5 wt.%, or 0.005 wt.% to 1.0 wt.% abrasives.

5. The Chemical Mechanical Planarization (CMP) polishing composition according to any one of Claims 1 - 4, wherein the oxidizer is a peroxy compound selected from the group consisting of hydrogen peroxide, urea peroxide, peroxyformic acid, peracetic acid, propaneperoxoic acid, substituted or unsubstituted butaneperoxoic acid, hydroperoxy-acetaldehyde, potassium periodate, ammonium peroxymonosulfate; and non-per-oxy compound selected from the group consisting of ferric nitrite, $KClO_4$, $KBrO_4$, $KMnO_4$; and combinations thereof.

6. The Chemical Mechanical Planarization (CMP) polishing composition according to any one of Claims 1 - 5, wherein the oxidizer is hydrogen peroxide.

7. The Chemical Mechanical Planarization (CMP) polishing composition according to any one of Claims 1 - 6, wherein 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.

8. The Chemical Mechanical Planarization (CMP) polishing composition according to any one of Claims 1 - 7, wherein the non-triazole corrosion inhibitor has the structure of (1).

9. The Chemical Mechanical Planarization (CMP) polishing composition according to any one of Claims 1 - 7, wherein the non-triazole corrosion inhibitor has the structure of (2).

10. The Chemical Mechanical Planarization (CMP) polishing composition according to any one of Claims 1 - 7, wherein the non-triazole corrosion inhibitor has the structure of (3).

11. The Chemical Mechanical Planarization (CMP) polishing composition according to any one of Claims 1 - 7, wherein the non-triazole corrosion inhibitor has the structure of (4).

12. The Chemical Mechanical Planarization (CMP) polishing composition according to any one of Claims 1 - 7, wherein the non-triazole corrosion inhibitor is selected from the group consisting of 2-(1*H*-pyrazol-3-yl)pyridine, 2-(1*H*-pyrazol-3-yl)pyrazine, 2-(5-methyl-1*H*-pyrazol-3-yl)pyridine, 2-(1*H*-pyrazol-4-yl)pyrazine, 2-(1*H*-pyrazol-4-yl)pyridine, 5-(pyridin-2-yl)-1*H*-pyrazol-4-amine, 1*H*-pyrazolo[3,4-*b*]pyridine, 1*H*-pyrazolo[3,4-*d*]pyrimidine, 6-methyl-1*H*-pyrazolo[3,4-*b*]pyridine, 1*H*-pyrazolo[3,4-*d*]pyrimidine-4-amine, 3-methyl-1*H*-pyrazolo[3,4-*b*]pyridine, 1*H*-pyrazolo[3,4-*b*]pyridine-5-amine, 1*H*-pyrazolo[3,4-*d*]pyrimidin-6-amine, 4-methyl-1*H*-pyrazolo[3,4-*b*]pyridine, 4-(1*H*-pyrazol-4-yl)pyrimidine, 1*H*-pyrazolo[3,4-*b*]pyrazine, 1*H*-pyrazolo[3,4-*b*]pyridine-6-amine, allopurinol, oxypurinol, tisopurine, and combinations thereof.

13. The Chemical Mechanical Planarization (CMP) polishing composition according to any one of Claims 1 - 7, wherein the non-triazole corrosion inhibitor is selected from the group consisting of allopurinol, 1*H*-pyrazolo[3,4-*b*]pyridine, 2-(1*H*-pyrazol-4-yl)pyrazine, 2-(1*H*-pyrazol-4-yl)pyridine, and combinations thereof.

14. The Chemical Mechanical Planarization (CMP) polishing composition according to any one of Claims 1 - 13, wherein the CMP polishing composition contains

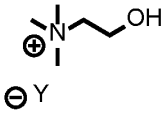
0.005 wt.% to 1.0 wt.%, 0.01 wt.% to 0.5 wt.%; or 0.02 wt.% to 0.2 wt.% non-triazole corrosion inhibitor.

15. The Chemical Mechanical Planarization (CMP) polishing composition according to any one of Claims 1 - 14, wherein the CMP polishing composition contains the chemical additive selected from the group consisting of amino acids and derivatives, organic amines; choline salts, and combinations thereof.

16. The Chemical Mechanical Planarization (CMP) polishing composition according to any one of Claims 1 - 14, wherein the CMP polishing composition contains the chemical additive selected from the group consisting of amino acid or their derivatives selected from the group consisting of glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, valine, leucine, isoleucine, phenylamine, proline, serine, threonine, tyrosine, glutamine, asparagine, glutamic acid, aspartic acid, tryptophan, histidine, arginine, lysine, methionine, cysteine, iminodiacetic acid, and combinations thereof.

17. The Chemical Mechanical Planarization (CMP) polishing composition according to any one of Claims 1 - 14, wherein the CMP polishing composition contains organic amine as the chemical additive selected from the group consisting of ethylenediamine, propylenediamine, butylenediamine, and combinations thereof.

18. The Chemical Mechanical Planarization (CMP) polishing composition according to any one of Claims 1 - 14, wherein the CMP polishing composition contains choline salt as the chemical additive wherein the choline salt has a general molecular structure of:



wherein anion Y^- can be bicarbonate, hydroxide, p-toluene-sulfonate, bitartrate, and other suitable anionic counter ions.

19. The Chemical Mechanical Planarization (CMP) polishing composition according to any one of Claims 1 - 18, wherein the CMP polishing composition contains 0.1

wt.% to 18 wt.%, 0.5 wt.% to 10 wt.%; or 0.75 wt.% to 2.5 wt.% of the chemical additive.

20. The Chemical Mechanical Planarization (CMP) polishing composition according to any one of Claims 1 - 19, wherein the CMP polishing composition contains biocide comprising ingredient selected from the group consisting of methyl isothiazolinone, 5-chloro-2-methyl-4-isothiazolin-3-one, 2-methyl-4-isothiazolin-3-one, and combinations thereof.

21. The Chemical Mechanical Planarization (CMP) polishing composition according to any one of Claims 1 - 20, wherein 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.

22. The Chemical Mechanical Planarization (CMP) polishing composition according to any one of Claims 1 - 21, wherein the CMP polishing composition contains the pH adjusting agent selected from the group consisting of(a)nitric acid, sulfuric acid, tartaric acid, succinic acid, citric acid, malic acid, malonic acid, various fatty acids, various polycarboxylic acids, and mixtures thereof to lower the pH; and (b) potassium hydroxide, sodium hydroxide, ammonia, tetraethylammonium hydroxide, piperazine, polyethyleneimine, modified polyethyleneimine, and mixtures thereof to raise the pH.

23. The Chemical Mechanical Planarization (CMP) polishing composition according to any one of Claims 1 - 22, wherein 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.

24. The Chemical Mechanical Planarization (CMP) polishing composition according to any one of Claims 1 - 23, wherein the CMP polishing composition comprises at least one selected from the group consisting of colloidal silica , fumed silica, and metal oxide-coated inorganic oxide particles; at least one selected from the group consisting of 2-(1*H*-pyrazol-3-yl)pyridine, , 2-(5-methyl-1*H*-pyrazol-3-yl)pyridine, 2-(1*H*-pyrazol-4-yl)pyrazine, 2-(1*H*-pyrazol-4-yl)pyridine, 5-(pyridin-2-yl)-1*H*-pyrazol-4-amine, 1*H*-pyrazolo[3,4-*b*]pyridine, 1*H*-pyrazolo[3,4-*d*]pyrimidine, 6-

methyl-1*H*-pyrazolo[3,4-*b*]pyridine, 1*H*-pyrazolo[3,4-*d*]pyrimidine-4-amine, 3-methyl-1*H*-pyrazolo[3,4-*b*]pyridine, 1*H*-pyrazolo[3,4-*b*]pyridine-5-amine, 1*H*-pyrazolo[3,4-*d*]pyrimidin-6-amine, 4-methyl-1*H*-pyrazolo[3,4-*b*]pyridine, 4-(1*H*-pyrazol-4-yl)pyrimidine, 1*H*-pyrazolo[3,4-*b*]pyrazine, 1*H*-pyrazolo[3,4-*b*]pyridine-6-amine, allopurinol, oxypurinol, and tisopurine; and the CMP polishing composition has a pH of 5 to 9, or 6 to 8.

25. The Chemical Mechanical Planarization (CMP) polishing composition according to any one of Claims 1 - 24, wherein the CMP polishing composition comprises at least one selected from the group consisting of colloidal silica fumed silica, and metal oxide-coated inorganic oxide particles; at least one selected from the group consisting of 2-(1*H*-pyrazol-3-yl)pyridine, , 2-(5-methyl-1*H*-pyrazol-3-yl)pyridine, 2-(1*H*-pyrazol-4-yl)pyrazine, 2-(1*H*-pyrazol-4-yl)pyridine, 5-(pyridin-2-yl)-1*H*-pyrazol-4-amine, 1*H*-pyrazolo[3,4-*b*]pyridine, 1*H*-pyrazolo[3,4-*d*]pyrimidine, 6-methyl-1*H*-pyrazolo[3,4-*b*]pyridine, 1*H*-pyrazolo[3,4-*d*]pyrimidine-4-amine, 3-methyl-1*H*-pyrazolo[3,4-*b*]pyridine, 1*H*-pyrazolo[3,4-*b*]pyridine-5-amine, 1*H*-pyrazolo[3,4-*d*]pyrimidin-6-amine, 4-methyl-1*H*-pyrazolo[3,4-*b*]pyridine, 4-(1*H*-pyrazol-4-yl)pyrimidine, 1*H*-pyrazolo[3,4-*b*]pyrazine, 1*H*-pyrazolo[3,4-*b*]pyridine-6-amine, allopurinol, oxypurinol, and tisopurine; at least one amino acid, diamine; and a choline salt; and the CMP polishing composition has a pH of 5 to 9, or 6 to 8.

26. The Chemical Mechanical Planarization (CMP) polishing composition according to any one of Claims 1 - 25, wherein the CMP polishing composition comprises colloidal silica, at least one selected from the group consisting of allopurinol, 1*H*-pyrazolo[3,4-*b*]pyridine, 2-(1*H*-pyrazol-4-yl)pyrazine, and 2-(1*H*-pyrazol-4-yl)pyridine; at least one of glycine and DL-alanine; and the CMP polishing composition has a pH of 5 to 9, or 6 to 8.

27. A Chemical Mechanical Planarization (CMP) polishing method for polishing a semiconductor substrate comprising at least one surface containing Cu, comprising, consisting essentially of, or consisting of:
contacting the at least one surface with a polishing pad;
delivering the chemical mechanical planarization (CMP) polishing composition according to any one of Claims 1 -26;

polishing the at least one surface containing Cu with the chemical mechanical planarization composition.

28. The Chemical Mechanical Planarization (CMP) polishing method according to claim 27, wherein the semiconductor substrate comprising at least another surface containing a second material; removal selectivity of Cu vs the second material is > 1, >5, or > 6; and
the second material is selected from the group consisting of Ta; Ti; TaN; TiN; Ta; TaN; Ti; TiN; SiO_2, SiN, SiC; and low-k and ultra-low-k material.

29. A Chemical Mechanical Planarization (CMP) polishing system, comprising:
a semiconductor substrate comprising at least one surface containing Cu;
a polishing pad; and
the chemical mechanical planarization (CMP) polishing composition according to any one of claims 1 to 26;
wherein the at least one surface containing Cu is in contact with the polishing pad and the chemical mechanical planarization composition.

30. The Chemical Mechanical Planarization (CMP) polishing system according to claim 29;
wherein the semiconductor substrate comprising at least another surface containing a second material; removal selectivity of Cu vs the second material is > 1, >5, or > 6; and
the second material is selected from the group consisting of Ta; Ti; TaN; TiN; Ta; TaN; Ti; TiN; SiO_2; SiN; SiC; and low-k and ultra-low-k material.