

SELECTIVE DEPOSITION OF ALUMINUM-CONTAINING DIELECTRIC MATERIAL ON DIELECTRIC OVER METAL UTILIZING ALKYNES

CROSS-REFERENCE TO RELATED APPLICATIONS

[001] This application claims priority to United States Provisional Patent Application number 63/520,228, filed on August 17, 2023, and United States Provisional Patent application number 63/560,138, filed on March 1, 2024, the disclosures of which are hereby incorporated by reference.

FIELD

[002] The present application relates to selective formation of a passivation layer on a first surface of a substrate relative to a second surface. In addition, further processing can be used to subsequently deposit a different material on the second surface relative to the first.

BACKGROUND

[003] Selective deposition processes are gaining a lot of momentum mostly because of the limitations of contemporary lithographic processes to enable the fabrication of advanced semiconductor devices based on ever diminishing physical dimensions. Traditionally, patterning in the microelectronics industry has been accomplished using various lithography and etch processes. However, since lithography is becoming exponentially more complex and expensive the use of selective deposition to form self-aligned features is becoming much more attractive. The fabrication of self-aligned via structures would benefit significantly from manufacturable selective deposition processes. Another potential application for selective deposition is gap fill. In gap fill, the dielectric “fill” film is grown selectively from the bottom of a trench towards the top. Selective deposition could be used for other applications such as selective sidewall deposition where films are selectively deposited on exposed surfaces of three dimensional FIN-FET structures. This would enable the deposition of a sidewall spacer without the need for complex patterning steps. Selective deposition processes for metal

and metal oxide films that are used as gate dielectrics and capacitor dielectrics would also be of great utility in semiconductor device manufacturing.

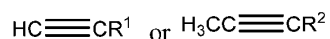
[004] There are previous examples within the technical literature related to the selective formation of surface passivation coatings on wafers with multiple, different chemical surfaces that are exposed. This has been done with the purpose of retarding or preventing the deposition of films through ALD processes on these passivated surfaces, but not preventing deposition on the surfaces where the ALD deposition process is desired to deposit a film. In general, the selectivity of the processes has been less than adequate due to incomplete passivation of the surfaces and / or due to physisorption of ALD precursor molecules and subsequent formation of the ALD film material either within the passivation layer itself or on the surfaces where deposition is not desired.

[005] Selectively passivation of metal over dielectric to achieve area selective deposition (ASD) of dielectric on dielectric remains great challenge due to the similarity in their surface chemistry natures, so far relatively few passivation chemistries have been reported that can selectively passivate metal over dielectric to successfully allow the atomic layer deposition of dielectric films on the dielectric.

[006] The present disclosure seeks to overcome the limitations of the prior art and provide improved methods for selective deposition of ultra-thin film materials using ALD deposition processes.

SUMMARY

[007] In a first aspect, a method is provided for forming an aluminum-containing dielectric film selectively on at least one surface of a substrate. The method for forming an aluminum-containing dielectric film selectively on at least one surface of a substrate comprising: (a) providing the substrate in a reaction vessel, the substrate having a first surface comprising a metal and a second surface comprising a dielectric material, wherein the first surface and the second surface are coplanar; (b) forming at least one passivated layer on the first surface by exposing the first surface and the second surface to a passivating composition comprising an alkyne having one of the following formulae:



IA IB;

wherein R^1 and R^2 are each selected from the group consisting of a linear or branched C_6 to C_{14} alkyl or a linear or branched C_6 to C_{14} arylalkyl; (c) purging the reactor with inert gas; (d) introducing an aluminum precursor into the reactor to react with the dielectric material to form an aluminum-containing layer; (e) purging the reactor with inert gas; (f) introducing a vapor comprising water into the reactor to react with the aluminum-containing layer to form an aluminum oxide layer; (g) purging the reactor with inert gas; and (h) repeating steps (d) through (g) to deposit a desired thickness of the aluminum-containing dielectric film on top of the dielectric material.

[008] In a further aspect of the first main aspect, the thickness of the aluminum-containing dielectric film can range from about 1 Å to about 100 Å, or about 5 Å to about 90 Å, or about 5 Å to about 80 Å, or about 5 Å to about 70 Å or about 5 Å to about 60 Å, or about 5 Å to about 50 Å, or about 5 Å to about 40 Å, or about 5 Å to about 30 Å or about 5 Å to about 20 Å.

[009] In a further aspect of the first main aspect, the aluminum precursor is selected from the group consisting of triethylaluminum, dimethylaluminum iso-propoxide, and diethylaluminum iso-propoxide.

[0010] In a further aspect of the first main aspect, the alkyne of Formula IA is selected from the group consisting of 1-octyne, 1-nonyne, 1-decyne, 1-undecyne, 1-dodecyne, 1-tridecyne, 1-tetradecyne, ethynylbenzene, 3-phenyl-1-propyne, 4-phenyl-1-butyne, 5-phenyl-1-pentyne, and 6-phenyl-1-hexyne.

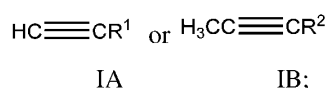
[0011] In a further aspect of the first main aspect, the alkyne of Formula IB is selected from the group consisting of 2-octyne, 2-nonyne, 2-decyne, 2-undecyne, 2-dodecyne, 2-tridecyne, and 2-tetradecyne.

[0012] In a further aspect of the first main aspect, the passivating composition comprises or consists essentially of 1-decyne, 1-dodecyne, or 5-phenyl-1-pentyne.

[0013] In a further aspect of the first main aspect, a deposition selectivity of the second surface to the first surface is greater than about 0.3, more preferably greater than about 0.5, and most preferably greater than about 0.6.

[0014] In a further aspect of the first main aspect, a deposition selectivity of the second surface to the first surface is greater than about 0.6 and the thickness of the aluminum-containing dielectric film is about 50 Å or less.

[0015] In a second main aspect, a method for forming an aluminum doped silicon oxide dielectric film selectively on at least one surface of a substrate is provided. The method comprising: (a) loading the substrate into a reactor, the substrate comprising a first surface comprising a metal and a second surface comprising a dielectric material, wherein the first surface and the second surface are coplanar; (b) introducing an alkyne into the reactor to selectively form an organic layer on the metal surface, the alkyne having the following formula:



wherein R¹ and R² are each selected from the group consisting of a linear or branched C₆ to C₁₄ alkyl or a linear or branched C₆ to C₁₄ arylalkyl; (c) purging the reactor with inert gas; (d) introducing an aluminum precursor into the reactor to react with the dielectric material to form an aluminum-containing layer; (e) purging the reactor with inert gas; (f) introducing a vapor comprising an alkoxysilanol into the reactor to react with the aluminum-containing layer to form an aluminum silicon oxide layer and; (g) purging the reactor with inert gas; and optionally (h) repeating steps (d) to (g) to deposit a desired thickness of the aluminum doped silicon oxide dielectric film on top of the dielectric material.

[0016] In a further aspect of the second main aspect, the aluminum doped silicon oxide dielectric film has a thickness ranging from about 1 Å to about 100 Å, or about 5 Å to about 90 Å, or about 5 Å to about 80 Å, or about 5 Å to about 70 Å or about 5 Å to about 60 Å, or about 5 Å to about 50 Å, or about 5 Å to about 40 Å, or about 5 Å to about 30 Å or about 5 Å to about 20 Å.

[0017] In a further aspect of the second main aspect, the aluminum precursor is selected from the group consisting of triethylaluminum, dimethylaluminum isopropoxide, and diethylaluminum isopropoxide.

[0018] In a further aspect of the second main aspect, the alkyne with Formula IA is selected from the group consisting of 1-octyne, 1-nonyne, 1-decyne, 1-undecyne, 1-

dodecyne, 1-tridecyne, 1-tetradecyne, ethynylbenzene, 3-phenyl-1-propyne, 4-phenyl-1-butyne, 5-phenyl-1-pentyne, and 6-phenyl-1-hexyne.

[0019] In a further aspect of the second main aspect, the alkyne with Formula IB can be selected from the group consisting of 2-octyne, 2-nonyne, 2-decyne, 2-undecyne, 2-dodecyne, 2-tridecyne, and 2-tetradecyne.

[0020] In a further aspect of the second main aspect, the alkoxysilanol is selected from the group consisting of tris(tert-butoxy)silanol, tris(tert-pentoxysilanol, bis(tert-butoxy)(tert-pentoxysilanol, and bis(tert-pentoxysilanol.

[0021] In a further aspect of the second main aspect, the dielectric material is selected from the group consisting of silicon oxide, carbon doped silicon oxide, silicon oxynitride, carbon doped oxynitride, silicon nitride, and metal oxide such as zirconium oxide, hafnium oxide, silicon doped zirconium oxide, or silicon doped hafnium oxide, or a combination thereof.

[0022] In a further aspect of the second main aspect, the metal of the metal or metal oxide is selected from selected from the group consisting of cobalt, aluminum, copper, tantalum, ruthenium, molybdenum, tungsten, platinum, iridium, nickel, titanium, silver, gold, or a combination thereof.

[0023] In a further aspect of the second main aspect, a deposition selectivity of the second surface to the first surface is greater than about 0.6, more preferably greater than about 0.8, and most preferably greater than about 0.9 and the thickness of the aluminum doped silicon oxide dielectric film is about 100 Å or less.

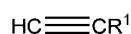
[0024] In a further aspect of the second main aspect, steps (d) to (g) are conducted at a temperature of between about 150 and about 350 degrees Celsius.

[0025] In a further aspect of the second main aspect, a preclean step is conducted prior to step (a), the preclean step comprising exposing the first surface to an acid, a reducing environment, heating, or a combination thereof.

[0026] In a further aspect of the second main aspect, the preclean step comprises exposing the substrate to citric acid, followed by exposing the substrate to H₂ at a temperature ranging from about 250 to about 500 degrees Celsius.

[0027] In a further aspect of the second main aspect, the substrate is subjected to a chemical mechanical planarization step, wherein the chemical mechanical planarization step is conducted prior to the preclean step in order to provide coplanarity of the first surface and the second surface.

[0028] In a third main aspect, a method for passivating a metal-containing surface of a substrate is provided. The method comprising: (a) providing the substrate in a reaction vessel at temperatures ranging from 20°C to 400°C, the substrate having a first surface comprising a metal and a second surface comprising a dielectric material; (b) forming at least one passivation layer on the first surface by exposing both the first surface and the second surfaces to a passivating composition comprising an alkyne having the following formula:



wherein R¹ a linear or branched C₆ to C₁₄ arylalkyl; and (c) purging the reactor with inert gas.

[0029] In a further aspect of the third main aspect, steps (a) to (c) are repeated to provide a fully covered passivation layer on the second surface.

[0030] In a further aspect of the third main aspect, the first surface comprises a metal or metalloid chosen from the group consisting of ruthenium (Ru), cobalt (Co), copper (Cu), titanium, (Ti), tantalum (Ta), nickel (Ni), tungsten (W), molybdenum (Mo), and combinations thereof, or wherein the first surface comprises a metal nitride chosen from the group consisting of tantalum nitride (TaN), titanium nitride (TiN), tungsten nitride (WN), tungsten carbonitride (WCN), molybdenum nitride (MoN), copper silicon nitride (CuSiN), silicon, germanium, and combinations thereof.

[0031] In a further aspect of the third main aspect, the second surface is selected from the group consisting of silicon oxide and carbon doped silicon oxide, or wherein the second surface is selected from the group consisting of silicon nitride.

[0032] In a further aspect of the third main aspect, the alkyne is selected from the group consisting of ethynylbenzene, 3-phenyl-1-propyne, 4-phenyl-1-butyne, 5-phenyl-1-pentyne, and 6-phenyl-1-hexyne.

[0033] The embodiments of the disclosure can be used alone or in combination with each other.

BRIEF DESCRIPTION OF THE DRAWINGS

[0034] The accompanying drawings, which are included to provide a further understanding of the disclosed subject matter and are incorporated in and constitute a part of this specification, illustrate embodiments of the disclosed subject matter and together with the description serve to explain the principles of the disclosed subject matter. In the drawings:

[0035] FIG. 1 illustrates an exemplary comprising: a surface pre-clean, metal passivation, and selective deposition wherein a dielectric film is selectively deposited on a dielectric film, while metal surface is passivated;

[0036] FIG. 2 illustrates the selectivity comparison of a 1-alkyne and a 5-alkyne across aluminum oxide films of varying thicknesses (Å);

[0037] FIG. 3 illustrates the selectivity comparison of a 1-alkyne at different temperatures across aluminum oxide films of varying thicknesses (Å);

[0038] FIG. 4 illustrates the selectivity comparison of a 5-phenyl-1-pentyne and 1-dodecyne at 250°C with various thickness (Å) of aluminum oxide films; and

[0039] FIG. 5 illustrates the selectivity comparison of a 5-phenyl-1-pentyne and 1-dodecyne at 250°C with various thickness of aluminum doped silicon oxide films (Å).

DETAILED DESCRIPTION

[0040] All references, including publications, patent applications, and patents, cited herein are hereby incorporated by reference to the same extent as if each reference were individually and specifically indicated to be incorporated by reference and were set forth in its entirety herein.

[0041] The use of the terms "a" and "an" and "the" and similar referents in the context of describing the disclosure (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The terms "comprising," "having," "including," and

“containing” are to be construed as open-ended terms (i.e., meaning “including, but not limited to,”) unless otherwise noted. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (*e.g.*, “such as”) provided herein, is intended merely to better illuminate the disclosure and does not pose a limitation on the scope of the claims unless otherwise stated explicitly. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the subject matter of this disclosure.

[0042] Preferred embodiments of this disclosure are described herein, including the best mode known to the inventors for carrying out the claimed subject matter. Variations of those preferred embodiments may become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventor expects skilled artisans to employ such variations as appropriate, and the inventor intends for the claimed subject matter to be practiced otherwise than as specifically described herein. Accordingly, this disclosure includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the claimed subject matter unless otherwise indicated herein or otherwise clearly contradicted by context.

[0043] There are a variety of methods that could be used for selective depositions. Embodiments of the disclosure are directed to methods that employ surface deactivation by taking advantage of the surface chemistry of two different surfaces. Since two different surfaces will have different reactive handles, the differences can be taken advantage of by utilizing molecules that will react with one surface (to deactivate that surface) and not react with the other surface.

[0044] In this disclosure, it has been conceived and demonstrated that a metal such as copper can be selectively passivated using 1-alkynes therefore allowing great inhibition

of dielectric growth on passivated metal surface, but highly selective growth of dielectric film such as aluminum-containing dielectric film on dielectric surface such as silicon oxide or carbon doped silicon oxide only at relative higher temperatures than thiol-based inhibitors.

[0045] Various aspects of the disclosure will now be described with reference to the drawings and tables disclosed herein, if applicable, with like reference numbers referring to like elements, unless specified otherwise. As described above, a need exists in the art to deposit aluminum-containing dielectric materials, such as aluminum oxide or silicon doped aluminum oxide, selectively on top of a dielectric surface relative to a metal surface in a semiconductor manufacturing process using a thermal process without using a plasma at temperatures ranging from 150 to 350 C with high selectivity.

[0046] In the illustrated embodiments, the selectivity is defined as (the thickness of aluminum-containing film on the dielectric material (growth surface) - the thickness of aluminum-containing film on the metal material (non-growth surface))/(the thickness of aluminum-containing film on the dielectric material (growth surface) + the thickness of aluminum-containing film on the metal material (non-growth surface)).

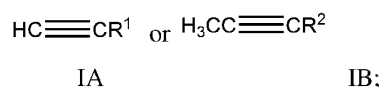
[0047] Selectivity is calculated by using formula: $\frac{Thk [GS] - Thk [NGS]}{Thk [GS] + Thk [NGS]}$.

[0048] The selectivity is preferably 80% or greater, more preferably 85% or greater, 90% or greater, or most preferably 95% or greater.

[0049] Accordingly, disclosed herein is a novel, and non-obvious, selective thermal atomic layer deposition (ALD) process, that selectively deposits aluminum-containing dielectric materials on top of a dielectric material relative to a metal, in an ALD reactor. This method comprises:

(a) loading the substrate comprising a dielectric material, and the metal into a reactor;

(b) introducing a passivating composition comprising an alkyne having one of the following formulae to selectively form an organic layer on the metal surface:



wherein R^1 and R^2 are each selected from the group consisting of a linear or branched C_6 to C_{14} alkyl or arylalkyl;

(c) purging the reactor with inert gas;

(d) introducing an aluminum precursor into the reactor to react with the dielectric material to form an aluminum-containing layer;

(e) purging the reactor with inert gas;

(f) introducing a vapor comprising water into the reactor to react with the aluminum-containing layer to form an aluminum oxide layer; and

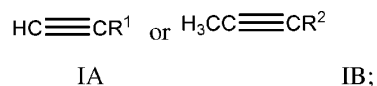
(g) purging the reactor with inert gas.

Steps (d) to (g) may be repeated to deposit a desired aluminum-containing dielectric films on top of the dielectric material. In some embodiments, step (b) and (c) can be conducted after Step (d) to (g) are repeated to deposit a desired aluminum oxide, followed by repeating Step (d) to (g) to provide a thicker aluminum oxide. The thickness of the aluminum-containing dielectric films can range from about 1 Å to about 100 Å, or about 5 Å to about 90 Å, or about 5 Å to about 80 Å, or about 5 Å to about 70 Å or about 5 Å to about 60 Å, or about 5 Å to about 50 Å, or about 5 Å to about 40 Å, or about 5 Å to about 30 Å or about 5 Å to about 20 Å, depending on a targeted thickness for a required selectivity. The aluminum precursor can be selected from the group consisting of triethylaluminum, dimethylaluminum iso-propoxide, diethylaluminum iso-propoxide. Examples of the alkynes with Formula IA can be selected from the group consisting of 1-octyne, 1-nonyne, 1-decyne, 1-undecyne, 1-dodecyne, 1-tridecyne, 1-tetradecyne, ethynylbenzene, 3-phenyl-1-propyne, 4-phenyl-1-butyne, 5-phenyl-1-pentyne, and 6-phenyl-1-hexyne. Examples of the alkynes with Formula IB can be selected from the group consisting of 2-octyne, 2-nonyne, 2-decyne, 2-undecyne, 2-dodecyne, 2-tridecyne, and 2-tetradecyne.

[0050] In second aspect, a thermal atomic layer deposition (ALD) process, that selectively deposits aluminum-containing dielectric materials on top of a dielectric material relative to a metal, in an ALD reactor. This method comprises:

(a) loading the substrate comprising a dielectric material, and the metal into a reactor;

(b) introducing a passivating composition comprising an alkyne to selectively form an organic layer on the metal surface, the alkyne comprising one of the following formulae:



wherein R^1 and R^2 are each selected from the group consisting of a linear or branched C_6 to C_{14} alkyl or arylalkyl;

(c) Purging the reactor with inert gas;

(d) introducing an aluminum precursor into the reactor to react with the dielectric material to form an aluminum-containing layer;

(e) purging the reactor with inert gas;

(f) introducing a vapor comprising an alkoxysilanol into the reactor to react with the aluminum-containing layer to form an aluminum silicon oxide layer; and

(g) purging the reactor with inert gas.

Steps (d) to (g) may be repeated to deposit a desired thickness of the aluminum doped silicon oxide dielectric film on top of the dielectric material. In some embodiments, steps (b) and (c) can be conducted after steps (d) to (g) are repeated to deposit a desired aluminum oxide, followed by repeating steps (d) to (g) to provide a thicker aluminum silicon oxide. The thickness of the aluminum-containing dielectric films can range from about 1 Å to about 100 Å, or about 5 Å to about 90 Å, or about 5 Å to about 80 Å, or about 5 Å to about 70 Å or about 5 Å to about 60 Å, or about 5 Å to about 50 Å, or about 5 Å to about 40 Å, or about 5 Å to about 30 Å or about 5 Å to about 20 Å, depending on what targeted thickness for a required selectivity. The aluminum precursor is selected from the group consisting of triethylaluminum, dimethylaluminum iso-propoxide (DMAI), diethylaluminum iso-propoxide. Examples of the alkynes with Formula IA can be selected from the group consisting of 1-octyne, 1-nonyne, 1-decyne, 1-undecyne, 1-dodecyne, 1-tridecyne, 1-tetradecyne. Examples of the alkynes with Formula IB can be selected from the group consisting of 2-octyne, 2-nonyne, 2-decyne, 2-undecyne, 2-dodecyne, 2-tridecyne, 2-tetradecyne, 3-phenyl-1-propyne, 4-phenyl-1-butyne, 5-phenyl-1-pentyne, and 6-phenyl-1-hexyne. The alkoxysilanol is selected from the

group consisting of tris(tert-butoxy)silanol, tris(tert-pentoxy)silanol, bis(tert-butoxy)(tert-pentoxy)silanol, and bis(tert-pentoxy)(tert-butoxy)silanol.

[0051] In a preferred embodiment of this method, the dielectric material may be selected from the group consisting of silicon oxide, carbon doped silicon oxide, silicon oxynitride, carbon doped oxynitride, silicon nitride, and metal oxide such as zirconium oxide, hafnium oxide, silicon doped zirconium oxide, silicon doped hafnium oxide, or any other high k materials. The metal in a preferred embodiment may be selected from the group consisting of cobalt, aluminum, copper, tantalum, ruthenium, molybdenum, tungsten, platinum, iridium, nickel, titanium, silver, gold, or a combination thereof.

[0052] As used in this specification and the appended claims, the term “substrate” and “wafer” are used interchangeably, both referring to a surface, or portion of a surface, upon which a process acts. It will also be understood by those skilled in the art that reference to a substrate can also refer to only a portion of the substrate, unless the context clearly indicates otherwise. Additionally, reference to depositing on a substrate can mean both a bare substrate and a substrate with one or more films or features deposited or formed thereon.

[0053] A “substrate” as used herein, refers to any substrate or material surface formed on a substrate upon which film processing is performed during a fabrication process. For example, a substrate surface on which processing can be performed include materials such as silicon, silicon oxide, strained silicon, silicon on insulator (SOI), carbon doped silicon oxides, silicon nitride, doped silicon, germanium, gallium arsenide, glass, sapphire, and any other materials such as metals, metal nitrides, metal alloys, and other conductive materials, depending on the application. Substrates include, without limitation, semiconductor wafers. Substrates may be exposed to a pretreatment process to polish, etch, reduce, oxidize, hydroxylate, anneal and/or bake the substrate surface. In addition to film processing directly on the surface of the substrate itself, in the present disclosure, any of the film processing steps disclosed may also be performed on an underlayer formed on the substrate as disclosed in more detail below, and the term “substrate surface” is intended to include such underlayer as the context indicates. For example, where a film/layer or partial film/layer has been

deposited onto a substrate surface, the exposed surface of the newly deposited film/layer becomes the substrate surface. What a given substrate surface comprises will depend on what films are to be deposited, as well as the particular chemistry used. In one or more embodiments, the first substrate surface will comprise a metal, and the second substrate surface will comprise a dielectric, or vice versa. In some embodiments, a substrate surface may comprise certain functionality (e.g., -OH, -NH, etc.).

[0054] Likewise, the surface comprising a metal that can be used in the methods described herein are quite varied. In some embodiments, the films may comprise, or consist essentially of a metal or metal nitride. Examples of metal surface include, but are not limited to, ruthenium (Ru), cobalt (Co), copper (Cu), titanium, (Ti), tantalum (Ta), nickel (Ni), tungsten (W), molybdenum (Mo), etc., and combinations thereof. Examples of metal nitride films include, but are not limited to, tantalum nitride (TaN), titanium nitride (TiN), tungsten nitride (WN), tungsten carbonitride (WCN), molybdenum nitride (MoN), copper silicon nitride (CuSiN), etc., and combinations thereof.

[0055] In some embodiments, the deposition film comprises a dielectric. Examples include, SiO₂, carbon doped silicon oxide, SiN, HfO₂, ZrO₂ etc.

[0056] In embodiments of the present disclosure, the substrate has at least two discrete surfaces wherein each discrete surface is characterized by a different chemistry. For example, in an embodiment, the surface of the substrate comprises at least a first surface comprising copper and at least a second surface comprising a dielectric material such as silicon dioxide.

[0057] The at least one second surface comprising a dielectric material can be, for example, any of the materials selected from the group consisting of SiO₂, a metal oxide, copper, cobalt, tungsten, amorphous silicon, polysilicon, monocrystalline silicon, germanium, and amorphous hydrogenated germanium. In some embodiments the at least one second surface comprises SiO₂ is a dielectric surface, such as a SiO₂ surface. In some embodiments the surface comprising SiO₂ may comprise silicon oxides, fluorinated silica glass (FSG), carbon doped silicon oxide (SiOC) and/or materials containing more than about 50% silicon oxide. In some embodiments the surface

comprising SiO₂ comprises –OH groups and may also comprise, for example, an alumina (Al₂O₃) surface with –OH surface groups.

[0058] Embodiments of the disclosure provide methods of selectively depositing a film such as, for example, a dielectric film, onto one surface of a substrate over a second surface on the same substrate wherein the two surfaces are co-planar created by chemical mechanical planarization. As used in this specification and the appended claims, the term “selectively depositing a film on one surface over another surface,” and the like, means that one of the first or second surface is passivated to substantially prevent deposition on the passivated layer and a film is deposited on the second (non-passivated) surface. The term “over” used in this regard does not imply a physical orientation of one surface on top of another surface, rather a relationship of the thermodynamic or kinetic properties of the chemical reaction with one surface relative to the other surface. For example, selectively depositing a cobalt film onto a copper surface over a dielectric surface means that the cobalt film deposits on the copper surface and less or no cobalt film deposits on the dielectric surface; or that the formation of the cobalt film on the copper surface is thermodynamically or kinetically favorable relative to the formation of a cobalt film on the dielectric surface.

[0059] The method of the present disclosure includes the optional step of contacting the surface of the substrate with a wet chemical composition to obtain a treated substrate. Exemplary wet chemical treatments include known chemical treatments such as, for example, RCA clean chemicals SC-1 and SC-2, aqueous HF, peroxide, H₂SO₄ / H₂O₂, NH₄OH, buffered HF solutions, and mixtures thereof.

[0060] In preferred embodiments, the wet chemical composition comprises at least one selected from the group consisting of a composition comprising H₂O₂ (28 % aq.), NH₄OH (28-30 %), and H₂O; HF (0.01 % - 10% (aq.)); peroxide; RCA clean chemicals SC-1 and SC-2; and a mixture of H₂SO₄ / H₂O₂.

[0061] As is known in the art, “RCA clean chemicals” refers to compositions comprising an ammonium hydroxide and hydrogen peroxide mixture wherein the basic cleaning procedure developed by the Radio Corporation of America in the 1960s. The RCA Standard-Clean-1 (SC-1) procedure uses an ammonium hydroxide and hydrogen peroxide solution and water heated to a temperature of about 70 °C. The SC-1

procedure dissolves films and removes Group I and II metals. The Group I and II metals are removed through complexing with the reagents in the SC-1 solution. The RCA Standard-Clean-2 (SC-2) procedure utilizes a mixture of hydrogen peroxide, hydrochloric acid, and water heated to a temperature of about 70 °C. The SC-2 procedure removes the metals that are not removed by the SC-1 procedure.

[0062] Contacting with the wet chemical composition can occur by any method known to those skilled in the art such as, for example, dipping or spraying. The contacting step can be one discrete step or more than one step.

[0063] In some embodiments, the temperature of the wet chemical composition during the contacting step can be, for example, from about ambient temperature to about 100 °C. In other embodiments, the temperature of the wet chemical composition during the contacting step can be, for example, from about 55 °C to about 95 °C. In other embodiments, the temperature of the wet chemical composition during the contacting step can be, for example, from about 60 °C to about 90 °C.

[0064] Embodiments also include the step of rinsing the surface of the substrate with deionized water after the step of contacting the surface of the substrate with the wet chemical composition. The rinsing step is typically carried out by any suitable means, for example, rinsing the surface of the substrate with de-ionized water by immersion or spray techniques.

[0065] Embodiments also include the step of drying at least the surface of the substrate after the rinsing step. The drying step is typically carried out by any suitable means, for example, the application of heat, isopropyl alcohol (IPA) vapor drying, or by centripetal force.

[0066] Embodiments also optionally include the step of treating the surface with hydrogen plasma, argon plasma, or ammonia plasma. Suitable processes include plasma processes (hydrogen plasma, NH_3 / NF_3 plasmas, water plasmas, and the like). The optional plasma step functions to remove undesired deposits on the surface and activate the surface for subsequent deposition of passivation reagents. Such plasma treatments may be most preferably applied after some deposition on the surface has been performed in order to remove non-selectively deposited material from the

previously passivated surface and to remove residual passivation reagents after the desired deposition thickness has been achieved.

[0067] As employed throughout the description, the term “alkyl” means a saturated hydrocarbon group which is straight-chained or branched. In some embodiments, the alkyl group has from 1 to 20 carbon atoms, from 2 to 20 carbon atoms, from 1 to 10 carbon atoms, from 2 to 10 carbon atoms, from 1 to 8 carbon atoms, from 2 to 8 carbon atoms, from 1 to 6 carbon atoms, from 2 to 6 carbon atoms, from 1 to 4 carbon atoms, from 2 to 4 carbon atoms, from 1 to 3 carbon atoms, or 2 or 3 carbon atoms. Examples of alkyl groups include, but are not limited to, methyl (Me), ethyl (Et), propyl (e.g., n-propyl and isopropyl), butyl (e.g., n-butyl, t-butyl, isobutyl), pentyl (e.g., n-pentyl, isopentyl, neopentyl), hexyl, isohexyl, heptyl, octyl, nonyl, 4,4dimethylpentyl, 2,2,4-trimethylpentyl, decyl, undecyl, dodecyl, 2-methyl-1-propyl, 2-methyl-2-propyl, 2-methyl-1-butyl, 3-methyl-1-butyl, 2-methyl-3-butyl, 2-methyl-1-pentyl, 2,2-dimethyl-1-propyl, 3-methyl-1-pentyl, 4-methyl-1-pentyl, 2-methyl-2-pentyl, 3-methyl-2-pentyl, 4-methyl-2-pentyl, 2,2-dimethyl-1-butyl, 3,3-dimethyl-1-butyl, 2-ethyl-1-butyl, and the like.

[0068] As employed throughout the description, the term “cyclic alkyl” denotes a cyclic functional group having from 3 to 10 or from 4 to 10 carbon atoms. Exemplary cyclic alkyl groups include, but are not limited to, cyclobutyl, cyclopentyl, cyclohexyl, and cyclooctyl groups.

[0069] As used herein, the term “aryl” means a monocyclic, bicyclic, or polycyclic (e.g., having 2, 3 or 4 fused rings) aromatic hydrocarbon. In some embodiments, the aryl group has from 6 to 20 carbon atoms or from 6 to 10 carbon atoms. Examples of aryl groups include, but are not limited to, phenyl, naphthyl, anthracenyl, phenanthrenyl, indanyl, indenyl, and tetrahydronaphthyl, and the like.

[0070] As used herein, the term “arylalkyl” means a hydrogen in an alkyl group is substituted by an aryl. In some embodiments, the alkyl group is a C₁₋₆ alkyl group. It may be further substituted by a halide such as Cl, F, or Br. In other embodiments, one or more hydrogens in the aryl ring may be substituted by alkyl or halide or halide-containing alkyl.

[0071] As employed throughout the description, the term “alkenyl group” denotes a group which has one or more carbon-carbon double bonds and has from 2 to 18 or from 2 to 10 carbon atoms. Exemplary alkenyl groups include, but are not limited to, vinyl or allyl groups.

[0072] As used herein, the term “alkynyl” means a straight or branched alkyl group having 2 to 20 carbon atoms and one or more triple carbon-carbon bonds. In some embodiments, the alkynyl group has from 2 to 10 carbon atoms, from 2 to 8 carbon atoms, from 2 to 6 carbon atoms, or from 2 to 4 carbon atoms. Examples of alkynyl groups include, but are not limited to, acetylene, 1-propylene, 2-propylene, and the like.

[0073] As used herein, the phrase “optionally substituted” means that a substitution is optional and, therefore, includes both unsubstituted and substituted atoms and moieties. A “substituted” atom or moiety indicates that any hydrogen atom on the designated compound or moiety can be replaced with a selection from the indicated substituent groups, provided that the normal valency of the designated compound or moiety is not exceeded, and that the substitution results in a stable compound. For example, if a methyl group is optionally substituted, then 1, 2, or 3 hydrogen atoms on the carbon atom within the methyl group can be replaced with 1, 2, or 3 of the recited substituent groups.

[0074] As used herein, the term “phenyl” means $-C_6H_5$. A phenyl group can be unsubstituted or substituted with one, two, or three suitable substituents.

[0075] As used herein, the term “halo” means halogen groups and includes, but is not limited to, fluoro, chloro, bromo, and iodo.

[0076] Vapor phase or gas phase reactions include the exposure of the heated substrate to the precursor molecule(s) and / or co-reactants in a suitable chamber that must be capable of providing the necessary pressure control and that can also supply heat to the substrate and / or chamber walls; the chamber should also provide suitable purity for the reactions that will take place, generally through high leak integrity and the use of ultra-high purity carrier and reactive gases.

[0077] As used in this specification and the appended claims, the terms “reactive gas”, “precursor”, “reactant”, and the like, are used interchangeably to mean a gas that includes a species which is reactive with a substrate surface. For example, a first

“reactive gas” may simply adsorb onto the surface of a substrate and be available for further chemical reaction with a second reactive gas. They may be used in conjunction with ultra-high purity carrier gases (as defined previously) and in any desired mixtures with one another (i.e., more than one type of precursor can be used either together or in discrete, independent steps to form the desired passivation layer with whatever order of precursor introduction is desired).

[0078] The precursor(s) and / or co-reactants may be delivered to the reactor using mass flow controllers (perhaps with heated lines), liquid injection vaporizers (perhaps with heated lines) or with no metering device (i.e., neat introduction of the vapor and or gas from a vessel that is isolated from the reactor using a simple valve). Any of the foregoing may also be used in combination with one another. Any means of providing the gas and / or vapor(s) to the reaction chamber that provides sufficient purity and repeatability may be used.

[0079] The precursor(s) and / or co-reactants may be introduced independently to the reactor, mixed prior to introduction to the reactor, mixed in the reactor or in any combination of the preceding in multiple, independent steps that might include differences in how the precursors are introduced between steps.

[0080] The temperature range of the reactions may be between room temperature and 400° C. In some cases, the temperature range of the reactions may be between room temperature and 200 °C. In yet other cases, the temperature range of the reactions may be between room temperature and 100° C. The pressure may range from 10-10 Torr to 3000 Torr and may be maintained under dynamic flow conditions (i.e., with a valve and a butterfly valve type arrangement) or may be maintained under static conditions (i.e., an evacuated chamber is exposed to the desired precursor(s) and / or co-reactant(s) until a total desired pressure is achieved and then the chamber is isolated from both the precursor(s) and / or co-reactant(s) source(s) and the vacuum pump). The reactor can be evacuated fully and re-exposed to fresh precursor(s) and / or co-reactants as many times as necessary. Precursor(s) and / or co-reactants may be introduced using any mixtures and / or concentrations desired.

[0081] The exposure of the surface can be conducted for 0.1-60 minutes, preferably in 1-5 minutes and most preferably for 1 minute. The partial pressure of the organic

halide in the reaction chamber can vary from about 1% of its saturated vapor pressure at the substrate temperature up to almost 100% of its saturation vapor pressure. Most preferably, it will be between 20 and 50% of its saturation vapor pressure. The chamber pressure can be the same as the partial pressure of the organic halide vapors but can be higher with the balance of the atmosphere comprising a carrier gas. Preferred carrier gases include N₂, He, and Ar, but also other gases such as H₂, CO₂ and dry O₂ may be used. The exposure vapors can be static (not flowing) for all or part of the exposure period. The preferred embodiment is to flow the vapors of the organic halide along with the optional carrier gas through the exposure chamber so that fresh vapors are exposed to the surface of the substrate for at least a portion of the exposure period.

[0082] The exposure chamber can be kept at near ambient temperature or can optionally be heated. Heat can be supplied to the outer walls of the chamber (hot wall) or only to the substrate (cold-wall reactor). Substrate heating in a cold wall reactor can be achieved by use of incident radiation through a transparent window (lamp heating), by resistive heating of the substrate itself or from resistive heating elements in the platform that the substrate is contacting, through induction or by other means known in the art. The temperature of the treatment is preferably between about 20 °C to about 400 °C, preferably between 20°C to about 200 °C, and most preferably between 20 °C to about 100 °C. The temperature can be constant during the exposure period or can vary within the specified temperature range.

[0083] Unreacted vapor of the at least one organic halide can then optionally be removed by evacuation or purging of the chamber with suitable inert gas before removing the substrate from the chamber or before chemical vapor or atomic-layer deposition processing. Optionally, the exposure chamber might also be used for subsequent processing steps to improve process efficiency so that the process may be repeated from step c), if necessary, to strip the protective film and any non-selective ALD deposit and then re-form a protective film.

[0084] The choice of the at least one alkyne and the exposing conditions used in this method should be optimized by standard experimentation to optimize selectivity of the protection afforded the metal surface against potential non-selective passivation, processing time, reagent cost, etc. depending on the requirements imposed by

subsequent processing steps. For example, selectivity can be adjusted/optimized by varying the nature of the R' or R'' group of the at least one alkyne having the structure represented by Formula IA or IB. Typically, since reactivity and selectivity are often inversely related, if the two surfaces are similar in chemistry, experimenting with the R group may be required to optimize the process. There is a difference in reactivity, for example between alkyl R-groups and aryl R-groups; typically, aryl groups are more reactive with active hydrogen bearing surfaces compared to alkyl groups. As a result, in some cases the alkyl groups might be needed to selectively passivate the metal without also passivating an adjacent surface that also has less reactive active hydrogen atoms.

[0085] Disclosed and Claimed Passivating Composition

[0086] Given the forgoing, in one embodiment the disclosed and claimed subject relates to passivating compositions that include, consist essentially of and/or consist of an alkyne. The passivating compositions are particularly well-suited for performing enhanced passivation of metallic substrates. In one aspect of this embodiment, the alkyne, consists essentially of or consists of one or more one 1-alkyne (an alkyne having a triple bond and the 1- position) or a 2-alkyne (an alkyne having a triple bond at the 2-position).

[0087] In one embodiment, the alkyne having formula IA or IB is a high-purity alkyne that is substantially free of water. In one aspect of this embodiment, the high-purity alkyne has a residual concentration of water of less than about 500 ppm. In one aspect of this embodiment, the high-purity alkyne has a residual concentration of water of less than about 100 ppm. In one aspect of this embodiment, the high-purity alkyne has a residual concentration of water of less than about 50 ppm. In one aspect of this embodiment, the alkyne having formula IA or IB has a residual concentration of water of less than about 25 ppm. In one aspect of this embodiment, the high-purity alkyne has a residual concentration of water of less than about 10 ppm. In one aspect of this embodiment, the high-purity alkyne is free of detectable water. In one aspect of this embodiment, the high-purity alkyne is free of water.

[0088] In one embodiment, the alkyne having formula IA or IB is substantially free of carboxylic acids. In one aspect of this embodiment, the alkyne having formula IA

or IB has a residual concentration of carboxylic acids of less than about 1000 ppm. In one aspect of this embodiment, the alkyne having formula IA or IB has a residual concentration of carboxylic acids of less than about 500 ppm. In one aspect of this embodiment, the alkyne having formula IA or IB has a residual concentration of carboxylic acids of less than about 100 ppm. In one aspect of this embodiment, the alkyne having formula IA or IB is free of detectable carboxylic acids. In one aspect of this embodiment, the alkyne having formula IA or IB is free of carboxylic acids.

[0089] In one embodiment, the alkyne having formula IA or IB is substantially free of impurities that may react with metallic surface during a passivation process. In one embodiment, the alkyne having formula IA or IB is substantially free of impurities that react with precursors during a deposition process.

[0090] In one embodiment, the alkyne having formula IA or IB is substantially free of impurities that passivate non-metallic surface and suppress growth on non-metallic surface.

[0091] In one embodiment, the alkyne having formula IA or IB is substantially free of halogen-containing impurities. In one aspect of this embodiment, the halogen-containing impurities are one or more of a fluorohydrocarbon, a chlorohydrocarbon, a bromohydrocarbon and an iodohydrocarbon. In one aspect of this embodiment, the alkyne having formula IA or IB has a residual concentration of halogen-containing impurities of less than about 1000 ppm. In one aspect of this embodiment, the alkyne having formula IA or IB has a residual concentration of halogen-containing impurities of less than about 500 ppm. In one aspect of this embodiment, the alkyne having formula IA or IB has a residual concentration of halogen-containing impurities of less than about 100 ppm. In one aspect of this embodiment, the alkyne having formula IA or IB has a residual concentration of halogen-containing impurities of less than about 50 ppm. In one aspect of this embodiment, the alkyne having formula IA or IB has a residual concentration of halogen-containing impurities of less than about 25 ppm. In one aspect of this embodiment, the alkyne having formula IA or IB has a residual concentration of halogen-containing impurities of less than about 10 ppm. In one aspect of this embodiment, the alkyne having formula IA or IB is free of halogen-containing impurities. In the forgoing aspects, the residual concentration of halogen-containing

impurities is detected by one or more of the following: Gas Chromatography (GC) and its associated hyphenated techniques comprising but not limited to GC-FID, GC-ECD, GC-MS; Liquid Chromatography (as defined as to encompass LC, HPLC, or UPLC variations) and its associated hyphenated techniques comprising but not limited to LC-DAD and LC-MS; Ion Chromatography (IC) and its associated forms; Spectroscopic techniques comprising but not limited to infrared (IR), Ultraviolet/Visible (UV/Vis), Near infrared (NIR), Raman and Nuclear Magnetic Resonance (NMR) spectroscopies; Inductively Coupled Plasma spectroscopy or spectrometry (ICP) and their associated hyphenated techniques comprising but not limited to ICP-MS, ICP-OES, GC-ICP-MS, and GC-ICP-OES; Elemental analyses such as X-ray fluorescence spectroscopy (XRF) and its associated forms (example WD-XRF) or Atomic Absorbance spectroscopy (AA) and its forms; and finally wet chemical techniques comprising but not limited to Titration (example halogen titration by with silver nitrate) and electrochemical detection (examples, cyclic voltammetry, ion selective electrodes, etc.). In one embodiment of the forgoing aspects, the residual concentration of halogen-containing impurities is detected by one or more of GC-MS, GC-ICP-MS, GC-ICP-OES, GC-FID, GC-ECD, HPLC and UV/Vis.

[0092] In one embodiment, the alkyne having formula IA or IB is purified by exposure to molecular sieves. In one embodiment, the alkyne having formula IA or IB is purified by exposure to silica gel. In one embodiment, the alkyne having formula IA or IB is purified by exposure to one or more adsorbent materials.

[0093] In one embodiment, the alkyne having formula IA or IB is purified by treatment with one or more group 1 metal followed by a distillation process. In one aspect of this embodiment, the alkyne is treated with metallic sodium. In another aspect embodiment, the metal and the alkyne are separated by filtration and the alkyne is distilled to remove non-volatile products of the reaction of impurities with metals.

[0094] In one embodiment, the alkyne having formula IA or IB is purified by treatment with one or more group (II) metal followed by a distillation process. In one aspect of this embodiment, the alkyne is treated with metallic magnesium. In another aspect embodiment, the metal and the alkyne are separated by filtration and the alkyne is distilled to remove non-volatile products of the reaction of impurities with metals.

[0095] In one embodiment, the alkyne having formula IA or IB is purified by exposure to activated carbon. In one aspect of this embodiment the alkyne is separated by filtration and is distilled to remove non-volatile products after treatment with activated carbon.

[0096] Packing of terminal alkynes

[0097] Xtb-GFN simulations were conducted to compare enhanced packing density in 1-decyne and 1-dodecyne vs 4-decyne, 5-decyne, and 6-dodecyne on Cu surface. The anchored alkynes are packed on a copper slab that is 20 Å x20 Å and are placed as closely as possible based on the sizes of the alkyne molecules & in chemisorbed geometries with copper atoms. The packing density is demonstrated by comparing the number that can be packed on the surface & optimized in Xtb-GFN. The following Table shows the results which demonstrate 1-alkynes have much higher packing density than the alkynes in which the carbon-carbon triple bond in the positions other than the 1- position, suggesting that 1-alkynes may provide better blocking and higher selectivity than other alkynes.

Alkyne	Number of alkynes anchored on Cu surface	Relative Packing density
1-decyne	16	2x
4-decyne	8	1x
5-decyne	8	1x
1-dodecyne	16	2x
6-dodecyne	8	2x

[0098] Once the metal surface is passivated the second surface comprising, for example, silicon oxide, is active for further selective reactions such as, for example, a selective ALD deposition of alumina-containing film on the silicon oxide surface.

[0099] Selective depositions according to the present disclosure can be, for example, metal and metal oxide layers disclosed in Hamalainen et al., “Atomic Layer Deposition of Noble Metals and Their Oxides,” Chem. Mater. 2014, 26, 786-801; and Johnson et al., “A Brief review of Atomic layer Deposition: From Fundamentals to Applications”, Materials Today, Volume 17, Number 5, June 2014, both of which are incorporated herein by reference in their entireties.

[00100] In some embodiments, a metal film is selectively deposited on the second surface. In one example, the metal film may serve as a cap layer on the second surface. In another example, the metal film may serve as a conductive pathway on the second surface (i.e., a line, pad or plug). In another example the metal film can, for example, be deposited by atomic layer deposition (ALD), plasma-enhanced ALD (PEALD), chemical vapor deposition (CVD), plasma-enhanced CVD (PECVD), or pulsed CVD. According to one embodiment, the metal film may be selected from the group consisting of Ru, Al, Ti, Ta, Mo, Co, Rh, Ir, Fe, Ru, Os, Mo, Mn, Tc, Re, Cu, Ag, Au, Ni, Pd, Pt, and combinations thereof.

[00101] In some embodiments, a metal or metal nitride film is selectively deposited on the second surface. In one example, the metal or metal nitride film may serve as a cap layer on the second surface. In another example, the metal or metal nitride film may serve as a diffusion barrier layer. The metal or metal nitride film can, for example, be deposited by atomic layer deposition (ALD), plasma-enhanced ALD (PEALD), chemical vapor deposition (CVD), plasma-enhanced CVD (PECVD), or pulsed CVD. Examples are found in, for example, "IBM Research Report, "Atomic Layer Deposition of Metal and Metal Nitride Thin Films: Current Research Efforts and Applications for Semiconductor Device Processing," RC22737 (W0303-012), March 5, 2003.

[00102] During the selective deposition process, the aforementioned protective surface previously deposited selectively on silicon nitride surfaces with the at least one organic halide could begin to react or otherwise become less inert. An optional re-application of the at least one organic halide, either with or without any of the aqueous or plasma pre-treatment steps may optionally be performed repeatedly to prevent or delay non-selective deposition on the silicon nitride surface.

[00103] In some embodiments passivation on a first surface of a substrate as described herein, such a copper surface of the substrate, relative to a second surface of the substrate is at least about 90% selectivity, at least about 95% selectivity, at least about 96%, 97%, 98% or 99% or greater selectivity. In some embodiments passivation only occurs on the first surface and does not occur on the second surface. In some embodiments passivation on the first surface of the substrate relative to the second surface of the substrate is at least about 50% selectivity, or at least about 60%

selectivity, which may be selective enough for some particular applications. In some embodiments passivation on the first surface of the substrate relative to the second surface of the substrate is at least about 50% selective, which may be selective enough for some particular applications.

[00104] Wet chemistry cleans may be used to remove the passivation layer. Example wet chemistry cleans include acidic, basic, and oxidative (e.g., peroxide-containing) wet chemistry compositions known in the art and described above for the optional step of contacting the substrate with a wet chemical composition. Another method to remove the passivation layer is via the application of heat or other energy.

EXAMPLES

[00105] Alkynes (e.g., 1-alkynes, 2-alkynes, or 1-arylalkynes) selectively passivate the metal surface versus the silicon oxide (SiO_2) surface. This process is depicted in FIG. 1. The process results in the selectivity to grow a desired thickness of dielectric film on SiO_2 .

[00106] Processes:

[00107] An illustrative process is shown in FIG. 1. Step 1 comprises a precleaning of the first surface (Cu) and the second surface (SiO_2), preferably with an acid, H_2 , high temperature, or a combination thereof. Following the pre-clean, Preferably, the first surface and the second surface are coplanar, as a result of a chemical mechanical planarization (CMP) as shown in FIG. 1 prior to the precleaning step.

[00108] Step 2 comprises passivation of the metal surface by exposing the copper to form a passivating/blocking organic layer employing a passivating composition preferably comprising a 1-alkyne such as 1-decyne or 1-dodecyne, or a 1-arylalkyne such as 5-phenyl-1-pentyne. Following passivation of the first surface, Step 3 includes depositing the aluminum containing dielectric layer is formed on the second surface (SiO_2), preferably by ALD of an aluminum precursor and a second precursor comprising oxygen or an alkoxysilanol.

[00109] Embodiments:

[00110] Example: Adsorption of 1-Alkyne on “Naked” Copper Surface, dielectric on dielectric (DoD) of aluminum oxide

[00111] This example evaluated the adsorption of 1-decyne (3E) on “naked” copper surface. It was calculated that 5-decyne strongly chemisorbs on copper (100) surface with an adsorption energy of -43 kcal/mol, and on copper (111) surface with an adsorption energy of -40 kcal/mol.

[00112] In this example, the first surface comprising Cu is pre-cleaned by dipping PVD Cu substrate in 2 wt.% citric acid solution for 3 minutes, and then the Cu is loaded together with SiO₂ as growth substrate to pre-clean chamber within 10 minutes to minimize the air exposure. After loading, Cu and SiO₂ are further cleaned by H₂ thermal annealing at 350°C for 10 minutes. After surface preparation, the substrates are moved to passivation chamber without air break, and SAM grafting is done at 250°C using a soaking mode for 15 minutes until passivation layer reaches saturation, and then the substrates are transferred to deposition chamber where a dielectric (preferably aluminum oxide or aluminum doped silicon oxide) is deposited using DMAI-H₂O ALD process at 250-350°C with DMAI-H₂O ALD sequence of DMAI 1s dose and 40s Ar purge followed by H₂O 1s dose and 60s Ar purge at 1 Torr process pressure. The thickness of aluminum oxide on Cu (non-growth surface, NGS) and SiO₂ (growth surface, GS) is measured by XRF-XRR thickness calibration, and selectivity is calculated by using formula: $\frac{Thk [GS] - Thk [NGS]}{Thk [GS] + Thk [NGS]}$.

[00113] FIG. 2 illustrates dielectric on dielectric selectivity vs aluminum oxide film thickness in angstroms (Å). demonstrates 1-alkyne has much better selectivity than 5-alkyne for aluminum-containing films with thickness less than 6nm (60 Å). FIG. 3 shows selectivity more than 0.6 can be achieved even at higher deposition temperatures such as 350°C.

[00114] FIG. 4 illustrates the selectivity comparison of an alkyne having Formula IA $HC\equiv CR^1$ wherein R¹ a linear or branched C₆ to C₁₄ alkyne or arylalkyl such as 5-phenyl-1-pentyne and 1-dodecyne at 250°C with various thickness of aluminum oxide films, demonstrating that the copper surface passivated with 5-phenyl-1-pentyne shows slightly DoD selectivity up to 90% for 25 Å aluminum oxide at 250 °C deposition temperature, which is slightly better than 1-dodecyne. Importantly the DoD selectivity of the copper surface passivated with 5-phenyl-1-pentyne is much better than that of 1-dodecyne for thicker aluminum oxide films.

[00115] FIG. 5 illustrates the selectivity comparison of an alkyne having Formula IA $\text{HC}\equiv\text{CR}^1$ wherein R^1 a linear or branched C_6 to C_{14} arylalkyl such as 5-phenyl-1-pentyne and 1-dodecyne at 250°C with various thickness of aluminum doped silicon oxide films, demonstrating that the copper surface passivated with 5-phenyl-1-pentyne shows slightly DoD selectivity up to 95% for 80 Å aluminum doped silicon oxide at 250 °C deposition temperature. Unexpectedly the DoD selectivity of the copper surface passivated with 5-phenyl-1-pentyne is much better than that of 1-dodecyne for thicker aluminum doped silicon oxide films. Both FIG 4 and FIG 5 indicate 1-arylalkylalkynes are better passivating composition than other alkynes and imply the aryl group seems provide better packing of the passivation layer than the linear alkyl. For purposes of this disclosure and claims, selectivity of the second surface to the first surface is found by the following equation: $\text{selectivity} = (\text{thickness of film on the second surface (SiO}_2) - \text{thickness of film on the first surface (Cu)}) / (\text{thickness of film on the second surface (SiO}_2) + \text{thickness of film on the first surface (Cu)})$. In the illustrated embodiments, the deposition selectivity of the second surface to the first surface is greater than about 0.3, more preferably greater than about 0.5 and most preferably greater than about 0.6.

[00116] It is anticipated that the disclosed and claimed methods could be used in conjunction with deposition tools commonly found at semiconductor manufacturing sites to produce molybdenum-containing layers for logic applications and other potential functions.

[00117] The foregoing description is intended primarily for purposes of illustration. Although the disclosed and claimed subject matter has been shown and described with respect to an exemplary embodiment thereof, it should be understood by those skilled in the art that the foregoing and various other changes, omissions, and additions in the form and detail thereof may be made therein without departing from the spirit and scope of the disclosed and claimed subject matter.

[00118] While the principles of the disclosure have been described above in connection with preferred embodiments, it is to be clearly understood that this description is made only by way of example and not as a limitation of the scope of the claimed subject matter.

CLAIMS

We claim:

1. A method for forming an aluminum-containing dielectric film selectively on at least one surface of a substrate comprising:
 - (a) providing the substrate in a reaction vessel, the substrate having a first surface comprising a metal and a second surface comprising a dielectric material, wherein the first surface and the second surface are coplanar;
 - (b) forming at least one passivated layer on the first surface by exposing the first surface and the second surface to a passivating composition comprising an alkyne having one of the following formulae:

$$\text{HC}\equiv\text{CR}^1 \quad \text{or} \quad \text{H}_3\text{CC}\equiv\text{CR}^2$$

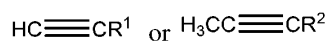
IA
IB;

 wherein R^1 and R^2 are each selected from the group consisting of a linear or branched C_6 to C_{14} alkyl or a linear or branched C_6 to C_{14} arylalkyl;
 - (c) purging the reactor with inert gas;
 - (d) introducing an aluminum precursor into the reactor to react with the dielectric material to form an aluminum-containing layer;
 - (e) purging the reactor with inert gas;
 - (f) introducing a vapor comprising water into the reactor to react with the aluminum-containing layer to form an aluminum oxide layer;
 - (g) purging the reactor with inert gas; and
 - (h) repeating steps (d) through (g) to deposit a desired thickness of the aluminum-containing dielectric film on top of the dielectric material.

2. The method of claim 1, wherein the thickness of the aluminum-containing dielectric film can range from about 1 Å to about 100 Å, or about 5 Å to about 90 Å, or about 5 Å to about 80 Å, or about 5 Å to about 70 Å or about 5 Å to about 60 Å, or about 5 Å to about 50 Å, or about 5 Å to about 40 Å, or about 5 Å to about 30 Å or about 5 Å to about 20 Å.

3. The method of claim 1, wherein the aluminum precursor is selected from the group consisting of triethylaluminum, dimethylaluminum iso-propoxide, and diethylaluminum iso-propoxide.
4. The method of claim 1, wherein the alkyne of Formula IA is selected from the group consisting of 1-octyne, 1-nonyne, 1-decyne, 1-undecyne, 1-dodecyne, 1-tridecyne, 1-tetradecyne, ethynylbenzene, 3-phenyl-1-propyne, 4-phenyl-1-butyne, 5-phenyl-1-pentyne, and 6-phenyl-1-hexyne.
5. The method of claim 1, wherein the alkyne of Formula IB is selected from the group consisting of 2-octyne, 2-nonyne, 2-decyne, 2-undecyne, 2-dodecyne, 2-tridecyne, and 2-tetradecyne.
6. The method of claim 1, wherein the passivating composition comprises or consists essentially of 1-decyne, 1-dodecyne, or 5-phenyl-1-pentyne.
7. The method of claim 1, wherein a deposition selectivity of the second surface to the first surface is greater than about 0.3, more preferably greater than about 0.5, and most preferably greater than about 0.6.
8. The method of claim 1, wherein a deposition selectivity of the second surface to the first surface is greater than about 0.6 and the thickness of the aluminum-containing dielectric film is about 50 Å or less.
9. A method for forming an aluminum doped silicon oxide dielectric film selectively on at least one surface of a substrate comprising:
 - (a) loading the substrate into a reactor, the substrate comprising a first surface comprising a metal and a second surface comprising a dielectric material, wherein the first surface and the second surface are coplanar;
 - (b) introducing an alkyne into the reactor to selectively form an organic

layer on the metal surface, the alkyne having the following formula:



IA

IB;

wherein R^1 and R^2 are each selected from the group consisting of a linear or branched C_6 to C_{14} alkyl or a linear or branched C_6 to C_{14} arylalkyl;

- (c) purging the reactor with inert gas;
- (d) introducing an aluminum precursor into the reactor to react with the dielectric material to form an aluminum-containing layer;
- (e) purging the reactor with inert gas;
- (f) introducing a vapor comprising an alkoxysilanol into the reactor to react with the aluminum-containing layer to form an aluminum silicon oxide layer and;
- (g) purging the reactor with inert gas; and
- (h) optionally repeating steps (d) to (g) to deposit a desired thickness of the aluminum doped silicon oxide dielectric film on top of the dielectric material.

10. The method of claim 9, wherein the aluminum doped silicon oxide dielectric film has a thickness ranging from about 1 Å to about 100 Å, or about 5 Å to about 90 Å, or about 5 Å to about 80 Å, or about 5 Å to about 70 Å or about 5 Å to about 60 Å, or about 5 Å to about 50 Å, or about 5 Å to about 40 Å, or about 5 Å to about 30 Å or about 5 Å to about 20 Å.
11. The method of claim 9, wherein the aluminum precursor is selected from the group consisting of triethylaluminum, dimethylaluminum isopropoxide, and diethylaluminum isopropoxide.
12. The method of claim 9, wherein the alkyne with Formula IA is selected from the group consisting of 1-octyne, 1-nonyne, 1-decyne, 1-undecyne, 1-dodecyne, 1-tridecyne, 1-tetradecyne, ethynylbenzene, 3-phenyl-1-propyne, 4-phenyl-1-butyne, 5-phenyl-1-pentyne, and 6-phenyl-1-hexyne.
13. The method of claim 9, wherein the alkyne with Formula IB can be selected from the group consisting of 2-octyne, 2-nonyne, 2-decyne, 2-undecyne, 2-

dodecyne, 2-tridecyne, and 2-tetradecyne.

14. The method of claim 9, wherein the alkoxysilanol is selected from the group consisting of tris(tert-butoxy)silanol, tris(tert-pentoxysilanol, bis(tert-butoxy)(tert-pentoxysilanol, and bis(tert-pentoxysilanol.
15. The method of claim 9, wherein the dielectric material of the second surface is selected from the group consisting of silicon oxide, carbon doped silicon oxide, silicon oxynitride, carbon doped oxynitride, silicon nitride, and metal oxide such as zirconium oxide, hafnium oxide, silicon doped zirconium oxide, or silicon doped hafnium oxide, or a combination thereof.
16. The method of claim 9, wherein the metal of the metal of the first surface is selected from selected from the group consisting of cobalt, aluminum, copper, tantalum, ruthenium, molybdenum, tungsten, platinum, iridium, nickel, titanium, silver, gold, or a combination thereof.
17. The method of claim 9, wherein a deposition selectivity of the second surface to the first surface is greater than about 0.6, more preferably greater than about 0.8, and most preferably greater than about 0.9 and the thickness of the aluminum doped silicon oxide dielectric film is about 100 Å or less.
18. The method of claim 9, wherein steps (d) to (g) are conducted at a temperature of between about 150 and about 350 degrees Celsius.
19. The method of claim 9, wherein a preclean step is conducted prior to step (a), the preclean step comprising exposing the first surface to an acid, a reducing environment, heating, or a combination thereof.
20. The method of claim 19, wherein the preclean step comprises exposing the substrate to citric acid, followed by exposing the substrate to H₂ at a temperature ranging from about 250 to about 500 degrees Celsius.

21. The method of claim 19, wherein the substrate is subjected to a chemical mechanical planarization step, wherein the chemical mechanical planarization step is conducted prior to the preclean step in order to provide coplanarity of the first surface and the second surface.
22. A method for passivating a metal-containing surface of a substrate comprising:
- (a) providing the substrate in a reaction vessel at temperatures ranging from 20°C to 400°C, the substrate having a first surface comprising a metal and a second surface comprising a dielectric material;
 - (b) forming at least one passivation layer on the first surface by exposing both the first surface and the second surfaces to a passivating composition comprising an alkyne having the following formula:
$$\text{HC}\equiv\text{CR}^1$$

wherein R¹ a linear or branched C₆ to C₁₄ arylalkyl; and
 - (c) purging the reactor with inert gas.
23. The method of claim 22, wherein steps (a) to (c) are repeated to provide a fully covered passivation layer on the second surface.
24. The method of claim 22, wherein the first surface comprises a metal or metalloid chosen from the group consisting of ruthenium (Ru), cobalt (Co), copper (Cu), titanium, (Ti), tantalum (Ta), nickel (Ni), tungsten (W), molybdenum (Mo), and combinations thereof, or wherein the first surface comprises a metal nitride chosen from the group consisting of tantalum nitride (TaN), titanium nitride (TiN), tungsten nitride (WN), tungsten carbonitride (WCN), molybdenum nitride (MoN), copper silicon nitride (CuSiN), silicon, germanium, and combinations thereof.

25. The method of claim 22, wherein the second surface is selected from the group consisting of silicon oxide and carbon doped silicon oxide, or wherein the second surface is selected from the group consisting of silicon nitride.
26. The method of claim 22, wherein the alkyne is selected from the group consisting of ethynylbenzene, 3-phenyl-1-propyne, 4-phenyl-1-butyne, 5-phenyl-1-pentyne, and 6-phenyl-1-hexyne.