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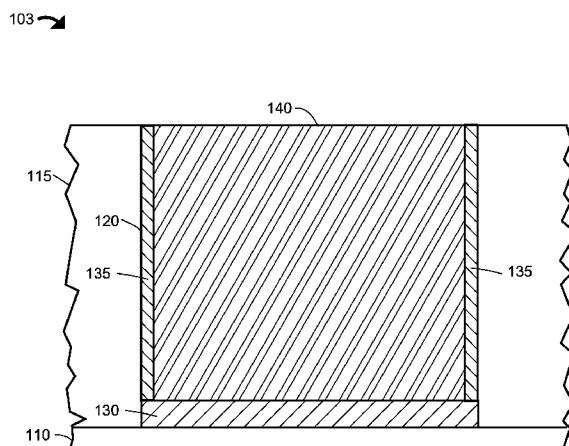


FIG. 3

(57) **Abstract:** One aspect of the present invention includes a method of fabricating an electronic device. According to one embodiment, the method comprises providing a substrate having dielectric oxide surface areas adjacent to electrically conductive surface areas, chemically bonding an anchor compound with the dielectric oxide surface areas so as to form an anchor layer, initiating the growth of a metal using the electrically conductive surface areas and growing the metal so that the anchor layer also bonds with the metal. The anchor compound has at least one functional group capable of forming a chemical bond with the oxide surface and has at least one functional group capable of forming a chemical bond with the metal. Another aspect of the present invention is an electronic device. A third aspect of the present invention is a solution comprising the anchor compound.

METHODS AND MATERIALS FOR ANCHORING GAPFILL METALS

CROSS REFERENCES

[0001] This application is related to U.S. Patent Application S/N 12/334,460, titled
5 “ACTIVATION SOLUTION FOR ELECTROLESS PLATING ON DIELECTRIC
LAYERS” to Artur KOLICS, filed 12/21/2007 which is incorporated herein, in its
entirety, by this reference.

BACKGROUND

[0002] This invention pertains to fabrication of electronic devices such as integrated
10 circuits; more specifically, this invention relates to methods and compositions to improve
the adhesion between gapfill metals and dielectrics for electronic devices.

[0003] Electroless deposition is a process that is frequently used in the fabrication of
electronic devices. The process is particularly important for applications requiring
deposition of metal layers such as gapfill metal on substrates comprising metal surface
15 areas and dielectric surface areas such as structures for damascene and/or dual damascene
devices. These processes are also in use for applications such as forming electrical
connections to metal contacts for integrated circuits. Electroless deposition processes can
readily proceed on certain catalytic or activated surfaces. The adhesion to the catalytic or
activated surfaces may be satisfactory. Similarly, chemical vapor deposition processes
20 used for depositing metals on the metal surfaces may also have satisfactory adhesion.
However, metals deposited by electroless deposition and metals deposited by chemical
vapor deposition may have poor adhesion to dielectric surfaces. Consequently, the
deposited metals may be attached or held only by the metal surface areas of the substrate.
Such surfaces may provide only a small portion of the contact surface area in comparison
25 to contact with the dielectric surfaces and the overall adhesion of the metal to the
substrate may be insufficient for subsequent processes.

[0004] There is a need for methods and materials for improving the adhesion of metal
such as gapfill metal to dielectric surfaces for the fabrication of a variety of electronic
devices.

SUMMARY

[0005] This invention pertains to electronic devices, more particularly, to
metallization of electronic devices. The present invention provides one or more

improvements in the solutions used for and methods of fabricating electronic devices such as for fabricating semiconductor devices that include integrated circuits.

[0006] One aspect of the present invention includes a method of fabricating an electronic device. According to one embodiment, the method comprises providing a substrate having dielectric oxide surface areas adjacent to electrically conductive surface areas, chemically bonding an anchor compound with the dielectric oxide surface areas so as to form an anchor layer, initiating the growth of a metal using the electrically conductive surface areas, and growing the metal so that the anchor layer also bonds with the metal. The anchor compound has at least one functional group capable of forming a chemical bond with the dielectric oxide surface and has at least one functional group capable of forming a chemical bond with the metal. Another aspect of the present invention is an electronic device. A third aspect of the present invention is a solution comprising the anchor compound.

[0007] It is to be understood that the invention is not limited in its application to the details of construction and to the arrangements of the components set forth in the following description or illustrated in the drawings. The invention is capable of other embodiments and of being practiced and carried out in various ways. In addition, it is to be understood that the phraseology and terminology employed herein are for the purpose of description and should not be regarded as limiting.

[0008] As such, those skilled in the art will appreciate that the conception upon which this disclosure is based may readily be utilized as a basis for the designing of other structures, methods, and systems for carrying out aspects of the present invention. It is important, therefore, that the claims be regarded as including such equivalent constructions insofar as they do not depart from the spirit and scope of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] FIG. 1 is a cross-section side view diagram of a substrate being processed according to an embodiment of the present invention.

[0010] FIG. 2 is a cross-section side view diagram of a substrate being processed according to an embodiment of the present invention.

[0011] FIG. 3 is a cross-section side view diagram of a substrate processed according to an embodiment of the present invention.

[0012] Skilled artisans appreciate that elements in the figures are illustrated for simplicity and clarity and have not necessarily been drawn to scale. For example, the
5 dimensions of some of the elements in the figures may be exaggerated relative to other elements to help to improve understanding of embodiments of the present invention.

DESCRIPTION

[0013] This invention pertains to electronic devices, more particularly, to
10 metallization of electronic devices. The present invention seeks to overcome one or more problems in fabricating electronic devices such as for fabricating semiconductor devices that use integrated circuits.

[0014] For the following defined terms, these definitions shall be applied, unless a different definition is given in the claims or elsewhere in this specification. All numeric
15 values are herein defined as being modified by the term "about," whether or not explicitly indicated. The term "about" generally refers to a range of numbers that a person of ordinary skill in the art would consider equivalent to the stated value to produce substantially the same properties, function, result, etc. A numerical range indicated by a low value and a high value is defined to include all numbers subsumed within the
20 numerical range and all subranges subsumed within the numerical range. As an example, the range 10 to 15 includes, but is not limited to, 10, 10.1, 10.47, 11, 11.75 to 12.2, 12.5, 13 to 13.8, 14, 14.025, and 15.

[0015] The term "metal" is used herein to refer to a metal element in the periodic table of the elements and/or to metal alloys comprising one or more metal elements mixed
25 with at least one other element; the metal and the metal alloys have the general properties of metal elements from the periodic table of the elements such as high electrical conductivity.

[0016] The term "valence" of a chemical element is defined here as the maximum number of univalent atoms that may combine with an atom of the element under
30 consideration, or with a fragment, or for which an atom of this element can be substituted in accordance with the International Union of Pure and Applied Chemist Compendium of Chemical Terminology, 2nd Edition (1997).

[0017] The term "anchor compound" is used herein to refer to a molecule or ion having one or more functional groups that form a chemical bond with an oxide surface and one or more functional groups that form a chemical bond with a metal or metal alloy having properties suitable for use as gapfill metal in an electronic device.

5 [0018] Embodiments of and the operation of embodiments of the present invention will be discussed below primarily in the context of processing semiconductor wafers such as silicon wafers used for fabricating integrated circuits. The following discussion is primarily directed towards silicon electronic devices that use metallization layers having metal layers formed on or in oxide dielectric structures such as metal layers used for
10 fabricating gate contacts. However, it is to be understood that embodiments in accordance with the present invention may be used for other semiconductor devices, a variety of metal layers, and semiconductor wafers other than silicon.

[0019] In the following description of the figures, identical reference numerals have been used when designating substantially identical elements or processes that are
15 common to the figures.

[0020] One aspect of the present invention includes a method of fabricating an electronic device. Reference is now made to Figure 1, Figure 2, and Figure 3, where there is shown a cross-section side view of a substrate being processed by methods according to one or more embodiments of the present invention. According to one
20 embodiment of the present invention, the method comprises providing a substrate 101. As shown in Figure 1, substrate 101 includes a base 110 and a dielectric oxide 115 on base 110. Dielectric oxide 115 has one or more vias and/or one or more trenches 120 formed therein. The one or more vias and/or one or more trenches 120 expose electrically conductive areas such as metal contact 130. Areas of dielectric oxide 115 are adjacent to
25 the electrically conductive areas such as metal contact 130. Metal contact 130 may be essentially the same as metal contacts such as those for semiconductor circuits. As an option for one or more embodiments of the present invention, the electrically conductive areas may be a silicide such as, but not limited to, nickel platinum silicide for a semiconductor circuit contact.

30 [0021] The method further comprises chemically bonding an anchor compound with the dielectric oxide surface areas to form an anchor layer 135 as illustrated in Figure 2. In general, the anchor compound has at least one functional group capable of forming a

chemical bond with the oxide surface and has at least one functional group capable of forming a chemical bond with a gapfill metal. The anchor compound has suitable properties and is applied under conditions so that the anchor compound substantially only forms a bond with the dielectric oxide to form anchor layer 135 on dielectric 115

5 substantially without forming a bond with metal contact 130. Consequently, anchor layer 135 is present on dielectric 115, but is not present on metal contact 130. Anchor layer 135 comprises a chemical reaction product from a reaction of dielectric oxide layer 115 with the anchor compound.

[0022] The method further comprises initiating the growth of a metal using the
10 electrically conductive surface area shown as metal contact 130 and growing the metal to fill the one or more trenches and/or one or more vias with a gapfill metal 140 so that the anchor compound also bonds with the metal contacting the dielectric oxide surface areas.

[0023] In one or more embodiments of the method of fabricating electronic devices, gapfill metal 140 is selectively deposited. Optionally, gapfill metal 140 may be
15 selectively deposited by a process such as electroless deposition or gapfill metal 140 may be selectively deposited by a process such as chemical vapor deposition. More specifically, the gapfill metal growth is started at a metal contact such as metal contact 130 at the bottom of a via or the bottom of a trench that has been formed in dielectric 115. The gapfill metal growth is continued so as to achieve a bottom-up fill of the via and/or
20 the trench.

[0024] According to one or more embodiments of the present invention, electroless deposition of gapfill metal 140 is accomplished by placing the substrate with anchor layer 135 into an electroless deposition solution. The electroless deposition solution is formulated so as to form a metal, metal alloy, or metal composite layer. Descriptions of
25 electroless deposition processes suitable for one or more embodiments of the present invention can be found in US Patent 6,794,288 to Kolics et al. and US Patent 6,911,076 to Kolics et al.; the contents of all of these patents are incorporated herein, in their entirety by this reference.

[0025] It should be noted that the diagrams in Fig. 1, Fig. 2, and Fig. 3 are not drawn
30 to scale. More specifically, the thickness of anchor layer 120 is exaggerated for the purpose of illustration. Furthermore, the diagram in Fig. 3 shows electronic device 103

having metal layer 140 as a gapfill metal. Still further, the diagram shown in Fig. 3 presents a planarized surface so as to form a damascene metallization structure.

[0026] According to one or more embodiments of the present invention, the method includes using an anchor compound that comprises an inorganic oxoanion, an amine, an imine, a cyanide, or combinations thereof. One or more other embodiments of the present invention use anchor compounds having functional groups that can form complexes with ions of the metal used for the gapfill and/or functional groups that adsorb strongly on the gapfill metal. Embodiments of the present invention that use cobalt in the gapfill metal comprise using anchor compounds having functional groups that can form complexes with ions of cobalt and/or functional groups that adsorb strongly on cobalt.

[0027] According to one or more embodiments of the present invention, the method includes using an anchor compound that comprises an inorganic oxoanion having the general formula $A_XO_Y^{Z-}$ wherein, A is a chemical element, O is oxygen, X is an integer, Y is an integer, and Z is an integer. Some examples of inorganic oxoanions for one or more embodiments of the present invention include, but are not limited to, phosphates and phosphites.

[0028] According to one or more embodiments of the present invention, the method includes using an anchor compound having the general formula:



M is germanium, hafnium, indium, silicon, tantalum, tin, titanium, or tungsten;

G is a functional group capable of forming a chemical bond with the metal;

R_1-O is a functional group capable of forming a chemical bond with the oxide surface, O is oxygen;

V is the valence of M; and

n is an integer from 1 to V-1.

According to one embodiment of the present invention, R_1 is an alkyl group, M is silicon, and G is an alkylamine.

[0029] One or more embodiments of the present invention include using anchor compounds of the formula presented above wherein G_n comprises groups such as, but not limited to, amine, imine, epoxy, hydroxyl, carboxy, carboxylate, phosphate, phosphonate, or combinations thereof. Optionally, one or more embodiments of the present invention include using anchor compounds wherein G_n comprises, sulfonate, boronate, carbonate,

bicarbonate, or combinations thereof. One or more embodiments of the present invention include using anchor compounds wherein $(R_1-O)_{V-n}$ comprises methoxy, ethoxy, propoxy, or combinations thereof. One or more embodiments of the present invention include using anchor compounds wherein $(R_1-O)_{V-n}$ comprises methoxy, ethoxy, propoxy, or combinations thereof and G comprises amine, imine, epoxy, hydroxyl, carboxy, carboxylate, phosphate, phosphonate, or combinations thereof.

[0030] According to one or more embodiments of the present invention, the method includes using an anchor compound that comprises mono-alkoxy silane or di-alkoxy silane and at least one from the group consisting of an amine group, an imine group, a carboxylate group, a cyanide group, a phosphate group, a phosphite group, a phosphonate group, and an epoxy group.

[0031] According to one or more embodiments of the present invention, the method further comprises making the surface of metallization contacts such as metal contact 130 substantially oxide free prior to the chemically bonding an anchor compound with dielectric oxide 115. This additional process is optional and may only be used for metallization contacts that are susceptible to oxide formation. The oxide is removed from the metallization contact so that the subsequent process of bonding the anchor compound to the dielectric oxide does not bond the anchor compound to oxide formed on the metallization contact.

[0032] Methods according to one or more embodiments of the present invention may also include a thermal process to more completely bond the anchor layer to the dielectric. The thermal process may include heating the substrate during and/or after exposing the substrate to the anchor compound. According to one or more embodiments of the present invention the thermal process is performed prior to beginning the growth of the gapfill metal.

[0033] According to one or more embodiments of the present invention, examples of dielectric oxides suitable for use as dielectric oxide 115 include, but are not limited to, aluminum oxide (Al_2O_3), silicon dioxide (SiO_2), carbon doped silicon dioxide ($SiOC$), silicon oxide-based low k dielectrics, and silicon oxides such as $SiOCH$, $SiON$, $SiOCN$, and $SiOCHN$. Alternative oxides for embodiments of the present invention include, but are not limited to, tantalum pentoxide (Ta_2O_5) and titanium dioxide (TiO_2). Optionally, the dielectric oxide, according to one or more embodiments of the present invention, may

be a surface oxide formed on a dissimilar material such as silicon oxide formed on materials such as, but not limited to, aluminum nitride, silicon nitride, silicon carbonitride, and silicon carbide.

[0034] One or more embodiments of the present invention may include using a variety of gapfill metals. Examples of gapfill metals suitable for one or more embodiments of the present invention include, but are not limited to, metals comprising cobalt, copper, gold, iridium, nickel, osmium, palladium, platinum, rhenium, ruthenium, rhodium, silver, tin, zinc, electrolessly plated alloys, or mixtures thereof. According to one embodiment of the present invention, the gapfill metal comprises cobalt. According to another embodiment of the present invention, the gapfill metal comprises cobalt and the metal contact comprises nickel platinum silicide. According to another embodiment of the present invention, the gapfill metal comprises cobalt, the metal contact comprises nickel platinum silicide, and the anchor compound comprises an oxoanion.

[0035] A variety of compounds can be used for anchor compounds according to one or more embodiments of the present invention. According to one embodiment of the present invention, the anchor compounds are applied to the substrates as liquids or as components of liquid solutions using wet chemical processes. According to one or more embodiments of the present invention, the anchor compounds are dissolved in liquids such as, but not limited to, water, water-soluble solvents, dimethylsulfoxide, formamide, acetonitrile, alcohol, or mixtures thereof. Other water-soluble solvents suitable for embodiments of the present invention will be clear to persons of ordinary skill in the art, in view of the present disclosure. According to another embodiment of the present invention, the anchor compounds are applied to the substrates as a gas or vapor using dry chemical processing or using substantially dry chemical processes. More specifically, according to one or more embodiments of the present invention, the anchor compound is applied to the substrates as a gas under conditions so that the anchor compound bonds to the dielectric oxide of the substrates. Optionally, the gas phase anchor compound may be mixed with another gas such as, but not limited to, a substantially inert carrier gas.

[0036] In another embodiment of the present invention, anchor layer 135 is formed by immersing the substrate in the anchor compound or in a solution containing the anchor compound to bond the anchor compound to the oxide surface for a time from about 30 seconds to about 600 seconds at a temperature from about 10°C to about 95°C.

According to another embodiment, the substrate is immersed in a solution containing the anchor compound to bond the anchor compound to the oxide surface from about 60 seconds to about 180 seconds at a temperature from about 50°C to about 70°C.

[0037] According to one or more embodiments of the present invention, the method comprises providing a substrate having metallization contacts and dielectric oxide. The dielectric oxide has vias to the metallization contacts. The method includes bonding an anchor compound with the dielectric oxide by exposing the dielectric oxide to the anchor compound and/or to a solution containing the anchor compound so as to form an anchor layer on the dielectric oxide. The method further includes initiating the selective growth of a gapfill metal using the metallization contacts. Optionally, the selective growth of the gapfill metal may be accomplished using processes such as, but not limited to, atomic layer deposition, chemical vapor deposition, and electroless deposition. The gapfill metal is grown so that the anchor layer formed by the anchor compound bonding with the dielectric oxide also bonds with the gapfill metal that is adjacent to or contacts the dielectric oxide. The anchor compound and the resulting anchor layer are selected so that they do not significantly cause growth of the gapfill metal. More specifically, the growth of the gapfill metal is the result of growth initiated by the metal contact at the bottom of the trench and/or via. The growth of the metal gapfill is continued so that the vias and/or trenches are at least filled with the gapfill metal. A planarization process may be used after completion of the gapfill. According to one or more embodiments of the present invention, the gapfill metal is a metal comprising cobalt or a cobalt alloy.

[0038] Another aspect of the present invention comprises an electronic device such as, but not limited to, an integrated circuit. Reference is again made to Fig. 3. According to one embodiment of the present invention, the electronic device comprises a base 110 such as a semiconductor wafer, a metallization contact 130, a dielectric oxide 115 having a via 120 to the metallization contact 130, a gapfill metal 140 grown from metallization contact 130 substantially filling via 120, and an anchor layer 135 chemically bonded between the surface of dielectric oxide 115 and gapfill metal 140. The electronic device has substantially none of the anchor layer between the interface at metallization contact 130 and gapfill metal 140.

[0039] According to one or more embodiments of the present invention, the anchor layer is a chemical reaction product from a reaction of the oxide surface and a reaction of the gapfill metal with an anchor compound having the general formula:

$(R_1-O)_{V-n}MG_n$ where

5 M is germanium, hafnium, indium, silicon, tantalum, tin, titanium, or tungsten;

G is a functional group capable of forming a chemical bond with the metal;

R_1-O is a functional group capable of forming a chemical bond with the oxide surface, O is oxygen;

V is the valence of M; and

10 n is an integer from 1 to V-1.

According to one embodiment of the present invention, R_1 is an alkyl group, M is silicon, and G is an alkylamine. As an option for one or more embodiments of the present invention, G comprises amine, imine, epoxy, hydroxyl, carboxy, carboxylate, phosphate, phosphonate, or combinations thereof. As an option for one or more embodiments of the present invention, R_1- is an alkyl group.

[0040] According to one or more embodiments of the present invention, the anchor compound comprises mono-alkoxy silane or di-alkoxy silane and at least one from the group consisting of an amine group, an imine group, a carboxylate group, a cyanide group, a phosphate group, a phosphite group, a phosphonate group, and an epoxy group.

20 **[0041]** According to one or more embodiments of the present invention, the anchor compounds have the formula presented above wherein G_n comprises groups such as, but not limited to, amine, imine, epoxy, hydroxyl, carboxy, carboxylate, phosphate, phosphonate, or combinations thereof. According to one or more embodiments of the present invention, the anchor compounds have the formula presented above wherein G_n comprises, sulfonate, boronate, carbonate, bicarbonate, or combinations thereof.

25 According to one or more embodiments of the present invention, the anchor compounds have the formula presented above wherein $(R_1-O)_{V-n}$ comprises methoxy, ethoxy, propoxy, or combinations thereof. According to one or more embodiments of the present invention, the anchor compounds have the formula presented above wherein $(R_1-O)_{4-n}$ comprises methoxy, ethoxy, propoxy, or combinations thereof and G comprises amine, imine, epoxy, hydroxyl, carboxy, carboxylate, phosphate, phosphonate, or combinations thereof.

[0042] According to one or more embodiments of the present invention, the anchor layer is a chemical reaction product from a reaction of the oxide surface and a reaction of the gapfill metal with an anchor compound that comprises an inorganic oxoanion, an amine, an imine, a cyanide, or combinations thereof. One or more other embodiments of the present invention use anchor compounds having functional groups that can form complexes with ions of the metal used for the gapfill and/or functional groups that adsorb strongly on the gapfill metal. Embodiments of the present invention that use cobalt in the gapfill metal comprise using anchor compounds having functional groups that can form complexes with ions of cobalt and/or functional groups that adsorb strongly on cobalt.

[0043] According to one or more embodiments of the present invention, the anchor layer is a chemical reaction product from a reaction of the oxide surface and a reaction of the gapfill metal with an anchor compound that comprises an inorganic oxoanion having the generic formula $A_XO_Y^{Z-}$ wherein, A is a chemical element, O is oxygen, X is an integer, Y is an integer, and Z is an integer. Some examples of inorganic oxoanions for one or more embodiments of the present invention include, but are not limited, phosphates and phosphites.

[0044] According to one or more embodiments of the present invention the dielectric oxide such as dielectric oxide 115 comprises oxides such as, but not limited to, aluminum oxide (Al_2O_3), silicon dioxide (SiO_2), carbon doped silicon dioxide ($SiOC$), silicon oxide-based low k dielectrics, and silicon oxides such as $SiOCH$, $SiON$, $SiOCN$, and $SiOCHN$. Alternative oxides for embodiments of the present invention include but are not limited to tantalum pentoxide (Ta_2O_5) and titanium dioxide (TiO_2). Optionally, the dielectric oxide, according to one or more embodiments of the present invention, may be a surface oxide formed on a dissimilar material such as oxide formed on materials such as, but not limited to, aluminum nitride, silicon nitride, silicon carbonitride, and silicon carbide.

[0045] One or more embodiments of the present invention may include using a variety of gapfill metals. Examples of gapfill metals suitable for one or more embodiments of the present invention include, but are not limited to, metals comprising cobalt, copper, gold, iridium, nickel, osmium, palladium, platinum, rhenium, ruthenium, rhodium, silver, tin, zinc, electrolessly plated alloys, or mixtures thereof. According to one embodiment of the present invention the gapfill metal comprises cobalt. According to another embodiment of the present invention the gapfill metal comprises cobalt and the

metal contact comprises nickel platinum silicide. According to another embodiment of the present invention gapfill metal comprises cobalt, the metal contact comprises nickel platinum silicide, and the anchor compound comprises an oxoanion.

[0046] According to one or more embodiments of the present invention, the method of making electronic devices described above and the electronic devices described above include using a liquid solution to bond an anchor compound to an oxide dielectric to form an anchor layer. The anchor compound has at least one functional group capable of forming a chemical bond with the oxide surface and has at least one functional group capable of forming a chemical bond with the metal.

[0047] According to one or more embodiments of the present invention, the solution comprises an anchor compound having the general formula:

$(R_1-O)_{V-n}MG_n$ where

M is germanium, hafnium, indium, silicon, tantalum, tin, titanium, or tungsten;

G is a functional group capable of forming a chemical bond with the metal;

R_1-O is a functional group capable of forming a chemical bond with the oxide surface, O is oxygen;

V is the valence of M; and

n is an integer from 1 to V-1.

According to one embodiment of the present invention, R_1 is an alkyl group, M is silicon, and G is an alkylamine. As an option for one or more embodiments of the present invention, G comprises amine, imine, epoxy, hydroxyl, carboxy, carboxylate, phosphate, phosphonate, or combinations thereof. As an option for one or more embodiments of the present invention, R_1- is an alkyl group.

[0048] According to one or more embodiments of the present invention, the anchor compound in the solution comprises mono-alkoxy silane or di-alkoxy silane and at least one from the group consisting of an amine group, an imine group, a carboxylate group, a cyanide group, a phosphate group, a phosphite group, a phosphonate group, and an epoxy group.

[0049] According to one or more embodiments of the present invention, the anchor compounds have the formula presented above wherein G_n comprises groups such as, but not limited to, amine, imine, epoxy, hydroxyl, carboxy, carboxylate, phosphate, phosphonate, or combinations thereof. According to one or more embodiments of the

present invention, the anchor compounds have the formula presented above wherein G_n comprises, sulfonate, boronate, carbonate, bicarbonate, or combinations thereof.

According to one or more embodiments of the present invention, the anchor compounds have the formula presented above wherein $(R_1-O)_{V-n}$ comprises methoxy, ethoxy,

5 propoxy, or combinations thereof. According to one or more embodiments of the present invention, the anchor compounds have the formula presented above wherein $(R_1-O)_{V-n}$ comprises methoxy, ethoxy, propoxy, or combinations thereof and G comprises amine, imine, epoxy, hydroxyl, carboxy, carboxylate, phosphate, phosphonate, or combinations thereof.

10 **[0050]** According to one or more embodiments of the present invention, the solution includes anchor compounds comprising an inorganic oxoanion, an amine, an imine, a cyanide, or combinations thereof. One or more other embodiments of the present invention, the solution includes anchor compounds having functional groups that can form complexes with ions of the metal used for the gapfill and/or functional groups that
15 adsorb strongly on the gapfill metal. For embodiments of the present invention that use cobalt in the gapfill metal, the solution comprises anchor compounds having functional groups that can form complexes with ions of cobalt and/or functional groups that adsorb strongly on cobalt.

[0051] According to one or more embodiments of the present invention, the solution
20 includes an anchor compound that comprises an inorganic oxoanion having the generic formula $A_XO_Y^{Z-}$ wherein, A is a chemical element, O is oxygen, X is an integer, Y is an integer, and Z is an integer. Some examples of inorganic oxoanions for one or more embodiments of the present invention include, but are not limited, phosphates and phosphites.

25 **[0052]** According to one or more embodiments of the present invention, the solution comprises an amount of water-soluble solvent which is optional; an amount of anchor compound having at least one functional group capable of forming a chemical bond with the oxide surface and having at least one functional group capable of forming a chemical bond with the gapfill metal; and an amount of water. According to one or more
30 embodiments of the present invention, the solution comprises a solvent and an anchoring agent without a water soluble solvent. According to one or more embodiments of the present invention the anchor compound comprises an inorganic oxoanion, such as but not

limited to, a phosphate, a phosphite, an amine, an imine, a cyanide, and combinations thereof or functional groups that can form complexes with metal ions and/or adsorb strongly on the gapfill metal.

5 [0053] According to one embodiment of the present invention, the solution comprises an amount of anchor compound. In general, the anchor compound has at least one functional group capable of forming a chemical bond with the oxide surface and has at least one functional group capable of forming a chemical bond with the gapfill metal. In another embodiment of the present invention, the solution comprises an amount of water-soluble solvent, an amount of anchor compound, and an amount of water.

10 [0054] The anchor compounds for embodiments of the present invention can have numerous chemical compositions. There are many choices for the at least one functional group capable of forming a chemical bond with the oxide surface and for the at least one functional group capable of forming a chemical bond with the metal. Some embodiments of the present invention may include anchor compounds having two or three or more
15 functional groups capable of forming a chemical bond with the oxide surface. Similarly, some embodiments of the present invention may include anchor compounds having two or three or more functional groups capable of forming a chemical bond with the gapfill metal. Optionally, anchor compounds may be selected that include different types of functional groups capable of forming chemical bonds with the oxide surface. Anchor
20 compounds may be selected that include different types of functional groups capable of forming chemical bonds with the metal. Embodiments of the present invention may also use mixtures of different types of anchor compounds.

[0055] According to one embodiment of the present invention, the anchor compound includes an alkoxysilane such as a mono-alkoxy silane, such as a di-alkoxy silane, and
25 such as a tri-alkoxy silane for forming the chemical bond with the oxide surface. The anchor compound further includes one or more polar groups such as, but not limited to, an amine group, an imine group, a carboxylate group, a phosphate group, a phosphonate group, and an epoxy group forming the chemical bond with the gapfill metal. As an option, anchor compounds according to some embodiments of the present invention may
30 include dissimilar polar groups or mixtures of dissimilar polar groups. For specific embodiments of the present invention, the type and amount of anchor compound is

selected so that the solution provides an effective amount of the anchor compound to the oxide surface to accomplish increased bonding between the oxide and the gapfill metal.

[0056] For another embodiment of the present invention, the solution includes an anchor compound having the general formula $(R_1-O)_{V-n}MG_n$ where M is germanium, hafnium, indium, silicon, tantalum, tin, titanium, or tungsten; G is the functional group capable of forming the chemical bond with the gapfill metal; R_1-O is the functional group capable of forming the chemical bond with the oxide surface, O is oxygen; V is the valence of M; and n is an integer from 1 to V-1. One embodiment of the present invention has G comprising one or more polar groups such as, but not limited to, amine, imine, epoxy, hydroxyl, carboxy, carboxylate, phosphate, phosphonate, sulfonate, boronate, carbonate, bicarbonate, or combinations thereof. Preferably, R_1 is an organic group such as an alkyl group and R_1-O is an alkoxy group such as methoxy, ethoxy, and propoxy. For another embodiment of the present invention, $(R_1-O)_{V-n}$ includes one or more groups such as, but not limited to, methoxy, ethoxy, propoxy, and combinations thereof and G_n comprises one or more groups such as, but not limited to, amine, imine, epoxy, hydroxyl, carboxy, carboxylate, phosphate, phosphonate, and combinations thereof. In another preferred embodiment, R_1 is an alkyl group, M is silicon, and G is an alkylamine.

[0057] Another embodiment of the present invention is a solution comprising components for electroless deposition and an anchor compound. The components for electroless deposition may comprise, but are not limited to, a solvent, a reducing agent for electroless deposition, and ions and/or complexes of one or more metals for electroless deposition of a gapfill metal. Descriptions of typical electroless deposition solutions and components of electroless deposition solutions can be found in commonly owned patents US Patent 6,794,288 to Kolics et al. and US Patent 6,911,076 to Kolics et al.; the contents of all of these patents are incorporated herein, in their entirety, by this reference. Descriptions of other electroless deposition solutions and components of electroless deposition solutions are also available elsewhere in the scientific and patent literature.

[0058] The anchor compound has at least one functional group capable of forming a chemical bond with an oxide surface and has at least one functional group capable of forming a chemical bond with the gapfill metal. Details and examples of anchor

compounds included in solution with components for electroless deposition according to one or more embodiments of the present invention are presented above.

[0059] A solution, according to one embodiment of the present invention, comprises components for electroless deposition and an anchor compound. The anchor compound
5 has the general formula $(R_1-O)_{V-n}MG_n$ where

M is germanium, hafnium, indium, silicon, tantalum, tin, titanium, or tungsten;

G is a functional group capable of forming the chemical bond with the metal;

R_1-O is the functional group capable of forming the chemical bond with the oxide surface, O is oxygen;

10 V is the valence of M; and

n is an integer from 1 to V-1.

[0060] A solution, according to one embodiment of the present invention, comprises components for electroless deposition and an anchor compound. The anchor compound comprises an inorganic oxoanion, a phosphate, a phosphite, a phosphonate, an amine, an
15 imine, a cyanide, or combinations thereof.

[0061] A solution, according to one embodiment of the present invention, comprises components for electroless deposition and an anchor compound. The anchor compound comprises inorganic oxoanions, amines, imines, cyanides, functional groups that form complexes with ions of the gapfill metal, functional groups that adsorb strongly on the
20 gapfill metal, or combinations thereof.

[0062] A solution, according to one embodiment of the present invention, comprises components for electroless deposition and an anchor compound. The anchor compound comprises inorganic oxoanions having the general formula $A_XO_Y^{Z-}$ wherein, A is a chemical element, O is oxygen, X is an integer, Y is an integer, and Z is an integer.

25 **[0063]** A solution, according to one embodiment of the present invention, comprises components for electroless deposition and an anchor compound. The anchor compound comprises mono-alkoxy silane, di-alkoxy silane, or tri-alkoxy silane and at least one member from the group consisting of an amine group, an imine group, a carboxylate group, a phosphate group, a phosphonate group, and an epoxy group.

30 **[0064]** In the foregoing specification, the invention has been described with reference to specific embodiments. However, one of ordinary skill in the art appreciates that various modifications and changes can be made without departing from the scope of the

present invention as set forth in the claims below. Accordingly, the specification and figures are to be regarded in an illustrative rather than a restrictive sense, and all such modifications are intended to be included within the scope of the present invention.

[0065] Benefits, other advantages, and solutions to problems have been described

5 above with regard to specific embodiments. However, the benefits, advantages, solutions to problems, and any element(s) that may cause any benefit, advantage, or solution to occur or become more pronounced are not to be construed as a critical, required, or essential feature or element of any or all the claims.

[0066] As used herein, the terms “comprises,” “comprising,” “includes,” “including,”

10 “has,” “having,” “at least one of,” or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of elements is not necessarily limited only to those elements but may include other elements not expressly listed or inherent to such process, method, article, or apparatus. Further, unless expressly stated to the contrary, “or” refers to an inclusive or
15 and not to an exclusive or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

CLAIMS

What is claimed is:

1. A method of fabricating an electronic device, the method comprising:
 - 5 providing a substrate having dielectric oxide surface areas adjacent to electrically conductive surface areas;
 - chemically bonding an anchor compound with the dielectric oxide surface areas so as to form an anchor layer;
 - initiating the growth of a metal using the electrically conductive surface areas and
 - 10 growing the metal so that the anchor layer bonds with the metal.
 2. The method of claim 1, wherein the anchor compound has at least one functional group capable of forming a chemical bond with the oxide surface and having at least one functional group capable of forming a chemical bond with the metal.
 3. The method of claim 1, wherein the anchor compound comprises an inorganic
 - 15 oxoanion, an amine, an imine, a cyanide, a functional group that form complexes with ions of the metal, a functional group that adsorbs strongly on the metal, or combinations thereof.
 4. The method of claim 1, wherein the anchor compound comprises an inorganic oxoanion having the generic formula $A_XO_Y^{Z-}$ wherein, A is a chemical element, O is
 - 20 oxygen, X is an integer, Y is an integer, and Z is an integer.
 5. The method of claim 1, wherein the anchor compound comprises phosphate, phosphite, or phosphonate.
 6. The method claim 1, wherein the anchor compound comprises mono-alkoxy silane, di-alkoxy silane, or tri-alkoxy silane and at least one from the group consisting of an
 - 25 amine group, an imine group, a carboxylate group, a cyanide group, a phosphate group, a phosphite group, a phosphonate group, and an epoxy group.
 7. The method of claim 1, wherein the anchor compound has the general formula $(R_1-O)_{v-n}MG_n$ where
 - 30 M is germanium, hafnium, indium, silicon, tantalum, tin, titanium, or tungsten;
 - G is a functional group capable of forming the chemical bond with the metal;

R_1-O is the functional group capable of forming the chemical bond with the oxide surface, O is oxygen;

V is the valence of M; and

n is an integer from 1 to V-1.

- 5 8. The method of claim 7, wherein R_1 is an alkyl group, M is silicon, and G is an alkylamine.
9. The method of claim 1, further comprising making the surface of the metallization contacts substantially oxide free prior to the chemically bonding an anchor compound with the dielectric oxide.
- 10 10. The method of claim 1, wherein the dielectric oxide is a surface oxide formed on a dissimilar material.
11. The method of claim 1, wherein the chemically bonding an anchor compound with the dielectric oxide surface areas is a dry chemical process using a gas comprising the anchor compound.
- 15 12. The method of claim 1, wherein chemically bonding an anchor compound with the dielectric oxide surface areas is a wet chemical process using a liquid solution comprising the anchor compound.
13. The method of claim 12, wherein the liquid solution further comprises dimethylsulfoxide, formamide, acetonitrile, alcohol, or mixtures thereof.
- 20 14. The method of claim 1, wherein the oxide surface comprises at least one selected from the group consisting of SiO_2 , SiOC, SiOCH, SiON, SiOCN, SiOCHN, Ta_2O_5 , and TiO_2 .
15. The method of claim 1, wherein the gapfill metal comprises cobalt, copper, gold, iridium, nickel, osmium, palladium, platinum, rhenium, ruthenium, rhodium, silver, tin,
- 25 zinc, electrolessly plated alloys, or mixtures thereof.
16. An electronic device fabricated using the method of claim 1.
17. An electronic device comprising:
 - a metallization contact;
 - a dielectric oxide having a via and/or a trench to the metallization contact;
 - 30 a gapfill metal grown from the metallization contact; and
 - an anchor layer formed by an anchor compound chemically bonded between the dielectric oxide and the gapfill metal.

18. The electronic device of claim 17, wherein the anchor layer comprises a chemical reaction product from a reaction of the dielectric oxide and a reaction of the gapfill metal with the anchor compound, the anchor compound comprises an inorganic oxoanion, an amine, an imine, a cyanide, or combinations thereof.
- 5 19. The electronic device of claim 17, wherein the anchor layer comprises a chemical reaction product from a reaction of the dielectric oxide and a reaction of the gapfill metal with the anchor compound, the anchor compound comprises functional groups that can form complexes with ions of the metal used for the gapfill metal and/or functional groups that adsorb strongly on the gapfill metal.
- 10 20. The electronic device of claim 17, wherein the gapfill metal comprises cobalt, the anchor layer comprises a chemical reaction product from a reaction of the dielectric oxide and a reaction of the gapfill metal with the anchor compound, the anchor compound comprises functional groups that can form complexes with ions of cobalt and/or functional groups that adsorb strongly on cobalt.
- 15 21. The electronic device of claim 17, wherein the anchor layer is a chemical reaction product from a reaction of the dielectric oxide and a reaction of the gapfill metal with an anchor compound that comprises an inorganic oxoanion having the generic formula $A_XO_Y^{Z-}$ wherein, A is a chemical element, O is oxygen, X is an integer, Y is an integer, and Z is an integer.
- 20 22. The electronic device of claim 17, wherein the anchor layer comprises a chemical reaction product from a reaction of the dielectric oxide and a reaction of the gapfill metal with the anchor compound, the anchor compound having the general formula:
 $(R_1-O)_{V-n}MG_n$ where
- 25 M is germanium, hafnium, indium, silicon, tantalum, tin, titanium, or tungsten;
- G is a functional group capable of forming the chemical bond with the metal;
- R_1-O is the functional group capable of forming the chemical bond with the oxide surface, O is oxygen;
- 30 V is the valence of M; and
- n is an integer from 1 to V-1.

23. The electronic device of claim 17, wherein the dielectric oxide comprises at least one of Al_2O_3 , SiO_2 , SiOC , SiOCH , SiON , SiOCN , SiOCHN , Ta_2O_5 , and TiO_2 .

24. The electronic device of claim 17, wherein the gapfill metal comprises at least one of copper, cobalt, nickel, tungsten, boron, phosphorus, and mixtures thereof.

5

25. The electronic device of claim 22, wherein the anchor layer comprises $\text{O}_{\text{V-n}}\text{MG}_n$ and G comprises amine, imine, epoxy, hydroxyl, carboxy, carboxylate, phosphate, phosphonate, or combinations thereof.

10 26. A solution to increase the bonding between an oxide surface and a gapfill metal, the solution comprising:

optionally, an amount of water-soluble solvent;

an amount of anchor compound having at least one functional group capable of forming a chemical bond with the oxide surface and having at least one functional group capable of forming a chemical bond with the gapfill metal; and

15 an amount of water.

27. The solution of claim 26, wherein the anchor compound comprises an inorganic oxoanion, a phosphate, a phosphite, a phosphonate, an amine, an imine, a cyanide, or combinations thereof.

20 28. The solution of claim 26, wherein the anchor compound comprises inorganic oxoanions, amines, imines, cyanides, functional groups that form complexes with ions of the gapfill metal, functional groups that adsorb strongly on the gapfill metal, or combinations thereof.

25 29. The solution of claim 26, wherein the anchor compound comprises inorganic oxoanions having the generic formula $\text{A}_x\text{O}_y^{z-}$ wherein, A is a chemical element, O is oxygen, X is an integer, Y is an integer, and Z is an integer.

30. The solution of claim 26, wherein the anchor compound comprises phosphate, phosphonate, or phosphite.

30 31. The solution of claim 26, wherein the anchor compound has at least one functional group capable of forming a chemical bond with the oxide surface and having at least one functional group capable of forming a chemical bond with the metal.

32. The solution claim 26, wherein the anchor compound comprises mono-alkoxy silane, di-alkoxy silane, or tri-alkoxy silane and at least one member from the group consisting

of an amine group, an imine group, a carboxylate group, a phosphate group, a phosphonate group, and an epoxy group.

33. A solution comprising:

a solvent;

5 an anchor compound having at least one functional group capable of forming a chemical bond with the oxide surface and having at least one functional group capable of forming a chemical bond with the gapfill metal;

a reducing agent for electroless deposition; and

ions of one or more metals for electroless deposition of a gapfill metal.

10 34. The method of claim 33, wherein the anchor compound has the general formula $(R_1-O)_{V-n}MG_n$ where

M is germanium, hafnium, indium, silicon, tantalum, tin, titanium, or tungsten;

15 G is a functional group capable of forming the chemical bond with the metal;

R_1-O is the functional group capable of forming the chemical bond with the oxide surface, O is oxygen;

V is the valence of M; and

n is an integer from 1 to V-1.

20 35. The solution of claim 33, wherein the anchor compound comprises an inorganic oxoanion, a phosphate, a phosphite, a phosphonate, an amine, an imine, a cyanide, or combinations thereof.

36. The solution of claim 33, wherein the anchor compound comprises inorganic oxoanions, amines, imines, cyanides, functional groups that form complexes with ions of
25 the gapfill metal, functional groups that adsorb strongly on the gapfill metal, or combinations thereof.

37. The solution of claim 33, wherein the anchor compound comprises inorganic oxoanions having the generic formula $A_XO_Y^{Z-}$ wherein A is a chemical element, O is oxygen, X is an integer, Y is an integer, and Z is an integer.

30 38. The solution claim 33, wherein the anchor compound comprises mono-alkoxy silane, di-alkoxy silane, or tri-alkoxy silane and at least one member from the group consisting

of an amine group, an imine group, a carboxylate group, a phosphate group, a phosphonate group, and an epoxy group.

101 

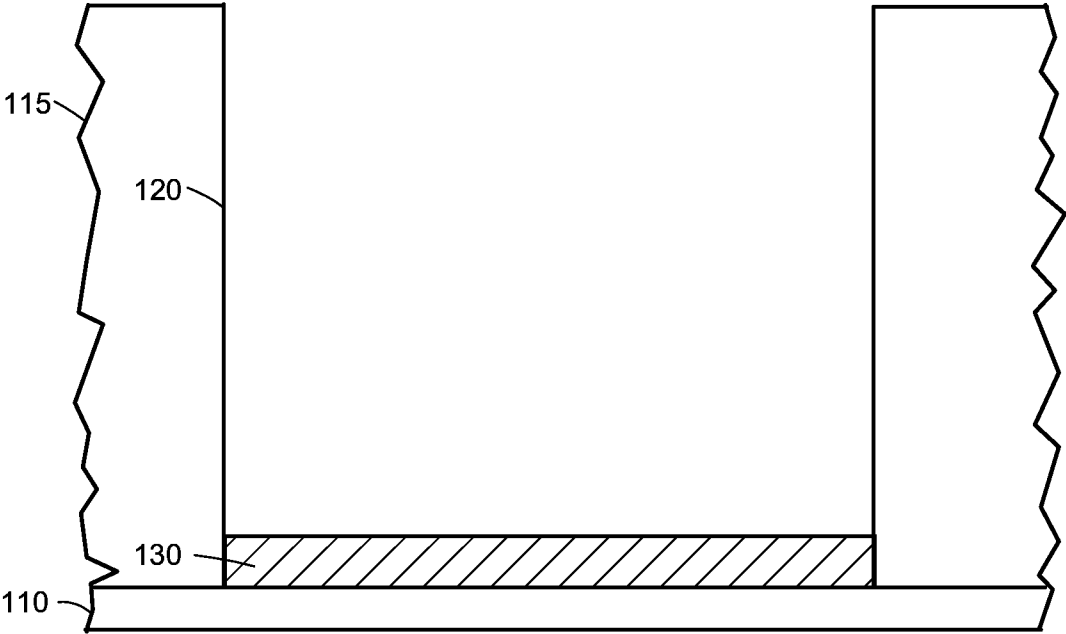


FIG. 1

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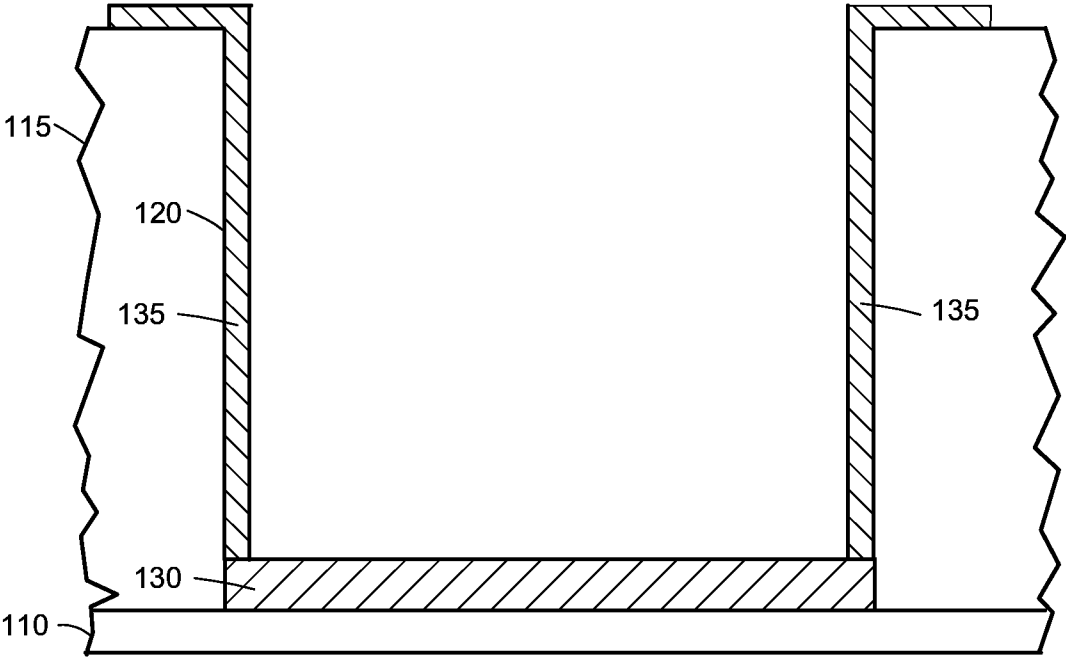


FIG. 2

103 ↗

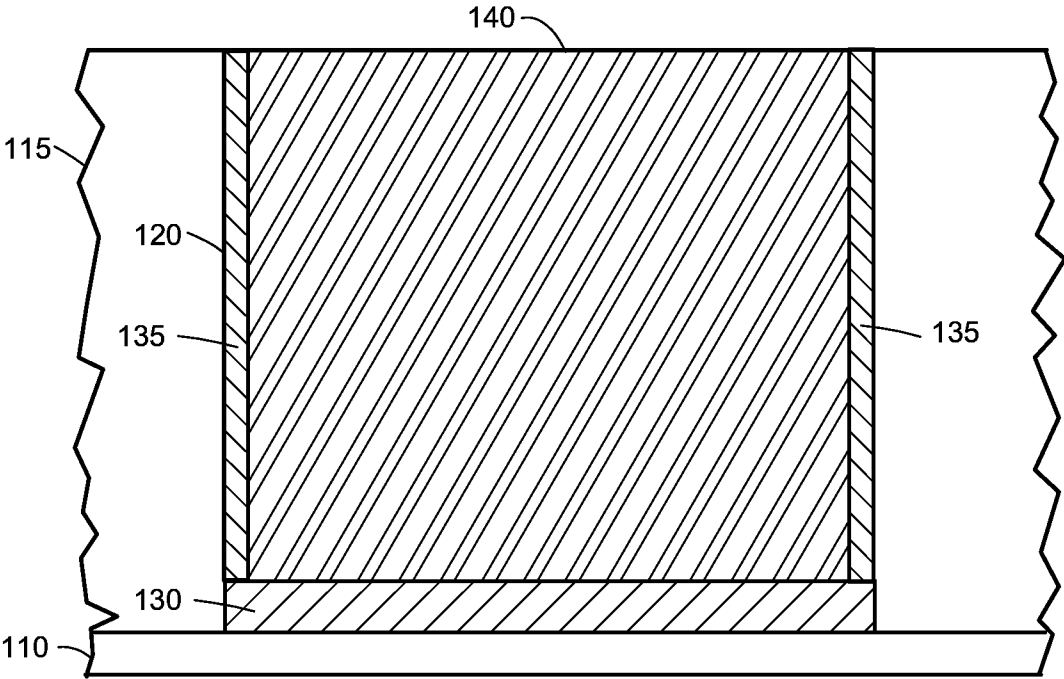


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/027425**A. CLASSIFICATION OF SUBJECT MATTER****H01L 21/28(2006.01)i, H01L 21/31(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01L 21/28; H01L 21/768; C23C 18/54; H01L 21/4763; H01G 9/07; H01G 9/15; H01G 4/12; H01L 23/522; C23C 18/16; H05K 3/38; H01L 21/44

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: anchor layer, compound, adhesive, bonding, dielectric oxide, metal, gap, trench, functional group

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2005-0181598 A (SRIDHAR K. KAILASAM) 18 August 2005	1,9-12,14-17,23-24
Y	See abstract, paragraphs [0014], [0032]-[0038], and figures 1-3.	2-3,7-8,19-20,22 ,25-26,28,31,33-34 ,36
A		4-6,13,18,21,27 ,29-30,32,35,37-38
Y	JP 2007-088506 A (MATSUSHITA ELECTRIC IND. CO., LTD.) 05 April 2007	2-3,7-8,19-20,22 ,25-26,28,31,33-34 ,36
A	See abstract, paragraphs [0031], [0045], [0049]-[0055], and claim 1.	
A	JP 2006-179742 A (NGK SPARK PLUG CO., LTD.) 06 July 2006	1-38
A	See abstract, paragraphs [0008]-[0023], claims 1-2, and figure 1.	
A	KR 10-2011-0086558 A (LAM RESEARCH CORP.) 28 July 2011	1-38
A	See abstract, paragraphs [0005]-[0006], [0010], [0024], claim 1, and figure 3.	
A	KR 10-2008-0086369 A (AVX CORP.) 25 September 2008	1-38
A	See abstract, paragraphs [0004], [0008], and claim 1.	



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

25 June 2013 (25.06.2013)

Date of mailing of the international search report

25 June 2013 (25.06.2013)

Name and mailing address of the ISA/KR

Korean Intellectual Property Office
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302-701, Republic of Korea

Facsimile No. 82-42-472-7140

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Telephone No. 82-42-481-3463



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/027425

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2005-0181598 A1	18.08.2005	US 6974768 B1 US 7425506 B1 US 7446032 B2	13.12.2005 16.09.2008 04.11.2008
JP 2007-088506 A	05.04.2007	JP 03986674 B2 JP 2000-058641 A	20.07.2007 25.02.2000
JP 2006-179742 A	06.07.2006	None	
KR 10-2011-0086558 A	28.07.2011	CN 102203319 A JP 2012-508819 A US 7682431 B1 WO 2010-056612 A2	28.09.2011 12.04.2012 23.03.2010 20.05.2010
KR 10-2008-0086369 A	25.09.2008	CN 101271770 A CN 101271770 B GB 2447729 A JP 2008-235908 A US 2008-0232035 A1 US 7460358 B2	24.09.2008 04.04.2012 24.09.2008 02.10.2008 25.09.2008 02.12.2008