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### Integrated circuit interconnect structures with graphene cap

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#### Abstract

Integrated circuitry interconnect structures comprising a first metal and a graphene cap over a top surface of the first metal. Within the interconnect structure an amount of a second metal, nitrogen, or silicon is greater proximal to an interface of the graphene cap. The presence of the second metal, nitrogen, or silicon may improve adhesion of the graphene to the first metal and/or otherwise improve electromigration resistance of a graphene capped interconnect structure. The second metal, nitrogen, or silicon may be introduced into the first metal during deposition of the first metal, or during a post-deposition treatment of the first metal. The second metal, nitrogen, or silicon may be introduced prior to, or after, capping the first metal with graphene.

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## Background/Summary

## BACKGROUND

- (1) Demand for higher performance integrated circuits (ICs) in electronic device applications has motivated increasingly dense transistor architectures. Interconnect parasitics become a greater challenge as the density of interconnect structures keeps pace with transistor density. For example, the resistance-capacitance (RC) delay associated with interconnects of an IC increases with the density of the interconnects.
  - (2) Conventional IC interconnect structures include electrically conductive lines within separate interconnect levels and electrically conductive vias linking together various metal lines between adjacent interconnect levels. In dual-damascene structures, vias and trenches etched into a dielectric material are filled with one or more conductive materials to form the conductive vias and lines. As interconnect line dimensions scale down, resistance of the interconnect structures increases, particularly the lines.
  - (3) The introduction of graphene can reduce electrical resistance of an interconnect structure, particularly a line. Graphene may, for example, be introduced onto a sidewall, bottom surface, or top surface of an interconnect line.
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## Description

### BRIEF DESCRIPTION OF THE DRAWINGS

- (1) The material described herein is illustrated by way of example and not by way of limitation in the accompanying figures. For simplicity and clarity of illustration, elements illustrated in the figures are not necessarily drawn to scale. For example, the dimensions of some elements may be exaggerated relative to other elements for clarity. Further, where considered appropriate, reference labels have been repeated among the figures to indicate corresponding or analogous elements. In the figures:
- (2) FIG. 1 is a flow diagram illustrating methods of forming an IC interconnect structure including a graphene cap, in accordance with some embodiments;
- (3) FIG. 2A illustrates a cross-sectional view of an IC interconnect structure including a graphene cap, in accordance with some damascene embodiments;
- (4) FIG. 2B illustrates a cross-sectional view of an IC interconnect structure including a graphene cap, in accordance with some subtractive embodiments;
- (5) FIG. 3 is a flow diagram illustrating methods of integrating a graphene gap into an IC interconnect structure, in accordance with some embodiments;
- (6) FIGS. 4A, 4B and 4C illustrate cross-sectional views of an IC interconnect structure evolving to include a graphene cap as operations in the methods illustrated in FIG. 3 are practiced, in accordance with some embodiments;
- (7) FIG. 5 is a flow diagram illustrating methods of a graphene cap into an IC interconnect structure, in accordance with some embodiments;
- (8) FIGS. 6A, 6B and 6C illustrate cross-sectional views of an IC interconnect structure evolving to include a graphene cap as operations in the methods illustrated in FIG. 5 are practiced, in accordance with some embodiments;
- (9) FIGS. 7A and 7B illustrate cross-sectional views of an IC interconnect structure evolving to include a graphene cap as operations in the methods illustrated in FIG. 5 are practiced, in accordance with some alternative embodiments;
- (10) FIG. 8 is a flow diagram illustrating methods of integrating a graphene cap into an IC interconnect structure, in accordance with some embodiments;
- (11) FIGS. 9A, 9B and 9C illustrate cross-sectional views of an IC interconnect structure evolving to include a graphene cap as operations in the methods illustrated in FIG. 8 are practiced, in accordance with some embodiments;

(12) FIG. 10 illustrates a mobile computing platform and a data server machine employing an IC including transistor structures with a source and drain stop layer, in accordance with embodiments; and

(13) FIG. 11 is a functional block diagram of an electronic computing device, in accordance with some embodiments.

#### DETAILED DESCRIPTION

(14) Embodiments are described with reference to the enclosed figures. While specific configurations and arrangements are depicted and discussed in detail, it should be understood that this is done for illustrative purposes only. Persons skilled in the relevant art will recognize that other configurations and arrangements are possible without departing from the spirit and scope of the description. It will be apparent to those skilled in the relevant art that techniques and/or arrangements described herein may be employed in a variety of other systems and applications other than what is described in detail herein.

(15) Reference is made in the following detailed description to the accompanying drawings, which form a part hereof and illustrate exemplary embodiments. Further, it is to be understood that other embodiments may be utilized and structural and/or logical changes may be made without departing from the scope of claimed subject matter. It should also be noted that directions and references, for example, up, down, top, bottom, and so on, may be used merely to facilitate the description of features in the drawings. Therefore, the following detailed description is not to be taken in a limiting sense and the scope of claimed subject matter is defined solely by the appended claims and their equivalents.

(16) In the following description, numerous details are set forth. However, it will be apparent to one skilled in the art, that embodiments may be practiced without these specific details. In some instances, well-known methods and devices are shown in block diagram form, rather than in detail, to avoid obscuring the embodiments. Reference throughout this specification to “an embodiment” or “one embodiment” or “some embodiments” means that a particular feature, structure, function, or characteristic described in connection with the embodiment is included in at least one embodiment. Thus, the appearances of the phrase “in an embodiment” or “in one embodiment” or “some embodiments” in various places throughout this specification are not necessarily referring to the same embodiment. Furthermore, the particular features, structures, functions, or characteristics may be combined in any suitable manner in one or more embodiments. For example, a first embodiment may be combined with a second embodiment anywhere the particular features, structures, functions, or characteristics associated with the two embodiments are not mutually exclusive.

(17) As used in the description and the appended claims, the singular forms “a”, “an” and “the” are intended to include the plural forms as well, unless the context clearly indicates otherwise. It will also be understood that the term “and/or” as used herein refers to and encompasses any and all possible combinations of one or more of the associated listed items.

(18) The terms “coupled” and “connected,” along with their derivatives, may be used herein to describe functional or structural relationships between components. It should be understood that these terms are not intended as synonyms for each other. Rather, in particular embodiments, “connected” may be used to indicate that two or more elements are in direct physical, optical, or electrical contact with each other. “Coupled” may be used to indicate that two or more elements are in either direct or indirect (with other intervening elements between them) physical or electrical contact with each other, and/or that the two or more elements co-operate or interact with each other (e.g., as in a cause and effect relationship).

(19) The terms “over,” “under,” “between,” and “on” as used herein refer to a relative position of one component or material with respect to other components or materials where such physical relationships are noteworthy. For example in the context of materials, one material or layer over or under another may be directly in contact or may have one or more intervening materials or layers.

Moreover, one material between two materials or layers may be directly in contact with the two materials/layers or may have one or more intervening materials/layers. In contrast, a first material or layer “on” a second material or layer is in direct physical contact with that second material/layer. Similar distinctions are to be made in the context of component assemblies.

(20) As used throughout this description, and in the claims, a list of items joined by the term “at least one of” or “one or more of” can mean any combination of the listed terms. For example, the phrase “at least one of A, B or C” can mean A; B; C; A and B; A and C; B and C; or A, B and C.

(21) Unless otherwise specified in the specific context of use, the term “predominantly” means more than 50%, or more than half. For example, a composition that is predominantly a first constituent means more than half of the composition is the first constituent (e.g., <50 at. %). The term “primarily” means the most, or greatest, part. For example, a composition that is primarily a first constituent means the composition has more of the first constituent than any other constituent. A composition that is primarily first and second constituents means the composition has more of the first and second constituents than any other constituent. The term “substantially” means there is only incidental variation. For example, composition that is substantially a first constituent means the composition may further include <1% of any other constituent. A composition that is substantially first and second constituents means the composition may further include <1% of any constituent substituted for either the first or second constituent.

(22) FIG. 1 is a flow diagram illustrating methods **100** of forming an IC interconnect structure including a graphene cap, in accordance with some embodiments. Methods **100** begin at input **105** with receipt of a workpiece. In some embodiments, the workpiece includes a semiconductor wafer, such as a large format (e.g., 300-450 mm) wafer. The wafer may include a Group IV semiconductor material layer (e.g., Si, Ge, SiGe, GeSn, etc.), a Group III-V semiconductor material layer, or a Group II-VI semiconductor material layer, for example. The workpiece may include one or more device layers including a semiconductor material layer, and may also have one or more interconnect levels interconnecting devices (e.g., transistors) of the device layers.

(23) In exemplary embodiments, a top surface of the workpiece comprises dielectric material, often referred to as an interlayer dielectric (ILD) as it may separate adjacent layers, or levels, of interconnect structures. Interconnect structures may be either conductive vias that provide a vertical electrically conductive pathway through an interconnect level and/or between levels, or conductive lines that provide a lateral or horizontal conductive pathway within an interconnect level. The dielectric material(s) may be directly over semiconductor device structures (e.g., gate, source and drain terminals of a transistor), or over any number of lower-level interconnect structures that are coupled to semiconductor device structures. In some damascene or dual-damascene embodiments, the dielectric material as received at input **105** has been patterned with trenches and/or via openings. In alternative subtractive interconnect embodiments, the insulator received at input **105** is substantially planar.

(24) Methods **100** continue at block **120** where an interconnect metal is deposited upon the dielectric material. In damascene or dual-damascene embodiments, the interconnect metal at least partially backfills the trenches and/or via openings within the dielectric material. In subtractive interconnect embodiments, planar interconnect metal layers deposited at block **120** may be subtractively patterned into an interconnect structure. For some metals more difficult to subtractively pattern, such as copper (Cu), a highly physical milling process may be practiced, for example with an ion beam etching (IBE) source where Ar or He ions are accelerated into the workpiece surface with high kinetic energies in order to sputter away exposed metal. For interconnect metal compositions that may be more readily etched, such as ruthenium (Ru), molybdenum (Mo) or tungsten (W), a chemical etching process may be practiced, for example with a plasma of one or more one or more of O.sub.2, Cl.sub.2, Br<sub>2</sub>, CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>4</sub>F<sub>8</sub>, H<sub>2</sub>, CH<sub>4</sub>, CH<sub>3</sub>CH<sub>3</sub>, CH<sub>3</sub>OH, CH<sub>3</sub>CH<sub>2</sub>OH, Ar, He, or Xe.

(25) Methods **100** continue at block **150** where a graphene cap is formed over a top surface of the interconnect metal. As described further below, the integrated circuit interconnect structure will therefore comprise a graphene cap over an underlying interconnect metal. For damascene or dual-damascene embodiments, the graphene may be advantageously formed on the underlying metal after a planarization process has reduced the interconnect metal into interconnect structures that are confined to the trenches and/or via openings within the dielectric material. The graphene formed at block **150** will therefore be a cap located on only a top surface of the interconnect structures. For subtractive patterning embodiments, the graphene may be formed on the interconnect metal before or after the subtractive patterning of the interconnect metal. For the former, the graphene cap will only be on a top surface of an interconnect structure, similar to (dual) damascene embodiments. For the latter, the graphene cap may be on both a top surface of the interconnect structure as well as on a sidewall of the interconnect structure.

(26) At block **150**, crystalline graphene is grown, or otherwise formed, upon exposed surfaces of interconnect lines. The graphene cap may be formed at block **150** according to a number of techniques with one example being chemical vapor deposition (CVD). The composition of the interconnect metal is advantageously suitable for nucleation of a graphene layer such that, during the CVD process, a carbon source such as methane gas is decomposed to form graphene crystals selectively upon metal nucleation sites with little to no graphene forming on adjacent dielectric material.

(27) A graphene cap over at least a top surface of an interconnect feature can significantly reduce the electrical resistance of the interconnect structure. For example, the inventors have measured a resistance reduction of 10-15% relative to a structure lacking a graphene cap. The resistance reduction may be a result of reduced charge carrier surface scattering. Although the reduced electrical resistance of a graphene-metal hybrid interconnect structure is promising, the inventors have further determined that structures with a graphene cap can suffer a reduced resistance to electromigration (EM).

(28) As further illustrated in FIG. **1**, at block **110** a dopant is introduced into the interconnect metal. The inventors have determined that EM resistance of an interconnect structure comprising a graphene capped metal can be improved by introducing one or more dopants into the underlying metal. With some component of lower electromigration resistance potentially attributable to poor adhesion between the graphene cap and the underlying metal, dopant(s) that can bond to the graphene more strongly may be particularly advantageous. However, the inventors have determined that the addition of certain dopants at block **110**, even if successful in improving EM resistance, can increase an interconnect structure's electrical resistance and may therefore at least partially counter the benefit of incorporating a graphene cap into an interconnect structure. The choice of dopant(s) to introduce at block **110** is therefore complicated by competing effects of the dopant within a graphene-metal interconnect structure.

(29) Methods **100** end at output **180** where an IC device is completed. For example, any upper-level interconnect structures may be fabricated to complete an IC according to any techniques. In some embodiments, output **180** may further comprise one or more additional iterations of blocks **120**, **110** and **150**, for example along with depositions of additional dielectric material. Either the dielectric material may be patterned in damascene interconnect embodiments, or the interconnect metal may be patterned in subtractive interconnect embodiments.

(30) FIG. **2A** illustrates a cross-sectional view of an IC device structure **200** in accordance with exemplary (dual) damascene embodiments. IC device structure **200** includes an interconnect level **202** and an interconnect level **203** over interconnect level **202**. Interconnect level **202** is over substrate **201**. Substrate **201** is illustrated in dashed line to emphasize substrate **201** may include any number of device layers comprising transistors (e.g., MOSFETs), any number of interconnect levels interconnect the transistors into circuitry, and any type of support substrate, such as, but not limited to monocrystalline semiconductor material. Over interconnect level **203**, IC device

structure **200** may include any number of additional interconnect levels **204**, also illustrated in dashed line as merely providing context to the interconnect levels **202** and **203** illustrated in solid line.

(31) Two adjacent interconnect levels **202** and **203** are illustrated to depict both transverse and longitudinal cross-sections of exemplary graphene-capped metal interconnect structures. The interconnect structure of interconnect level **202** comprises a line extending along the x axis over a dielectric material **205**, and a via extending along the z-axis through dielectric material **205**. The interconnect structure of interconnect level **203** comprises another line extending along the y axis (e.g., into the page) over dielectric material **205**, and another via extending along the z-axis through dielectric material **205** to intersect interconnect level **202**.

(32) Layers of dielectric material **205** are between another dielectric material **210** with dielectric material **210** being adjacent to the interconnect structures. Dielectric materials **205** and **210** are of different chemical composition, for example so that dielectric materials **205** may function as etch stops during a dielectric patterning process. Each of dielectric material **205** and dielectric material **210** may be any of any composition known to be suitable for IC interconnects. In some embodiments, dielectric material **210** is a low-k dielectric material (e.g., SiOC), for example having a relative permittivity below 3.5. In other examples, dielectric material **210** may be any of SiO, SiON, hydrogen silsesquioxane, methyl silsesquioxane, polyimide, polynorbornenes, benzocyclobutene, or the like. Dielectric material **205** may also be a low-k dielectric material having a relative permittivity less than about 3.5. Dielectric material **205** may also be a conventional dielectric material with a somewhat higher relative permittivity in the range of 3.5-9, or a high-k dielectric material having an even higher relative permittivity. For some embodiments where dielectric material **205** has a higher relative permittivity than that of dielectric material **210**, dielectric material **205** is a silicon-based dielectric, for example comprising predominantly Si and at least one of O (e.g., SiO<sub>x</sub>) or N (e.g., SiN<sub>x</sub>, SiON), any of which may also be carbon-doped (e.g., carbon-doped nitride).

(33) Interconnect structures within each of interconnect levels **202** and **203** have a graphene cap **250** over an interconnect metal **220**. Graphene cap **250** comprises one or more monolayers of crystalline graphene. Because of a minimal thickness  $T_{sub.G}$ , for example corresponding to only 1-2 monolayers of material, graphene cap **250** may be referred to as two-dimensional (2D). The microstructure of graphene cap **250** may be polycrystalline with discontinuities extending through the monolayers (e.g., in z-dimension) to define grain boundaries where the long range order within a grain of graphene cap **250** is disrupted. In some exemplary embodiments, individual grains within graphene cap **250** all have the full thickness  $T_{sub.G}$  with no two grains being stacked one atop the other. Hence, even when polycrystalline, each grain is 2D. Within an interconnect structure, a bottom surface of graphene cap **250** defines a substantially planar interface I, which in the illustrated example is co-planar with a bottom surface of dielectric material **205**. Dielectric material **205** is over a top surface **251** of graphene cap **250** except where a via passes through dielectric material **205**.

(34) In some exemplary embodiments, interconnect metal **220** is predominantly Cu, and may be substantially pure Cu, or a Cu-rich alloy. For such embodiments, interconnect metal **220** may be in direct contact with graphene cap **250** at interface I, as illustrated, because interconnect metal top surface **221** is then a suitable nucleation surface for the growth of graphene. Interconnect metal **220** may also be predominantly one or more metals other than Cu. In some alternative embodiments, interconnect metal **220** is predominantly Ru or Co, which have also been found to provide suitable graphene nucleation surface, and so can be in direct contact with graphene cap **250** at interface I. In still other embodiments, interconnect metal **220** may be predominantly another metal, such as, but not limited to, W or Mo. For interconnect metal compositions less suitable for direct contact with graphene cap **250**, an intervening cap or graphene seed layer (not depicted) of a suitable metal composition may be present between graphene cap **250** and interconnect metal **220**.

(35) Interconnect structures within each of interconnect levels **202** and **203** further comprise a barrier layer **240**. In the illustrated example, barrier layer **240** is between interconnect metal sidewall **222** and a sidewall of dielectric material **210**. Barrier layer **240** is also between interconnect metal bottom surface **223** and dielectric material **205**. Barrier layer **240** is of a composition distinct from interconnect metal **220**, and may be a metal, metal chalcogenide, metal oxide, or metal nitride, for example. In some exemplary embodiments, barrier layer **240** comprises tantalum (Ta), W, Mo, titanium (Ti), or cobalt (Co). In some embodiments where interconnect metal is predominantly Cu, barrier layer **240** is TaN.sub.x. In the illustrated embodiment, graphene cap **250** is confined to the area of interconnect metal top surface **221**, and is absent from the portion barrier layer **240** co-planar with interface I.

(36) Interconnect structures in accordance with embodiments herein may also include an adhesion layer (not depicted) between either barrier layer **240** and dielectric materials **205** and/or **210**, or being interconnect metal **220** and barrier layer **240**. The composition of adhesion materials may also vary, with Ti and TiN being two examples.

(37) As further illustrated in FIG. 2A, interconnect metal **220** comprises a dopant **225** that improves adhesion of graphene cap **250** and/or otherwise improves EM resistance of the interconnect structure. In advantageous embodiments, dopant **225** is concentrated within a thickness T.sub.D proximal to graphene cap interface I. Within thickness T.sub.D the amount of dopant **225** is greater than any portion of interconnect metal **220** more distal from interface I along interconnect metal thickness T.sub.1. Interconnect metal thickness T.sub.1 may be in the tens of nm, for example, while thickness T.sub.D is less than 10 nm, and advantageously less than 5 nm. As concentrated proximal to interface I, any electrical resistance penalty associated with dopant **225** can be minimized while improvement in EM resistance can be maximized.

(38) In some embodiments, dopant **225** is another metal. Dopant **225** may be, for example, one or more of manganese (Mn), zinc (Zn), magnesium (Mg), cobalt (Co), or aluminum (Al). The inventors have found Mn and Zn to be advantageous as readily migrating toward interconnect metal surface **221**. This migration concentrates the metal dopants proximal to graphene cap interface I even if they are first introduced into more distal regions of interconnect metal **220**, for example as described further below. The migration may be so complete that dopant **225** may be substantially absent from interconnect metal **220** at distances from interface I exceeding T.sub.D. The inventors have further found Mn to be particularly advantageous as incurring a negligible electrical resistance penalty. While Al was also found to improve EM resistance, it incurred a greater electrical resistance penalty. Although not bound by theory, the higher electrical resistance may indicate Al does not concentrate proximal to interface I as readily as Mn.

(39) In some alternative embodiments, dopant **225** is silicon or nitrogen. To limit the impact of these dopants on electrical resistance of the interconnect structure, silicon or nitrogen may be similarly confined to with dopant thickness T.sub.D, for example by exposing only interconnect metal top surface **221** to some surface treatment, as further described below.

(40) FIG. 2B illustrates a cross-sectional view of an IC interconnect structure **299** including graphene cap **250**, in accordance with some subtractive embodiments where interconnect structures in each of interconnect levels **202** and **203** have been subtractively patterned from planar metallization layers. Reference numbers introduced in the context of FIG. 2A are retained in FIG. 2B where the structural feature shares one or more of the attributes described above. For example, interconnect metal **220** may again be predominantly Cu. However, for subtractive embodiments, interconnect metal **220** may instead be a metal more readily etched, such as Ru, Co, W or Mo. Dopants **225** may likewise be any of those described above.

(41) For subtractively patterned interconnect structures, barrier layer **240** is only on a bottom surface (e.g., bottom surface **223**) of interconnect metal **220**. FIG. 2B illustrates an example where graphene cap **250** is on both a top surface (e.g., top surface **221**) and a sidewall (e.g., sidewall surface **222**) of interconnect metal **220**. Interconnect metal **220** was therefore patterned prior to



growth of graphene cap **250**. Dopants **225**, being concentrated within thickness T.sub.D, are therefore also present within top surface **221** and sidewall surface **222**. Dielectric material **205** may again be present (e.g., as an etch stop layer). However, planar interface I between top surface **221** and graphene cap **250** is in this example below a planar interface between two layers of dielectric material **210**.

(42) As noted above, graphene cap **250** may also be grown on a planar metallization layer prior to subtractive patterning of the interconnect structures, and graphene cap **250** would then be present only on the interconnect top surface **221**, substantially as illustrated in FIG. 2A. Dopants **225** would likewise then again be concentrated only within top surface **221**.

(43) FIG. 3 is a flow diagram illustrating methods **300** for introducing a dopant into an IC interconnect structure, in accordance with some embodiments. FIG. 4A-4C illustrate cross-sectional views of an IC interconnect structure evolving to include a graphene cap as operations in methods **300** are practiced, in accordance with some embodiments.

(44) Referring first to FIG. 3, methods **300** again begin at input **105** where a workpiece with ILD is received. In exemplary (dual)damascene embodiments, the ILD has been patterned with via openings and/or trenches. At block **320**, one or more barrier layer(s) and/or adhesion layer(s) is optionally deposited. For example, any of the barrier or adhesion materials described above may be deposited at block **320** with any suitable technique, such as, but not limited to, physical vapor deposition (PVD) or atomic layer deposition (ALD).

(45) Methods **300** continue at block **325** where a layer comprising the metal dopant is deposited, for example with any blanket deposition process (e.g., PVD). FIG. 4A illustrates an example where a seed layer **420** has been deposited directly onto barrier layer **240**. Any of the metal dopants described above may be readily deposited to any desired concentration by sputtering a target of a suitable alloy or by co-sputtering multiple targets. In some embodiments, seed layer **420** is predominantly Cu and further comprises at least one of Mn, Zn, Mg, Co, or Al. Seed layer **420** may be deposited to any thickness needed to facilitate a subsequent electrolytic deposition process, and/or to incorporate enough of the metal dopant.

(46) Returning to FIG. 3, methods **300** continue at block **330** where interconnect metal is deposited. For damascene embodiments, overburden may be removed at block **330** with a planarization process. In exemplary embodiments where interconnect metal is predominantly Cu, block **330** comprises an electrolytic plating process. However, other deposition techniques known to be suitable for other metals may also be practiced at block **330**. In the example illustrated in FIG. 4B, interconnect metal **220** has been deposited and planarized to thickness T.sub.1 so that top interconnect metal surface **221** is co-planar with a surface of dielectric material **210**. As further illustrated, following the formation of interconnect metal **220**, metal dopants **425** are concentrated proximal to seed layer **420**.

(47) Returning to FIG. 3, methods **300** continue at block **150** with formation of the graphene cap, for example substantially as described above. The IC device may then be completed at output **180**. In the example further illustrated in FIG. 4C, the composition of interconnect metal **220** is advantageously suitable for nucleation of a graphene passivation layer. Selective deposition of graphene is possible on an interconnect surface comprising predominantly Cu, Ru, or Co, for example. During the deposition process, crystals of graphene nucleate selectively upon interconnect metal sites with little to no graphene forming on dielectric material **210**. In embodiments where the composition of interconnect metal **220** is not suitable for nucleating graphene, a seed or cap layer (not depicted) may be first deposited upon interconnect metal top surface **221**. Graphene may then be grown upon the surface of that cap layer. For example, in an embodiment where interconnect metal **220** is predominantly other than Cu (e.g., W), a cap layer of predominantly Cu or Co may be deposited onto interconnect metal top surface **221**. Such a metal cap layer may be selectively deposited on interconnect metal top surface **221**, for example by either electroless deposition (ED), CVD, or atomic layer deposition (ALD). Alternatively, such a metal

cap layer may be unselectively formed with any blanket deposition (e.g., PVD). A blanket metal cap layer may then be subtractively patterned, for example to remain only interconnect metal top surface **221**.

(48) As further illustrated in FIG. **4C**, metal dopants **425** have migrated away from the seed layer to become dopants **225** concentrated proximal to graphene cap interface **I**. This dopant migration may be motivated through elevated temperature processing. For example, metal dopants may migrate sufficiently during (CVD) growth of graphene cap **250** conducted at a temperature of at least 250° C. for a majority of the dopants be within thickness  $T_{sub.D}$  of interconnect metal **220**.

Alternatively, a majority of the metal dopants may be driven into thickness  $T_{sub.D}$  during a BEOL thermal anneal, which may be performed at any point subsequent to the formation of graphene cap **250**. Such an anneal may be performed at a temperature of 200-350° C., for example. With the interconnect structure **402** substantially complete, methods **300** (FIG. **3**) may be repeated to form other interconnect structures at a next higher interconnect level, for example to arrive at the IC device structure **200** (FIG. **2**).

(49) As noted above, dopants may also be locally introduced into a top of an interconnect metal through a surface treatment. The surface treatment may be performed prior to, during, or after, a graphene cap is formed on the interconnect metal. FIG. **5** is a flow diagram illustrating methods **500** for integrating a graphene cap into an IC interconnect structure, in accordance with some embodiments. FIG. **6A-6C** illustrate cross-sectional views of an IC interconnect structure evolving to include a graphene cap as operations in the method **500** are practiced, in accordance with some embodiments.

(50) Referring first to FIG. **5**, methods **500** again begin with input **105**. Optionally, a barrier layer and/or adhesion layer is deposited at block **320**. At block **330**, interconnect metal is deposited, and may be planarized with surrounding dielectric material for damascene embodiments. For embodiments where block **330** entails an electrolytic plating process, a seed layer may be deposited, but the metal dopants that were incorporated into the seed layer for methods **300** (FIG. **3**) may be omitted. In the example illustrated in FIG. **6A**, interconnect metal **220** has been deposited, and top surface **221** planarized with a surface of dielectric material **210**. As illustrated, interconnect metal **220** is of a substantially homogenous composition. For example, the entirety of interconnect metal **220** may be a homogenous Cu-rich, Ru-rich, Mo-rich, W-rich or Co-rich alloy.

(51) Returning to FIG. **5**, methods **500** continue at block **540** where a dopant is introduced through a top surface of interconnect metal. In the example further illustrated in FIG. **6B**, doping **625** may be by any of a chemical vapor treatment, plasma treatment, ion implantation, wet chemical treatment, or thin film deposition, for example. Any of the dopants described above may be introduced by doping **625**. Dopant **225** may be introduced into top surface **221**, for example by solid state diffusion from a deposited thin film that may then be stripped off as sacrificial following a thermal drive. In some embodiments, doping **225** comprises a vapor phase process during which interconnect metal top surface **221** is exposed to one or more of the metal dopants described elsewhere herein. For example, Al may be deposited upon a copper interconnect metal top surface **221**. In other embodiments, doping **625** comprises a plasma and/or chemical vapor process during which interconnect metal top surface **221** is exposed to a nitrogen source gas, such as  $NH_{sub.3}$ ,  $N_{sub.2}H_{sub.4}$ ,  $N_{sub.2}O$ , or  $N_{sub.2}$ . In other embodiments, doping **625** comprises a plasma and/or chemical vapor phase process during which interconnect metal top surface **221** is exposed to a silicon source gas, such as a silane (e.g.,  $SiH_{sub.4}$ ).

(52) Methods **500** (FIG. **5**) continue at block **150** where the graphene cap is formed, for example substantially as described elsewhere herein. The IC device structure may then be completed at output **180**. In the example further illustrated in FIG. **6C**, graphene cap **250** is grown directly on interconnect top surface **221** in the presence of dopant **225**. Accordingly, dopant **225** may alter the initial nucleation of graphene cap **250**. If such alteration is undesirable, blocks **540** and **150** may be sequenced so that graphene cap **250** is at least partially formed prior to the surface doping.

(53) FIGS. 7A and 7B illustrate cross-sectional views of an IC interconnect structure evolving to include a graphene cap as operations in the methods **500** are practiced, in accordance with some alternative embodiments. FIG. 7A illustrates an example where doping **625** is performed after the nucleation of graphene grains **750**, but prior to coalescence of grains **750**. Dopant **225** may be localized to only those regions of interconnect metal **220** that are below spaces between grains **750**. Such localization of dopant **225** may further reduce a change in electrical resistivity of the interconnect structure attributable to dopant **225**. A dielectric material may be deposited over, and within spaces separate graphene grains **750**. Alternatively, before dielectric material is deposited, graphene growth may be continued to coalesce grains **750** into a contiguous graphene cap, for example substantially as described above. FIG. 7B illustrates another example where doping **625** is performed after graphene cap **250** has been formed. For such embodiments, graphene cap **250** (being polycrystalline with small grain size) does not fully mask doping **625**. Dopants **225** can enter interconnect metal **220**, for example through the many grain boundaries, to a depth of thickness  $T_{sub.D}$ .

(54) In accordance with some alternative embodiments, a graphene cap is formed instead formed upon an intervening metal cap that has good adhesion to both the interconnect metal and the graphene cap. The metal cap may also facilitate nucleation of graphene, and is advantageously a metal that also improves EM resistance of the interconnect structure. For example, one or more of the metal dopants described above may be deposited as a continuous thin film layer. FIG. **8** is a flow diagram illustrating methods **800** for integrating a graphene cap into an IC interconnect structure, in accordance with some embodiments. FIG. **9A-9C** illustrate cross-sectional views of an IC interconnect structure evolving to include a graphene cap as operations in the methods **800** are practiced, in accordance with some embodiments.

(55) Referring first to FIG. **8**, methods **800** being at input **105** and include blocks **320** and **330**, each of which may be practiced substantially as described elsewhere herein. At block **840**, a metal cap is formed on interconnect metal. A graphene cap is then formed on the metal cap at block **130**, and methods **800** are completed at output **180**. In the example illustrated in FIG. **9A**, an interconnect structure includes interconnect metal **220** substantially as described elsewhere herein. Metal cap **650** is formed upon interconnect metal top surface **221**, for example with a deposition process, such as ED, CVD or ALD, that is selective to interconnect metal **220**. In some exemplary embodiments where interconnect metal **220** is Cu-rich, metal cap **650** is predominantly Co. As further illustrated in FIG. **9C**, graphene cap **250** is nucleated on metal cap **650** and grows both on metal cap top surface **651** and metal cap sidewall **652**.

(56) The interconnect structures, and the methods of forming such structures, described herein may be integrated into a wide variety of ICs and computing systems that include such ICs. FIG. **10** illustrates a system in which a mobile computing platform **1005** and/or a data server machine **1006** employs an IC having a memory and/or microprocessor IC with one or more interconnect structures, for example in accordance with some embodiments described elsewhere herein. In some embodiments, the transistor structure is coupled to an I/O of the memory and/or microprocessor IC. The server machine **1006** may be any commercial server, for example including any number of high-performance computing platforms within a rack and networked together for electronic data processing, which in the exemplary embodiment includes a monolithic IC **1050**. The mobile computing platform **1005** may be any portable device configured for each of electronic data display, electronic data processing, wireless electronic data transmission, or the like. For example, the mobile computing platform **1005** may be any of a tablet, a smart phone, laptop computer, etc., and may include a display screen (e.g., a capacitive, inductive, resistive, or optical touchscreen), a chip-level integrated system **1010**, and a battery **1015**.

(57) Whether disposed within the integrated system **1010** comprising an assembly of multiple chips as illustrated in the expanded view **1011**, or as a stand-alone packaged IC chip within the server machine **1006**, a device may include memory circuitry (e.g., RAM), and/or a logic circuitry (e.g., a

microprocessor, a multi-core microprocessor, graphics processor, or the like). At least one of these circuitries further includes one or more interconnect structures, for example in accordance with some embodiments described elsewhere herein. A processor IC **1001**, for example may be further coupled to another IC chip or package substrate **1036** that further hosts one or more additional ICs, such as power management IC **1030** and radio frequency IC **1025**. RFIC **1025** may have an output coupled to an antenna (not shown) to implement any of a number of wireless standards or protocols, including but not limited to Wi-Fi (IEEE 802.11 family), WiMAX (IEEE 802.16 family), IEEE 802.20, long term evolution (LTE), Ev-DO, HSPA+, HSDPA+, HSUPA+, EDGE, GSM, GPRS, CDMA, TDMA, DECT, Bluetooth, derivatives thereof, as well as any other wireless protocols that are designated as 3G, 4G, 5G, and beyond.

(58) FIG. **11** is a functional block diagram of an electronic computing device **1100**, in accordance with some embodiments. Device **1100** further includes a motherboard **1102** hosting a number of components, such as, but not limited to, processor **1001** (e.g., an applications processor). Processor **1001** may be physically and/or electrically coupled to motherboard **1102**. In some examples, processor **1001** is part of an IC including one or more interconnect structures, for example in accordance with some embodiments described elsewhere herein. In general, the term “processor” or “microprocessor” may refer to any device or portion of a device that processes electronic data from registers and/or memory to transform that electronic data into other electronic data that may be further stored in registers and/or memory.

(59) In various examples, one or more communication chips **1106** may also be physically and/or electrically coupled to the motherboard **1102**. In further implementations, communication chips **1106** may be part of processor **1001**. Depending on its applications, computing device **1100** may include other components that may or may not be physically and electrically coupled to motherboard **1102**. These other components include, but are not limited to, volatile memory (e.g., DRAM **1132**), non-volatile memory (e.g., ROM **1135**), flash memory (e.g., NAND or NOR), magnetic memory (MRAM **1130**), a graphics processor **1122**, a digital signal processor, a crypto processor, a chipset **1112**, an antenna **1125**, touchscreen display **1115**, touchscreen controller **1165**, battery **1116**, audio codec, video codec, power amplifier **1121**, global positioning system (GPS) device **1140**, compass **1145**, accelerometer, gyroscope, speaker **1120**, camera **1141**, and mass storage device (such as hard disk drive, solid-state drive (SSD), compact disk (CD), digital versatile disk (DVD), and so forth, or the like.

(60) While certain features set forth herein have been described with reference to various implementations, this description is not intended to be construed in a limiting sense. Hence, various modifications of the implementations described herein, as well as other implementations, which are apparent to persons skilled in the art to which the present disclosure pertains are deemed to lie within the spirit and scope of the present disclosure.

(61) It will be recognized that the invention is not limited to the embodiments so described, but can be practiced with modification and alteration without departing from the scope of the appended claims. For example, the above embodiments may include specific combinations of features as further provided below.

(62) In first examples, an integrated circuit (IC) structure, comprises a plurality of transistors and an interconnect structure coupled to at least one of the transistors. The interconnect structure comprises a first metal, and graphene over a top surface of the first metal. An amount of a second metal, nitrogen or silicon within the interconnect structure is higher proximal to an interface of the graphene than distal from the interface.

(63) In second examples, for any of the first examples the amount of the second metal is higher proximal to the interface. The second metal is Mn, Zn, Mg, Co, or Al.

(64) In third examples, for any of the first through second examples the second metal is Mn or Zn.

(65) In fourth examples, for any of the first through third examples the second metal is Mn.

(66) In fifth examples, for any of the second through fourth examples the first metal is Cu, Ru, Co,

Mo, or W.

(67) In sixth examples, for any of the fifth examples the first metal is Cu.

(68) In seventh examples, for any of the first through sixth examples the second metal, nitrogen or silicon is substantially absent from the first metal at distances greater than 5 nm of the interface.

(69) In eighth examples, for any of the first through seventh examples the interconnect structure further comprises a third metal in contact with a bottom of the first metal, opposite the graphene, and between the first metal and an underlying dielectric material.

(70) In ninth examples, for any of the eighth examples the third metal is at least one of Co, Ta, or Ti.

(71) In tenth examples, for any of the eighth through ninth examples the third metal is in contact with a sidewall of the first metal, and between the first metal and an adjacent dielectric material.

(72) In eleventh examples, for any of the first through tenth examples the graphene comprises a plurality of grains spaced apart from adjacent grains. The amount of the second metal, nitrogen or silicon is higher proximal to the interface of the grains of graphene and the first metal. A dielectric material is over the graphene, and within spaces between the plurality of grains.

(73) In twelfth examples, a computer platform comprises a power supply, and an integrated circuit (IC) coupled to the power supply. The IC comprises a plurality of transistors, and an interconnect structure coupled to at least one of the transistors. The interconnect structure comprises a first metal, and graphene over a top surface of the first metal. An amount of a second metal, nitrogen or silicon within the interconnect structure is higher proximal to an interface of the graphene than distal from the interface.

(74) In thirteenth examples, for any of the twelfth examples the first metal is Cu, the amount of the second metal is higher proximal to the interface, and the second metal is Mn or Zn.

(75) In fourteenth examples, for any of the twelfth through thirteenth examples the interconnect structure further comprises a third metal in contact with a bottom of the first metal, opposite the graphene, and between a sidewall of the first metal and an adjacent dielectric material. The third metal is at least one of Co, Ta, or Ti.

(76) In fifteenth examples, for any of the twelfth through fourteenth examples the second metal is substantially absent from the first metal at distances greater than 5 nm of the interface.

(77) In sixteenth examples a method of forming an integrated circuit (IC) interconnect structure comprises depositing a first metal over a dielectric material, wherein the depositing further comprises doping the first metal with a second metal, nitrogen, or silicon. The method comprises forming graphene on a top surface of the first metal with a concentration of the second metal, nitrogen or silicon within the interconnect structure being higher proximal to an interface of the graphene and the first metal than distal from the interface.

(78) In seventeenth examples, for any of the sixteenth embodiments depositing the first metal comprises depositing a seed layer comprising Cu and the second metal, and electroplating Cu or a Cu alloy upon the seed layer.

(79) In eighteenth examples, for any of the sixteenth through seventeenth examples forming the graphene comprises heating the first metal to at least 200° C. and diffusing a majority of the second metal from the seed layer to within 5 nm of the interface.

(80) In nineteenth examples, for any of the sixteenth through eighteenth examples the second metal comprises Mn, Zn, Mg, or Co.

(81) In twentieth examples, for any of the sixteenth through nineteenth examples doping the first metal with the second metal, nitrogen, or silicon comprises introducing Al, N, or Si into at least the top surface of the first metal.

(82) In twenty-first examples, for any of the twentieth examples Al, N, or Si is introduced prior to forming the graphene on the top surface.

(83) However, the above embodiments are not limited in this regard and, in various implementations, the above embodiments may include the undertaking of only a subset of such

features, undertaking a different order of such features, undertaking a different combination of such features, and/or undertaking additional features than those features explicitly listed. The scope of the invention should, therefore, be determined with reference to the appended claims, along with the full scope of equivalents to which such claims are entitled.

## Claims

1. An integrated circuit (IC) structure, comprising: a plurality of transistors; and an interconnect structure coupled to at least one of the transistors, wherein the interconnect structure comprises: a first metal; and graphene over, and in direct contact with, a top surface of the first metal, wherein the graphene comprises a plurality of grains spaced apart from adjacent grains, wherein an amount of a second metal, nitrogen or silicon within the first metal is higher proximal to an interface of the graphene than distal from the interface, and higher within a first region of the first metal below spaces between the grains than within a second region of the first metal immediately below individual ones of the grains.
2. The IC structure of claim 1, wherein the amount of the second metal is higher proximal to the interface, and wherein the second metal is Mn, Zn, Mg, Co, or Al.
3. The IC structure of claim 2, wherein the second metal is Mn or Zn.
4. The IC structure of claim 3, wherein the second metal is Mn.
5. The IC structure of claim 2, wherein the first metal is Cu, Ru, Co, Mo, or W.
6. The IC structure of claim 5, wherein the first metal is Cu.
7. The IC structure of claim 1, wherein the second metal, nitrogen or silicon is substantially absent from the first metal at distances greater than 5 nm of the interface.
8. The IC structure of claim 1, wherein the interconnect structure further comprises a third metal in contact with a bottom of the first metal, opposite the graphene, and between the first metal and an underlying dielectric material.
9. The IC structure of claim 8, wherein the third metal is at least one of Co, Ta, or Ti.
10. The IC structure of claim 8, wherein the third metal is in contact with a sidewall of the first metal, and between the first metal and an adjacent dielectric material.
11. The IC structure of claim 1, wherein a dielectric material is over the graphene, and within the spaces between the grains.
12. A computer platform comprising: a power supply; and an integrated circuit (IC) coupled to the power supply, wherein the IC comprises the IC structure of claim 1.
13. The platform of claim 12, wherein: the first metal is Cu; and the second metal is Mn or Zn.
14. The platform of claim 13, wherein the interconnect structure further comprises a third metal in contact with a bottom of the first metal, opposite the graphene, and between a sidewall of the first metal and an adjacent dielectric material; the third metal is at least one of Co, Ta, or Ti.
15. The platform of claim 13, wherein the second metal is substantially absent from the first metal at distances greater than 5 nm of the interface.
16. A method of forming an integrated circuit (IC) interconnect structure, comprising: depositing a first metal over a dielectric material; forming graphene directly on a top surface of the first metal; and doping first regions of the first metal that are below spaces between grains of the graphene with a concentration of a second metal, nitrogen or silicon that is higher than within second regions of the first metal that are immediately below individual ones of the grains.
17. The method of claim 16, wherein: depositing the first metal comprises depositing a seed layer comprising Cu, and electroplating Cu or a Cu alloy upon the seed layer.
18. The method of claim 17, wherein the second metal comprises Mn, Zn, Mg, or Co.
19. The method of claim 16, wherein doping the first regions of the first metal with the second

metal, nitrogen, or silicon comprises introducing Al, N, or Si into at least the top surface of the first metal.

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