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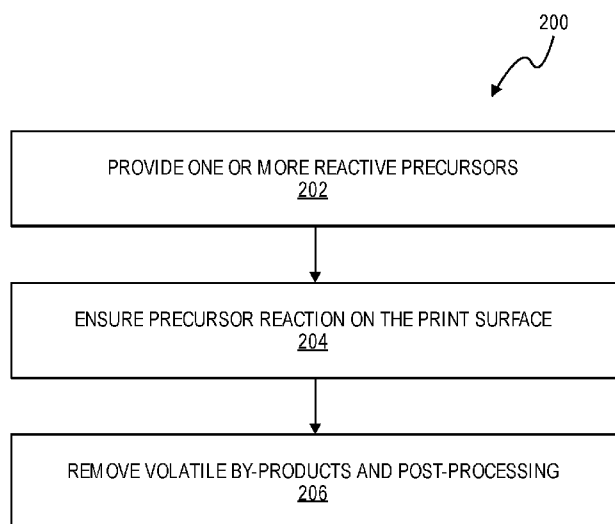


FIG. 2

(57) Abstract: Described herein are improved 3D printing methods for fabricating structures made of metals, including metal alloys, and dielectrics. Such structures may be used in various components of integrated circuits, such as e.g. interconnects, interlayer dielectrics, electrodes, and transistors. Methods provided herein are based on using reactive inks comprising molecular metal and dielectric precursors that react to form desired resulting materials once deposited on a print surface, i.e. 3D printing inks that need to react on the print surface in order to form the desired materials. Through the use of reactive inks, strong covalent or metallic bonds can be formed between printed layers, leading to more robust structures with improved isotropic properties. Because molecular precursors are reacted on the print surface, dense continuous traces may be fabricated. In addition, molecular precursors proposed herein enable 3D printing of intricate structures, e.g. with intricate internal cavities, made of materials with unique compositions.

MULTI-COMPONENT REACTIVE INKS FOR 3D-PRINTED ELECTRONICSTechnical Field

[0001] This disclosure relates generally to the field of integrated circuits and semiconductor manufacturing, and more specifically, to three-dimensional printed structures for use in electronic devices as well as to multi-component reactive inks and methods for manufacturing such structures.

Background

[0002] "Additive manufacturing" is a name generally used to refer to a process in which three-dimensional (3D) design data is used to manufacture a component by depositing one or more materials layer by layer. Such a process is also often referred to as "3D printing." As the name suggests, additive manufacturing techniques distinguish from conventional manufacturing methods in that materials are added, rather than being removed.

[0003] Additive manufacturing enables new possibilities for the free form, flexible integration of components into tailored packages encompassing non-traditional Printed Circuit Boards (PCBs), the Internet of Things (IoT), and wearables. However, implementation of these possibilities in real life is not without issue. For example, current inks used for the 3D printing of inorganic materials such as metals and ceramics are based on preformed micron-sized particles and nanoparticle formulations of the target material(s), leading to low density printed structures with poor physical properties such as e.g. resistivity and robustness. Improvements with respect to methods and materials used for manufacturing 3D-printed electronic devices are always desirable.

Brief Description of the Drawings

[0004] FIG. 1 provides a schematic illustration of mixing reactive inks for forming metals and dielectrics in the print zone, according to some embodiments of the present disclosure.

[0005] FIG. 2 provides a schematic flow chart illustrating a process of 3D printing using reactive inks for forming metals and dielectrics, according to some embodiments of the present disclosure.

[0006] FIG. 3 provides examples of various copper-based reactive precursors, according to various embodiments of the present disclosure.

[0007] FIG. 4 provides examples of various reactive precursors for 3D printing of carbon-doped silicon oxides, according to various embodiments of the present disclosure.

[0008] FIG. 5 provides an example of a metal oxide nanocluster, according to some embodiments of the present disclosure.

[0009] FIGs. 6A and 6B provide schematic illustrations of cross-sections of different exemplary structures fabricated using 3D reactive ink printing as described herein, according to some embodiments of the present disclosure.

[0010] FIG. 7 provides a schematic illustration of an interposer, according to some embodiments of the present disclosure.

[0011] FIG. 8 provides a schematic illustration of a computing device built in accordance with some embodiments of the present disclosure.

[0012] FIG. 9 provides examples of various diketonate-based reactive precursors, according to various embodiments of the present disclosure.

Detailed Description

[0013] In the following description, various aspects of the illustrative implementations will be described using terms commonly employed by those skilled in the art to convey the substance of their work to others skilled in the art. However, it will be apparent to those skilled in the art that the present disclosure may be practiced with only some of the described aspects. For purposes of explanation, specific numbers, materials and configurations are set forth in order to provide a thorough understanding of the illustrative implementations. However, it will be apparent to one skilled in the art that the present disclosure may be practiced without the specific details. In other instances, well-known features are omitted or simplified in order not to obscure the illustrative implementations.

[0014] Various operations will be described as multiple discrete operations, in turn, in a manner that is most helpful in understanding the present disclosure, however, the order of description should not be construed to imply that these operations are necessarily order dependent. In particular, these operations need not be performed in the order of presentation.

[0015] The terms “over,” “under,” “between,” and “on” as used herein refer to a relative position of one material layer or component with respect to other layers or components. For example, one layer disposed over or under another layer may be directly in contact with the other layer or may have one or more intervening layers. Moreover, one layer disposed between two layers may be directly in contact with the two layers or may have one or more intervening layers. In contrast, a first layer “on” a second layer is in direct contact with that second layer. Similarly, unless explicitly stated otherwise, one feature disposed between two features may be in direct contact with the adjacent features or may have one or more intervening layers.

[0016] Implementations of the disclosure may be formed or carried out on a substrate, such as a semiconductor substrate. In one implementation, the semiconductor substrate may be a crystalline substrate formed using a bulk silicon or a silicon-on-insulator substructure. In other implementations, the semiconductor substrate may be formed using alternate

materials, which may or may not be combined with silicon, that include but are not limited to germanium, indium antimonide, lead telluride, indium arsenide, indium phosphide, gallium arsenide, indium gallium arsenide, gallium antimonide, or other combinations of group III-V or group IV materials. Although a few examples of materials from which the substrate may be formed are described here, any material that may serve as a foundation upon which a semiconductor device may be built falls within the spirit and scope of the present disclosure.

[0017] In various embodiments, the interconnects as described herein may be used to connect various components associated with an integrated circuit. Components include, for example, transistors, diodes, power sources, resistors, capacitors, inductors, sensors, transceivers, receivers, antennas, etc. Components associated with an integrated circuit may include those that are mounted on an integrated circuit or those connected to an integrated circuit. The integrated circuit may be either analog or digital and may be used in a number of applications, such as microprocessors, optoelectronics, logic blocks, audio amplifiers, etc., depending on the components associated with the integrated circuit. The integrated circuit may be employed as part of a chipset for executing one or more related functions in a computer.

[0018] In the embodiments where at least some of the components associated with an integrated circuit are transistors, a plurality of transistors, such as metal-oxide-semiconductor field-effect transistors (MOSFET or simply MOS transistors), may be fabricated on the substrate. In various implementations of the disclosure, the MOS transistors may be planar transistors, nonplanar transistors, or a combination of both. Nonplanar transistors include FinFET transistors such as double-gate transistors and tri-gate transistors, and wrap-around or all-around gate transistors such as nanoribbon and nanowire transistors. Although the implementations described herein may illustrate only planar transistors, it should be noted that the disclosure may also be carried out using nonplanar transistors.

[0019] Each MOS transistor includes a gate stack formed of at least two layers, a gate interconnect support layer and a gate electrode layer. The gate interconnect support layer

may include one layer or a stack of layers. The one or more layers may include silicon oxide, silicon dioxide (SiO_2) and/or a high-k dielectric material. The high-k dielectric material may include elements such as hafnium, silicon, oxygen, titanium, tantalum, lanthanum, aluminum, zirconium, barium, strontium, yttrium, lead, scandium, niobium, and zinc. Examples of high-k materials that may be used in the gate interconnect support layer include, but are not limited to, hafnium oxide, hafnium silicon oxide, lanthanum oxide, lanthanum aluminum oxide, zirconium oxide, zirconium silicon oxide, tantalum oxide, titanium oxide, barium strontium titanium oxide, barium titanium oxide, strontium titanium oxide, yttrium oxide, aluminum oxide, lead scandium tantalum oxide, and lead zinc niobate. In some embodiments, an annealing process may be carried out on the gate interconnect support layer to improve its quality when a high-k material is used.

[0020] The gate electrode layer is formed on the gate interconnect support layer and may consist of at least one P-type workfunction metal or N-type workfunction metal, depending on whether the transistor is to be a PMOS or an NMOS transistor. In some implementations, the gate electrode layer may consist of a stack of two or more metal layers, where one or more metal layers are workfunction metal layers and at least one metal layer is a fill metal layer. Further metal layers may be included for other purposes, such as a barrier layer.

[0021] For a PMOS transistor, metals that may be used for the gate electrode include, but are not limited to, ruthenium, palladium, platinum, cobalt, nickel, and conductive metal oxides, e.g., ruthenium oxide. A P-type metal layer will enable the formation of a PMOS gate electrode with a workfunction that is between about 4.9 eV and about 5.2 eV. For an NMOS transistor, metals that may be used for the gate electrode include, but are not limited to, hafnium, zirconium, titanium, tantalum, aluminum, alloys of these metals, and carbides of these metals such as hafnium carbide, zirconium carbide, titanium carbide, tantalum carbide, and aluminum carbide. An N-type metal layer will enable the formation of an NMOS gate electrode with a workfunction that is between about 3.9 eV and about 4.2 eV.

[0022] In some implementations, when viewed as a cross-section of the transistor along the source-channel-drain direction, the gate electrode may consist of a “U”-shaped structure that includes a bottom portion substantially parallel to the surface of the substrate and two sidewall portions that are substantially perpendicular to the top surface of the substrate. In another implementation, at least one of the metal layers that form the gate electrode may simply be a planar layer that is substantially parallel to the top surface of the substrate and does not include sidewall portions substantially perpendicular to the top surface of the substrate. In further implementations of the disclosure, the gate electrode may consist of a combination of U-shaped structures and planar, non-U-shaped structures. For example, the gate electrode may consist of one or more U-shaped metal layers formed atop one or more planar, non-U-shaped layers.

[0023] In some implementations of the disclosure, a pair of sidewall spacers may be formed on opposing sides of the gate stack that bracket the gate stack. The sidewall spacers may be formed from a material such as silicon nitride, silicon oxide, silicon carbide, silicon nitride doped with carbon, and silicon oxynitride. Processes for forming sidewall spacers are well known in the art and generally include deposition and etching process steps. In an alternate implementation, a plurality of spacer pairs may be used, for instance, two pairs, three pairs, or four pairs of sidewall spacers may be formed on opposing sides of the gate stack.

[0024] As is well known in the art, source and drain regions are formed within the substrate adjacent to the gate stack of each MOS transistor. The source and drain regions are generally formed using either an implantation/diffusion process or an etching/deposition process. In the former process, dopants such as boron, aluminum, antimony, phosphorous, or arsenic may be ion-implanted into the substrate to form the source and drain regions. An annealing process that activates the dopants and causes them to diffuse further into the substrate typically follows the ion implantation process. In the latter process, the substrate may first be etched to form recesses at the locations of the source and drain regions. An epitaxial deposition process may then be carried out to fill the recesses with material that is used to fabricate the source and drain regions. In some implementations, the source and drain regions may be fabricated using a silicon alloy such as silicon germanium or silicon

carbide. In some implementations the epitaxially deposited silicon alloy may be doped in situ with dopants such as boron, arsenic, or phosphorous. In further embodiments, the source and drain regions may be formed using one or more alternate semiconductor materials such as germanium or a group III-V material or alloy. And in further embodiments, one or more layers of metal and/or metal alloys may be used to form the source and drain regions.

[0025] One or more interlayer dielectrics may be deposited over the MOS transistors. The ILD layers may be formed using dielectric materials known for their applicability in integrated circuit structures, such as dielectric materials. Examples of dielectric materials that may be used include, but are not limited to, silicon dioxide (SiO₂), carbon doped oxide (CDO), silicon nitride, organic polymers such as perfluorocyclobutane or polytetrafluoroethylene, fluorosilicate glass (FSG), and organosilicates such as silsesquioxane, siloxane, or organosilicate glass. The ILD layers may include pores or air gaps to further reduce their dielectric constant.

[0026] In general, an interlayer dielectric (ILD) or inter metal dielectric (IMD) film is the insulating material used between metal conductors and devices (such as transistors) in integrated circuit devices.

[0027] Various 3D printing techniques have been employed to fabricate different components used in integrated circuits, such as e.g. interconnects, interlayer dielectrics, electrodes, transistors, etc. To provide context, as mentioned in the Background section above, conventionally, inks used for the 3D printing of inorganic materials such as metals and ceramics have been based on preformed micron-sized particles and nanoparticle formulations of the target material(s). In such inks, particles of the material of interest are preformed and stabilized so as to not agglomerate, and are dissolved in a solvent to achieve the desired viscosity and material loading. Because the particles are preformed and stabilized, they form only weak bonds to each other when printed and require post-deposition processing, such as e.g. thermal annealing, to sinter particles and improve physical properties of the resulting printed structure. In addition, inter-layer bonding is

typically weaker than intra-layer bonding of the resulting materials, leading to anisotropic material properties. Still further, the polydispersity control of the constituent particles is often poor, leading to sub-optimal packing in the printed structure. Even with post-deposition processing, many voids exist between the particles, leading to poor mechanical properties as well as high resistivity for metals and increased tendency to oxidize due to high surface area.

[0028] To improve on one or more of these issues, a new 3D printing methodology is proposed based on rapid chemical reactivity in the print zone to direct-write high quality metallic and ceramic structures. In particular, some embodiments of the present disclosure provide improved 3D printing methods for fabricating structures made of metals, including metal alloys, and dielectrics. Such structures may be used in various components of integrated circuits, such as e.g. interconnects, interlayer dielectrics, electrodes, transistors, inductors, capacitors, antennas and sensors. Methods provided herein are based on using reactive inks comprising molecular metal and dielectric precursors that react to form desired resulting materials once deposited on a print surface, i.e. 3D printing inks that need to react on the print surface in order to form the desired materials. Through the use of reactive inks, strong covalent or metallic bonds can be formed between printed layers, leading to more robust structures with improved isotropic properties. Because molecular precursors are reacted on the print surface, dense continuous traces may be fabricated. In addition, molecular precursors proposed herein enable 3D printing of intricate structures, e.g. with intricate internal cavities, made of materials with unique compositions. As a result, highly dense traces of various metals, metal alloys, and dielectrics can be fabricated in a controlled, atomically precise manner.

[0029] FIG. 1 provides a schematic illustration of mixing reactive inks for forming metals and dielectrics in the print zone, according to some embodiments of the present disclosure. In FIG. 1, reference numeral 102 indicates a part of an additive manufacturing tool, e.g. a nozzle or a print head of a 3D printing apparatus, for providing inks A and B onto a print surface 104. Although the print surface 104 is shown in FIG. 1 to be substantially planar, embodiments of the present disclosure are applicable to any topography of the print

surface. Furthermore, as used herein, the term “print surface” refers not necessarily to the original surface onto which materials begin to be printed, as shown in the exemplary illustration of FIG. 1, but also to the surface of previously printed material layers (i.e. a surface of a structure, also referred to as a “work object”, being printed), since 3D printing is typically carried out layer by layer.

[0030] As shown in FIG. 1, ink A may comprise reactive molecular precursor components 106, while ink B may comprise reactive molecular precursor components 108. In various embodiments, any number of one or more reactive molecular precursors may be provided onto the print surface (FIG. 1 showing an example with two precursors – ink A and ink B), via any number of dispensing paths (FIG. 1 showing an example with three paths – two for ink A and one for ink B). Once provided onto the print surface, the one or more reactive molecular precursors react with one another and/or with functional groups of the print surface to form a predefined 3D structure of the resulting metallic or ceramic material 110.

[0031] In some embodiments, a print head includes containers for holding one or more reactive precursors. Preferably, each reactive precursor is held in a respective container (e.g. a source ampule), in order to prevent different precursors from reacting with one another. A print head may further include means for providing the one or more precursors onto a print surface, such as e.g. a gas jet dispenser, an aerosol dispenser, an ink jet dispenser, a capillary dispenser, etc. When two or more reactive precursors are used, a print head may be configured to focus provision of the different precursors on the same point of the print surface such that they would only mix there and rapidly react to form the desired material. In various embodiments, a print head may be configured to be heated to between 30-150 degrees Celsius in order to aid with the vaporization of the one or more precursors and to provide the thermal energy necessary for fast reactions on the (heated) print surface.

[0032] In some embodiments, for a solid or liquid precursor, a print head could be configured to heat the precursor to a temperature such that a sufficient vapor pressure is developed inside a source ampoule and deliver it to the print surface using an inert carrier

gas (N₂ or Ar) through a print head with micron size gas jets focusing the reactive gas on the print surface.

[0033] In some embodiments, a print head could be configured to deliver a liquid reactive precursor to a print surface as aerosol droplets with an inert carrier gas.

[0034] In some embodiments, a print head could be configured to deliver a liquid reactive precursor or solution of a liquid or solid reactive precursor using an ink jet print head.

[0035] In some embodiments, a print head could be configured to deliver a liquid reactive precursor or a solution of a liquid or solid reactive precursor using a direct liquid injection head where the precursor with or without a solvent is rapidly heated and vaporized in the print head and passed through gas delivery jets to the print surface.

[0036] In some embodiments, a print head could be configured to deliver a high viscosity “paste” like reactive precursor by micro-extruding the precursor onto a print surface using a thin capillary print head driven by e.g. a syringe pump.

[0037] In various embodiments, multiple print heads can be used to co-print different materials to build up 3D-printed electronics on planar or non-planar surfaces. The print heads may either be stationary or controlled in the x,y,z direction with tilt and rotation functions. The stage holding the work piece may be held stationary or capable of travel in the x,y,z direction with tilt and rotation functions. The motion of the stage and/or the print head(s) along with the dispensing of the reactive ink components and environmental control in the built structure may be remotely controlled by an appropriately configured computer.

[0038] FIG. 2 provides a schematic flow chart illustrating a process 200 of 3D printing using reactive inks for forming metals and dielectrics, according to some embodiments of the present disclosure. First, the process is described in general terms, with reference to boxes 202-206 shown in FIG. 2, followed by descriptions of various examples illustrating various exemplary 3D printing scenarios.

Delivery of one or more reactive precursors (box 202)

[0039] The process 200 may begin with providing one or more reactive precursors onto a print surface (box 202).

[0040] In general, a reactive ink may be formed by breaking down a non-reactive ink into one or more, typically two or more, reactive components which are then independently delivered to the print surface where they are combined to form the desired material through reaction with each other and surface functional groups on the built surface. For example, in a two component reactive ink, reactants A and B as shown in FIG. 1 may be delivered as either pure vapors or as droplets of reactive precursors in an appropriately chosen solvent. In various embodiments, solvents such as diethylene glycol mono butyl ether (DEGBE), terpinol, ethylene glycol, diethylene glycol mono ethyl ether acrylate (DEGMEA), hexadecane, mesitylene, toluene, amyl acetate, 2-heptanone, deionized water, isopropanol or cyclohexanone may be used. They pass through a print head 102 and are focused on the print surface 104 where they first meet, reacting rapidly to deposit a dense trace of either metal or dielectric (e.g. ceramic) material.

[0041] Depending on the chemical reactivity of the inks, the nozzle and/or the print surface may need to be heated, e.g. to a temperature between 30 and 300 degrees Celsius, including all values and ranges therein. It may also be necessary to house the reactive 3D printing tool inside an inert atmosphere environment such as a glove box filled with high purity inert gas, such as e.g. nitrogen or argon, to avoid undesired reactivity of the components or reaction by-products with the ambient atmosphere.

[0042] Inks in solutions may be delivered to the print head using any number of known mechanical pumping mechanisms. The final dispense of inks in solution may occur by standard methods such as ink-jetting or aerosol jetting. High viscosity paste-like inks may be extruded from the print head. Reactive vapors may also be used as ink components. High vapor pressure materials may be metered in using a mass flow controller (MFC) and/or a pulsing valve, while lower vapor pressure solids or liquids may be vaporized inside a source ampoule which may be held at a temperature between 0 and 250 degrees Celsius, including

all values and ranges therein. When a heated source is used for one of the reactants, a heated delivery line equipped with an MFC and/or a pulsing valve may be used such that an increasing temperature gradient can be maintained between the source and the print head. The print head and the work object may be housed inside a heated enclosure in order to avoid the condensation of reactants during the print process. In addition to channels to deliver the chemical reactants to the print surface, the print head may also be equipped with a focused light source of defined electromagnetic radiation spectrum for use in photolytic reactivity or curing.

[0043] In a reactive ink 3D printing process, the chemical reactivity of the ink components must be carefully tuned in order to obtain the desired material with useful print speeds and without clogging the print head. The reactive ink printing of high purity metals, for example, will typically involve a metal precursor in which the metal center(s) may be in the zero or higher oxidation state and a second reactive ink component which will remove any ligands around the metal center and reduce the metal center to the zero oxidation state if necessary. A single component reactive ink printing (i.e. 3D printing where only a single reactive precursor is used) may involve thermal decomposition on a hot build surface of a metal carbonyl or trifluorophosphine complex such as but not limited to $\text{Fe}(\text{CO})_5$, $\text{Co}_2(\text{CO})_8$, $\text{Ni}(\text{CO})_4$, $\text{Ni}(\text{PF}_3)_4$, $\text{Pt}(\text{PF}_3)_4$, $\text{Ru}_3(\text{CO})_{12}$ or $\text{H}_2\text{Ru}(\text{PF}_3)_4$. Either general or local heating in the build region results in the release of the carbonyl or trifluorophosphine ligands and deposition of a metallic trace. Similar metal direct-write may also be possible through the photolysis of the inks again causing release of the CO or PF_3 ligands.

Precursor reaction on the print surface (box 204)

[0044] Once one or more reactive precursors are provided onto the print surface, the process 200 includes ensuring that the one or more precursors react to form the desired material in a structure shaped as configured by the 3D printing design (box 204 in FIG. 2).

[0045] In some embodiments, reactions on the print surface may be facilitated by providing suitable excitation, such as e.g. heating the print surface at 30 to 300 degrees Celsius for 30 seconds to the duration of the print period plus an additional heat treatment period of up to

24 hours, providing optical excitation, or providing excitation in a form of charged particle beams directed onto the reactive materials deposited on the print surface. In some embodiments, reactive inks may be selected to have relatively low temperature reactivity, e.g. to allow co-printing of dissimilar materials such as metals and ceramics with a temperature envelope compatible with typical electronic device fabrication and/or packaging.

[0046] Depending on the choice of reactive inks used, reactions on the print surface may include one or more of thermal decomposition, transmetallation, reductive elimination, oxidative addition or complexing to form coordination polymers, or any other reactions based on organometallic and/or inorganic chemical solution based reactivity.

[0047] In general, “thermal decomposition” (also referred to as “thermolysis”) refers to chemical decomposition caused by heat. In general, “transmetallation” refers to a type of organometallic reaction that involved transfer of ligands from one metal to another. In general, “reductive elimination” refers to a reaction that is the reverse of oxidative addition. In general, “complexing” refers to forming a metal complex (also referred to as a “coordination complex”) where a central atom or ion, which is usually metallic, is surrounded by an array of bound molecules or ions, which are, in turn, known as ligands or complexing agents. Related term “complexing agent” (also referred to as “ligand”) refers to a non-metal compound in which independently existing molecules or ions form coordinate bonds with a metal atom or ion.

[0048] The above described dispensing of one or more reactive metal and dielectric precursor inks and ensuring that reactions take place on the print surface may be used to print a large variety of metallic and ceramic 3D structures with properties superior to those that may be achieved using 3D printing with conventional, non-reactive, inks for forming metals and dielectrics.

[0049] For example, it is known that the 3D printing of high density, high purity, low resistivity copper (Cu) objects has been a great challenge to the additive manufacturing community. This can be achieved, however, using reactive precursors

as described herein through the rapid reactivity of a Cu(I) or Cu(II) organometallic precursor with a second component reducing agent. Cu (I) precursors may include e.g. (*N,N'*-alkylacetemidinate)copper(I), (*N,N'*-alkylguanidinate)copper(I), β -diketonate copper phosphine complex, β -diketonate copper vinylsilane complex and *N*-heterocyclic carbene copper amide complex. Cu (II) precursors may include e.g. bis(dimethylamino-2-propoxide)copper(II) and related copper bis(aminoalkoxides), along with copper bis(β -diketonate) complexes, copper bis(β -diketoiminate) complexes and copper bis(pyrrylimine) complexes. FIG. 3 provides examples of various copper-based reactive precursors, according to various embodiments of the present disclosure. In particular, chemical structure 302 illustrates (*N,N'*-alkylacetemidinate)copper(I), if R and X are alkyl groups and (*N,N'*-alkylguanidinate)copper(I), if R is an alkyl group and X is an -NR₂ group; chemical structure 304 illustrates a β -diketonate copper phosphine complex; chemical structure 306 illustrates β -diketonate copper vinylsilane complex; chemical structure 308 illustrates *N*-heterocyclic carbene copper amide complex; chemical structure 310 illustrates bis(dimethylamino-2-propoxide)copper(II); chemical structure 312 illustrates copper bis(β -diketonate) complex; chemical structure 314 illustrates copper bis(β -diketoiminate) complex; and chemical structure 316 illustrates copper bis(pyrrylimine) complex.

[0050] As a coreactant, a variety of reducing agents such as trimethylaluminum, triethylaluminum, triethylboron, an amineborane such as dimethylamine-borane, dimethylzinc, diethylzinc or a hydrazine such as N₂H₄, 1,1-dimethylhydrazine or tertiary-butylhydrazine may be employed. In the case of reducing agents such as AlMe₃, AlEt₃, BEt₃, Me₂N-BH₃, ZnMe₂ or ZnEt₂, there may be traces of 0.1-10 at% of an alloying element such as Al, B or Zn left in the printed copper structure. The generality of this principle should be noted as the aforementioned reducing agents can be used with concentrated inks of other molecular metal precursors of elements such as manganese, iron, cobalt, nickel, ruthenium, palladium, silver, iridium, platinum and gold. For example, iron, cobalt, nickel, ruthenium, palladium, iridium and platinum homoleptic β -diketonate complexes precursors may be combined with diethylzinc or

triethylaluminum vapor or a concentrated solution in order to form a single element metal (i.e. a material comprising a single element of the elements of the periodic table, possibly with impurities which could be unavoidable, but not an alloy) or alloyed metallic deposits. For gold, a metal dissolved metal salt such as HAuCl_4 may be combined with a reducing agent such as citrate to form conductive traces.

[0051] In the case of printing dielectric materials, reactive inks may be based on sol-gel chemistry, or other linking chemistry such as dehydrogenative coupling in the presence of a catalyst or click chemistry. Early transition metal oxides including, TiO_x , ZrO_x or HfO_x can be direct-written using precursors including e.g. MCl_4 , $\text{M}(\text{OCH}(\text{CH}_3)_2)_4$ and other metal alkoxides. These precursors can be co-reacted with water and acids, including nitric acid (HNO_3), to form a dense metal-oxide network via hydrolysis-condensation. Acid catalysts are preferably selected from non-chelating catalysts, in order to prevent the formation of individual particles. Moderate surface temperatures (60 to 80 degrees Celsius, including all values and ranges therein) may be applied to activate cross-linking to form the resulting material. Silicon containing dielectric materials such as e.g. a carbon-doped oxide (CDO) may be deposited using reactive inks in which a mixture of one or more silicon-based precursors with reactive functional group is combined with a catalyst causing their crossing linking on the print surface.

[0052] One catalyst to be emphasized is $\text{B}(\text{C}_6\text{F}_5)_3$ (BCF), a catalyst which can couple Si-H bonds with other functionality to provide new Si-O or Si-C bonds. For example, BCF catalyzes the reaction of Si-H with Si-OR groups to make Si-O-Si and a volatile alkane RH. In this case, either two silicon precursors (one with SiH, one with Si-OEt) or one silicon precursor with both functionality can be introduced in parallel with small amount of the BCF catalyst. Upon contact, catalysis will ensue and new high molecular weight material will be created in place, with minimal byproduct formation.

[0053] Subsequent annealing and curing of deposited material can be carried out to form final material desired, again with minimum outgassing of byproducts.

[0054] In some embodiments, hexaethoxytrisilacyclohexane and 1,3,5-trisilacyclohexane in various ratios may be utilized. As an alternative, one precursor such as 1,3,5-triethoxy-1,3,5-trisilacyclohexane could be used where both functionalities (i.e., Si-H and Si-OR functionalities) are present. FIG. 4 provides examples of various reactive precursors for 3D printing of carbon-doped silicon oxides, according to various embodiments of the present disclosure. In particular, chemical structure 402 illustrates 1,3,5-trisilacyclohexane and chemical structure 404 illustrates 1,3,5-triethoxy-1,3,5-trisilacyclohexane.

[0055] Other chemical reactivity that can be catalyzed to form Si, C, O containing dielectric films includes hydrosilation where SiH bond is reacted with alkenes or alkynes to create new SiC bonds. As an example 1,3,5-trivinyl-1,3,5-trisilacyclohexane could be used as a single component precursor (i.e. when only a single reactive precursor is used in box 202). In various embodiments, silicon-containing precursors may either be delivered without solvent if they are liquids or dissolved in a solvent such as but not limited to toluene, mesitylene, xylenes, dichloromethane, dichloroethane, or chlorobenzene if they are either liquids or solids. The cross-linking catalyst may be dissolved a solvent such as but not limited to those mentioned above. The concentrations of silicon precursors may be in the 0.01-10.0M range while the concentration of the catalyst may be in the 0.0001-0.01M range.

[0056] Ceramic materials may also be direct-written using the reaction of nanoclusters of ceramic materials with reactive surface ligands with coreactants causing rapid cross-linking. Pre-formed metal oxide nanoclusters (HfO_2 , TiO_2 , ZrO_2 , SnO_2 , etc.) may be co-deposited with water and/or ultraviolet (UV) light to form a cross-linked network. These clusters may be comprised of a metal oxide core, capped with carboxylate stabilizing ligands. UV irradiation can break the C-O bond at the particle surface, leading to ligand dissociation and destabilized particles. In the presence of water, these destabilized particles can condense to form M-O-M bonds, thereby crosslinking the metal oxide cores. FIG. 5 provides an example of metal oxide nanocluster 502,

according to some embodiments of the present disclosure, where M could be a metal such as e.g. Hf, Zr, Ti, Sn, etc, and R is a functional group shown as 504.

Optional: removal of byproducts and post processing (box 206)

[0057] The process 200 may also include, optionally, removing byproducts of the precursor reaction on the print surface and post processing (box 206 in FIG. 2).

[0058] For example, volatile byproducts may be removed from the surface through appropriate ventilation and/or vacuum.

[0059] In some embodiments, once the solid metallic or ceramic material is set into a cross-linked network, the structure can be subjected to higher temperature outgassing bakes, e.g. at 150-450 degrees Celsius, including all values and ranges therein, for 1-30 minutes, including all values and ranges therein, in order to remove any thermally labile species. Preferably, the outgassing bake is carried out under inert atmosphere, such as e.g. nitrogen gas. As used herein, the term “outgassing” is used to describe release of zero or more gases that may have been dissolved, trapped, absorbed, or otherwise included within the resulting printed material.

[0060] Additionally or alternatively, the printed work object may undergo appropriate post processing including e.g. thermal anneal, solvent rinse, and/or curing. For example, the resulting printed material may be cured, e.g. by using heat, UV photons or/and electron beams, in order to mechanically harden and/or change the properties of the material. In some embodiments, curing may involve heating the structure between e.g. 150-450 degrees Celsius, including all values and ranges therein, while simultaneously exposing the structure to optical radiation of 170-254 nm wavelengths (i.e., deep ultraviolet light), including all values and ranges therein. In other embodiments, curing may involve heating the structure between 200-450 degrees Celsius, including all values and ranges therein, and exposing the structure to electrons.

[0061] Next, some exemplary particular combinations of reactive precursors for forming metallic and ceramic structures using 3D printing are described.

3D printing example # 1

[0062] In this example of a single component organometallic precursor ink, only a single reactive precursor may be used to print a structure comprising iron (Fe), cobalt (Co), nickel (Ni), or ruthenium (Ru) in its elemental form, or iron carbide. The first and only precursor would include a metal carbonyl complex, such as e.g. iron pentacarbonyl ($\text{Fe}(\text{CO})_5$), dicobalt octacarbonyl ($\text{Co}_2(\text{CO})_8$), nickel tetracarbonyl ($\text{Ni}(\text{CO})_4$), or triruthenium dodecacarbonyl ($\text{Ru}_3(\text{CO})_{12}$). No second precursor would be used in this example because thermal decomposition under an inert atmosphere of a concentrated organic solvent solution of any one of the first precursors of this example may be used to deposit metals in their single element forms or metallic alloys.

[0063] In some cases, between 0.1 and 15 atomic percent phosphorus could be detected in 3D structures printed from $\text{Ni}(\text{PF}_3)_4$, $\text{Pt}(\text{PF}_3)_4$, or $\text{H}_2\text{Ru}(\text{PF}_3)_4$. Resulting printed structures would comprise single element metal or metal alloy having porosity of less than 10% (where, as used herein, an expression of “having porosity of less than X%” refers to “having physical density of at least $(100-X)\%$ ”), thus yielding structures that are more dense compared to analogous materials that could be printed using non-reactive inks. Hot stage and local vacuum may be used to remove volatile byproducts, e.g. trifluorophosphine or dihydrogen.

3D printing example # 2

[0064] In another example of a single component ink, metal trifluorophosphine complexes such as e.g. tetrakis(trifluorophosphine)nickel(0) ($\text{Ni}(\text{PF}_3)_4$), tetrakis(trifluorophosphine)platinum(0) ($\text{Pt}(\text{PF}_3)_4$), or dihydrido-tetrakis(trifluorophosphine)ruthenium(II) ($\text{H}_2\text{Ru}(\text{PF}_3)_4$) may be used as the first and single precursor. Again, thermal decomposition would be the reaction responsible for the formation of metals in their single elemental forms, possibly with impurities of 0.1-15 atomic percent.

3D printing example # 3

[0065] In this example of a two component reactive ink system for 3D printing of high density, low resistivity single element copper or copper alloy traces having porosity of less than 10%, two reactive precursors could be used.

[0066] The first precursor could be a copper-based precursor comprising one or more of a (N,N'-alkylacetemidinate)copper(I), a (N,N'-alkylguanidinate)copper(I), a β -diketonate copper phosphine complex, a β -diketonate copper vinylsilane complex, a N-heterocyclic carbene copper amide complex. The first precursor could also be a Cu(II) precursor including e.g. a bis(dimethylamino-2-propoxide)copper(II) and related copper bis(aminoalkoxides) along with copper bis(β -diketonate) complexes, copper bis(β -diketoiminate) complexes and copper bis(pyrrylimine) complexes.

[0067] The second reactive precursor could include trimethylgallium (GaMe₃), triethylgallium (GaEt₃), trimethylaluminum (AlMe₃), triethylaluminum (AlEt₃), triethylborane (BEt₃), an amineborane such as dimethylamineborane (Me₂HN-BH₃), dimethylzinc (ZnMe₂), diethylzinc (ZnEt₂) or a hydrazine such as N₂H₄, 1,1-dimethylhydrazine (H₂NNMe₂), or tertiary-butylhydrazine (tBu(H)NNH₂).

[0068] In various embodiments, these coreactants could be delivered as gases/vapors or as organic solutions (when such solutions would be stable). Similar to Example # 1, the printing could be carried out under an inert atmosphere and hot stage and local vacuum could be used to remove volatile byproducts.

[0069] In this example, transmetallation followed by spontaneous reductive elimination would be the reaction responsible for the formation of copper metal or metal alloy on the print surface.

[0070] In some cases, traces of elements such as Al, Ga, B, Zn, and/or N, between 0.1 and 15 atomic percent, could be detected in 3D structures, resulting from the use of reducing agents.

3D printing example # 4

[0071] In this example of a two component reactive ink system for 3D printing of high density, low resistivity Fe, Co, Ni, Ru, Pd, Pt, or Ag single element structures or structures of their alloys with Zn, Al or Ga of 10% porosity or less, two reactive precursors could be used.

[0072] The first precursor could be Fe, Co, Ni, Ru, Pd, or Pt beta-diketonates (e.g. acac's) or a silver diketonate phosphine complex.

[0073] FIG. 9 provides examples of various diketonate-based reactive precursors, according to various embodiments of the present disclosure. In particular, chemical structure 902 illustrates a Fe, Co, Ni, Pd, or Pt beta-diketonate, chemical structure 904 illustrates a Fe or Ru beta-diketonate, while chemical structure 906 illustrates a silver diketonate phosphine complex.

[0074] The second precursor could be ZnEt₂, AlEt₃, GaEt₃, ZnMe₂, AlMe₃, or GaMe₃ (either vapor or concentrated solutions). Again, the printing could be carried out under an inert atmosphere and hot stage and local vacuum could be used to remove volatile byproducts.

[0075] In this example, transmetallation followed by reductive elimination would be the reaction responsible for the formation of final printed materials on the print surface.

[0076] In some cases, traces of elements such as Al, Ga, and/or Zn, between 0.1 and 15 atomic percent, could be detected in 3D structures.

3D printing example # 5

[0077] In this example of a two component inorganic and organic reducing agent ink system, the first precursor could be tetrachloroauric(III) acid (HAuCl₄), while the second precursor could be sodium citrate (HOC(COONa)(CH₂COONa)₂) to fabricate high density, low resistivity gold (Au) structures having porosity of less than 10%.

[0078] In some cases, traces of elements such as sodium and chlorine, between 0.1 and 5 atomic percent, could be detected in 3D structures.

3D printing example # 6

[0079] In this example of a two component inorganic ink system for 3D printing of dielectric metal oxides and ceramics, the first precursor could be selected from titanium(IV) chloride (TiCl_4), zirconium(IV) chloride (ZrCl_4), hafnium(IV) chloride (HfCl_4), while the second precursor could be water and a suitable acid, such as e.g. nitric acid (HNO_3). Metal chloride ink reacts with aqueous (acidic) co-reactant causing hydrolysis and crosslinking on the print surface. As a result, metal oxide structures having porosity of 10% or less could be printed, possibly with traces of chlorine.

3D printing example # 7

[0080] In another example of a two component inorganic ink system for 3D printing of dielectric metal oxides and ceramics, the first precursor could be selected from tetra-alkoxytitanium(IV) (Ti(OR)_4), tetra-alkoxyzirconium(IV) (Zr(OR)_4), or tetra-alkoxyhafnium(IV) (Hf(OR)_4), where R is one of a methyl (Me) substituent, an ethyl (Et) substituent, a propyl (Pr) substituent, or a butyl (Bu) substituent, while the second precursor could be water and a suitable acid, such as e.g. nitric acid (HNO_3). Metal alkoxide ink reacts with aqueous (acidic) co-reactant causing hydrolysis and crosslinking on the print surface. As a result, metal oxide structures having porosity of 10% or less could be printed.

3D printing example # 8

[0081] In yet another example, the first reactive precursor could include metal oxide nanoclusters (e.g. hafnia (HfO_2) nanoclusters, titania (TiO_2) nanoclusters, zirconia (ZrO_2) nanoclusters, stannic oxide (SnO_2) nanoclusters, etc) with carboxylate capping ligands. In various embodiments, water and/or UV radiation may be used as the second reactive precursor to trigger a reaction on the print surface and form metal or metal oxide structures in the form of nanoclusters having porosity of 50% or less, e.g. between 5% and 50%, including all values and ranges therein. Unique metal oxide nanoparticles may remain visible in printed structures.

[0082] UV irradiation can break the carboxylate C-O bond at the particle surface, leading to ligand dissociation and destabilized particles. In the presence of water, these destabilized particles can condense to form M-O-M bonds, crosslinking the metal oxide cores.

3D printing example # 9

[0083] In this example, carbon-doped silicon oxide (i.e. a low-k dielectric material) having porosity of 15% or less may be 3D printed using a formulation of hexaethoxytrisilacyclohexane and 1,3,5-trisilacyclohexane (shown as compound 502 in FIG. 5) or 1,3,5-triethoxy-1,3,5-trisilacyclohexane (shown as compound 504 in FIG. 5) as the first precursor and BCF as the second precursor. BCF catalyzes the reaction of Si-H with Si-OR groups to make Si-O-Si and a volatile alkane RH, where R is an alkyl group such as methyl, ethyl, propyl or butyl. Traces of B and F, e.g. 0.1-5 atomic percent, from the catalyst may be present in printed structures.

Exemplary 3D printed structures

[0084] 3D structures of materials comprising one or more metals, metal alloys, and ceramics printed using reactive inks in the manner described herein may be included as a part of a semiconductor device or an IC package, such as e.g. interlayer dielectrics, electrodes, transistors, memory devices, etc. The 3D printed structures fabricated as described herein could also be parts of interconnects, e.g. backend interconnects, used for providing electrical conductivity in the semiconductor device or the IC package. As used herein, the term “backend interconnect” is used to describe a region of an IC chip containing wiring between transistors and other elements, while the term “frontend interconnect” is used to describe a region of an IC chip containing the rest of the wiring. Printed structures described herein may e.g. be used in any devices or assemblies where one electrically conductive element of the wiring needs to be separated from another electrically conductive element, which could be done both in backend and frontend interconnects. Such devices or assemblies would typically provide an electronic component, such as e.g. a transistor, a die, a sensor, a processing device, or a memory device, and an interconnect for

providing electrical connectivity to the component. The interconnect includes a plurality of conductive regions, e.g. trenches and vias filled with electrically conductive materials. Another term commonly used in the art for a plurality of trenches and vias filled with electrically conductive materials is a “metallization stack.” For example, a plurality of openings such as e.g. shown in FIG. 6B, could be filled with dielectric materials to electrically isolate at least some of the conductive regions from one another. For example, the printed structure with the openings could be made of a conductive material.

[0085] 3D structures of materials comprising one or more metals, metal alloys, and ceramics printed using reactive inks in the manner described herein may also be included as waveguides (due to low resistivity and low roughness), inductors, antennas, standard transmission lines and vias, and wirebond replacements (e.g. for stacked die solutions).

[0086] Depending on the reactive inks used and/or possible further agents such as e.g. reducing agents, surfaces of such 3D printed structures may include characteristic trace amounts of e.g. phosphorous (P), nitrogen (N), carbon (C), zinc (Zn), aluminum (Al), gallium (Ga), or boron (B), typically in concentration between 0.5 and 15 atomic percent, including all ranges and values therein. These residual trace elements present in the final structures can be detectable by e.g. transmission electron microscopy (TEM) with energy-dispersive X-ray spectroscopy (EDX) or electron energy loss spectroscopy (EELS) elemental analysis or X-ray photoelectron spectroscopy (XPS).

[0087] FIGs. 6A and 6B provide schematic illustrations of cross-sections of different exemplary structures, 600A and 600B, fabricated using 3D reactive ink printing as described herein. As can be seen, FIGs. 6A and 6B are drawn to reflect example real world process limitations, in that the features are not drawn with precise right angles and straight lines.

[0088] With reference to FIG. 6A, the 3D printed structure 600A may include at least a portion 602 fabricated using 3D reactive ink printing as described herein. The material of the portion 602 may include one or more metals, either in their single element form, or in alloys with other elements, or dielectrics. As a result of the 3D printing process, the material 602 may be built on top of a portion comprising one or more other materials,

shown in FIG. 3A as materials 604, 606, 608, which, in turn could also be part of the structure 600A and could have been built using the 3D printing as described herein. In various embodiments, one or more of portions 602, 604, 606, and 608 may be made from the same or different materials. The portions 604, 606, and 608 could also be parts of a substrate on which the 3D structure comprising only the portion 602 is printed, and may be e.g. comprised of one or more of silicon, silicon dioxide, germanium, indium, antimonide, lead telluride, indium arsenide, indium phosphide, gallium arsenide and gallium antimonide.

[0089] With reference to FIG. 6B, the 3D printed structure 600B may include one or more portions 610, made from the same or different materials using 3D printing techniques described herein, and disposed over a substrate 612. FIG. 6B illustrates that 3D printing using reactive inks allows fabricating structures comprising a plurality of openings that may include openings, holes, or gaps (referred to herein as simply “openings”) of various aspect ratios, where, as used herein, “aspect ratio” refers to a ratio between a height or a depth of an opening to a width of an opening. In various embodiments, openings described herein may have aspect ratios between 1 and 20, including all values and ranges therein, e.g. between 1 and 15, between 5 and 10, etc. Preferably, dimensions of the openings are on the nanometer scale, e.g. with a width of an opening being about 20 nm and a depth of an opening being about 100 nm, i.e. aspect ratio of 5. Therefore, such structures with openings are sometimes described as nanostructures or nanopatterned structures.

Implementation in an interposer

[0090] In accordance with embodiments of the disclosure, 3D structures comprising one or more metallic or ceramic materials printed using one or more reactive inks disclosed herein may be used in the fabrication of an interposer, such as e.g. the one shown in FIG. 7. In particular, such 3D structures may be used in the fabrication of various interconnects of the interposer shown in FIG. 7. For example, the 3D printed materials described herein may be used in forming at least some of the trenches 708 and vias 710, which could be done instead of or in addition to a conventional dual damascene process.

[0091] FIG. 7 illustrates an interposer 700 that includes one or more embodiments of the disclosure. The interposer 700 is an intervening substrate used to bridge a first substrate 702 to a second substrate 704. The first substrate 702 may be, for instance, an integrated circuit die. The second substrate 704 may be, for instance, a memory module, a computer motherboard, or another integrated circuit die. Generally, the purpose of an interposer 700 is to spread a connection to a wider pitch or to reroute a connection to a different connection. For example, an interposer 700 may couple an integrated circuit die to a ball grid array (BGA) 706 that can subsequently be coupled to the second substrate 704. In some embodiments, the first and second substrates 702/804 may be attached to opposing sides of the interposer 700. In other embodiments, the first and second substrates 702/804 may be attached to the same side of the interposer 700. In further embodiments, three or more substrates may be interconnected by way of the interposer 700.

[0092] The interposer 700 may be formed of an epoxy resin, a fiberglass-reinforced epoxy resin, a ceramic material, or a polymer material such as polyimide. In further implementations, the interposer may be formed of alternate rigid or flexible materials that may include the same materials described above for use in a semiconductor substrate, such as silicon, germanium, and other group III-V and group IV materials.

[0093] The interposer may include metal interconnect trenches 708 and vias 710, including but not limited to through-silicon vias (TSVs) 712. The vias 710 may be enclosed by first and second diffusion barrier layers as described herein. The interposer 700 may further include embedded devices 714, including both passive and active devices. Such devices include, but are not limited to, capacitors, decoupling capacitors, resistors, inductors, fuses, diodes, transformers, sensors, and electrostatic discharge (ESD) devices. More complex devices such as radio-frequency (RF) devices, power amplifiers, power management devices, antennas, arrays, sensors, and MEMS devices may also be formed on the interposer 700.

Implementation in a computing device

[0094] In accordance with embodiments of the disclosure, 3D structures comprising one or more metallic or ceramic materials printed using one or more reactive inks disclosed herein

may be used in the fabrication of a computing device, such as e.g. the one shown in FIG. 8. In particular, such 3D printed materials may be used in the fabrication of various interconnects of the computing device shown in FIG. 8 or/and in the fabrication of various memory elements shown in FIG. 8, such as e.g. on-die memory 806.

[0095] Figure 8 illustrates a computing device 800 in accordance with one embodiment of the disclosure. The computing device 800 may include a number of components. In one embodiment, these components may be attached to one or more motherboards. In an alternate embodiment, some or all of these components may be fabricated onto a single system-on-a-chip (SoC) die. The components in the computing device 800 include, but are not limited to, an integrated circuit die 802 and at least one communications logic unit 808. In some implementations the communications logic unit 808 may be fabricated within the integrated circuit die 802 while in other implementations the communications logic unit 808 may be fabricated in a separate integrated circuit chip that may be bonded to a substrate or motherboard that may be shared with or electronically coupled to the integrated circuit die 802. The integrated circuit die 802 may include a CPU 804 as well as on-die memory 806, often used as cache memory, that can be provided by technologies such as embedded DRAM (eDRAM) or spin-transfer torque memory (STTM or STT-MRAM).

[0096] Computing device 800 may include other components that may or may not be physically and electrically coupled to the motherboard or fabricated within an SoC die. These other components include, but are not limited to, volatile memory 810 (e.g., DRAM), non-volatile memory 812 (e.g., ROM or flash memory), a graphics processing unit 814 (GPU), a digital signal processor 816, a crypto processor 842 (a specialized processor that executes cryptographic algorithms within hardware), a chipset 820, an antenna 822, a display or a touchscreen display 824, a touchscreen controller 826, a battery 828 or other power source, a power amplifier (not shown), a voltage regulator (not shown), a global positioning system (GPS) device 828, a compass 830, a motion coprocessor or sensors 832 (that may include an accelerometer, a gyroscope, and a compass), a speaker 834, a camera 836, user input devices 838 (such as a keyboard, mouse, stylus, and touchpad), and a mass storage device 840 (such as hard disk drive, compact disk (CD), digital versatile disk (DVD), and so forth).

[0097] The communications logic unit 808 enables wireless communications for the transfer of data to and from the computing device 800. The term “wireless” and its derivatives may be used to describe circuits, devices, systems, methods, techniques, communications channels, etc., that may communicate data through the use of modulated electromagnetic radiation through a non-solid medium. The term does not imply that the associated devices do not contain any wires, although in some embodiments they might not. The communications logic unit 808 may 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. The computing device 800 may include a plurality of communications logic units 808. For instance, a first communications logic unit 808 may be dedicated to shorter range wireless communications such as Wi-Fi and Bluetooth and a second communications logic unit 808 may be dedicated to longer range wireless communications such as GPS, EDGE, GPRS, CDMA, WiMAX, LTE, Ev-DO, and others.

[0098] The processor 804 of the computing device 800 may include one or more interconnects or other lithographically patterned features that are formed in accordance with embodiments of the present disclosure. The term “processor” 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 stored in registers and/or memory.

[0099] The communications logic unit 808 may also include one or more interconnects or other lithographically patterned features that are formed in accordance with embodiments of the present disclosure.

[00100] In further embodiments, another component housed within the computing device 800 may contain one or more interconnects or other lithographically patterned features that are formed in accordance with embodiments of the present disclosure.

[00101] In various embodiments, the computing device 800 may be a laptop computer, a netbook computer, a notebook computer, an ultrabook computer, a smartphone, a tablet, a personal digital assistant (PDA), an ultra mobile PC, a mobile phone, a desktop computer, a server, a printer, a scanner, a monitor, a set-top box, an entertainment control unit, a digital camera, a portable music player, or a digital video recorder. In further implementations, the computing device 800 may be any other electronic device that processes data.

[00102] Some further Examples in accordance with various embodiments of the present disclosure are now described.

[00103] Example 1 provides a method for 3D printing of a predefined 3D structure, the method including: providing one or more functional groups on a print surface, and depositing a first reactive precursor onto the print surface to react with the one or more functional groups to form the structure comprising a metal or a dielectric.

[00104] Example 2 provides the method according to Example 1, where the first reactive precursor includes a metal carbonyl complex.

[00105] Example 3 provides the method according to Example 2, where the metal carbonyl complex includes iron pentacarbonyl ($\text{Fe}(\text{CO})_5$) and the structure includes an iron (Fe) metal or an iron carbide having porosity of 10% or less.

[00106] Example 4 provides the method according to Example 2, where the metal carbonyl complex includes dicobalt octacarbonyl ($\text{Co}_2(\text{CO})_8$) and the structure includes a cobalt (Co) metal having porosity of 10% or less.

[00107] Example 5 provides the method according to Example 2, where the metal carbonyl complex includes nickel tetracarbonyl ($\text{Ni}(\text{CO})_4$) and the structure includes a nickel (Ni) metal having porosity of 10% or less.

[00108] Example 6 provides the method according to Example 2, where the metal carbonyl complex includes triruthenium dodecacarbonyl ($\text{Ru}_3(\text{CO})_{12}$) and the structure includes a ruthenium (Ru) metal having porosity of 10% or less.

[00109] Example 7 provides the method according to any one of the preceding Examples, where the first reactive precursor is provided onto the print surface in an inert atmosphere.

[00110] Example 8 provides the method according to any one of the preceding Examples, further including providing an excitation to facilitate reaction of the first reactive precursor on the print surface.

[00111] Example 9 provides the method according to Example 8, where the excitation includes heating the print surface at 30 to 300 degrees Celsius for 30 seconds to the duration of the print period plus an additional heat treatment period of up to 24 hours.

[00112] Example 10 provides the method according to Examples 8 or 9, where the excitation includes optical excitation.

[00113] Example 11 provides the method according to Example 1, where the first reactive precursor includes metal oxide nanoclusters (e.g. hafnia (HfO_2) nanoclusters, titania (TiO_2) nanoclusters, zirconia (ZrO_2) nanoclusters, stannic oxide (SnO_2) nanoclusters, etc) with carboxylate capping ligands, the structure includes the metal of the metal oxide nanoclusters having porosity of 50% or less, and Example 2 provides the method further includes providing an optical excitation to facilitate reaction of the first reactive precursor on the print surface.

[00114] The method according to any one of the preceding Examples could further include removing volatile by-products from the print surface.

[00115] Example 12 provides a method for 3D printing of a predefined 3D structure, the method including: providing a first reactive precursor onto a print surface, and providing

a second reactive precursor onto the print surface to react with the second reactive precursor on the print surface to form the structure comprising a metal or a dielectric.

[00116] Example 13 provides the method according to Example 12, where the first reactive precursor includes a copper (Cu) based precursor, the second reactive precursor includes trimethylgallium (GaMe₃) or triethylgallium (GaEt₃), and the structure includes a single element copper metal or a copper alloy having porosity of 10% or less.

[00117] Example 14 provides the method according to Example 13, where reaction of the first reactive precursor with the second reactive precursor on the print surface includes transmetallation followed by spontaneous reductive elimination to form the structure including the single element copper metal or the copper alloy.

[00118] In various embodiments of Examples 13 and 14, the Cu-based precursor may include one or more of a (N,N'-alkylacetemidinate)copper(I), a (N,N'-alkylguanidinate)copper(I), a β -diketonate copper phosphine complex, a β -diketonate copper vinylsilane complex, a N-heterocyclic carbene copper amide complex, while Cu(II) precursor may include a bis(dimethylamino-2-propoxide)copper(II) and related copper bis(aminoalkoxides) along with copper bis(β -diketonate) complexes, copper bis(β -diketoiminate) complexes and copper bis(pyrrylimine) complexes.

[00119] In various embodiments of Examples 13 and 14, instead of or in addition to trimethylgallium (GaMe₃) and triethylgallium (GaEt₃), the second reactive precursor may include one or more of trimethylaluminum (AlMe₃), triethylaluminum (AlEt₃), triethylborane (BEt₃), an amineborane such as dimethylamineborane (Me₂HN-BH₃), dimethylzinc (ZnMe₂), diethylzinc (ZnEt₂) or a hydrazine such as N₂H₄, 1,1-dimethylhydrazine (H₂NNMe₂), or tertiary-butylhydrazine (tBu(H)NNH₂). In various embodiments, these coreactants could be delivered as gases or as organic solutions (when such solutions would be stable).

[00120] Example 15 provides the method according to Example 12, where the first reactive precursor includes an iron (Fe) diketonate, the second reactive precursor includes

trimethylgallium (GaMe₃) or triethylgallium (GaEt₃), and the structure includes a single element iron metal or an alloy or iron and gallium having porosity of 10% or less.

[00121] Example 16 provides the method according to Example 12, where the first reactive precursor includes a cobalt (Co) diketonate, the second reactive precursor includes trimethylgallium (GaMe₃) or triethylgallium (GaEt₃), and the structure includes a single element cobalt metal or an alloy of cobalt and gallium having porosity of 10% or less.

[00122] Example 17 provides the method according to Example 12, where the first reactive precursor includes a nickel (Ni) diketonate, the second reactive precursor includes trimethylgallium (GaMe₃) or triethylgallium (GaEt₃), and the structure includes a single element nickel metal or an alloy of nickel and gallium having porosity of 10% or less.

[00123] Example 18 provides the method according to Example 12, where the first reactive precursor includes a ruthenium (Ru) diketonate, the second reactive precursor comprises trimethylgallium (GaMe₃) or triethylgallium (GaEt₃), and the structure comprises a single element ruthenium metal or an alloy of ruthenium and gallium having porosity of 10% or less.

[00124] Example 19 provides the method according to Example 12, where the first reactive precursor includes a palladium (Pd) diketonate, the second reactive precursor comprises trimethylgallium (GaMe₃) or triethylgallium (GaEt₃), and the structure comprises a single element palladium metal or an alloy of palladium and gallium having porosity of 10% or less.

[00125] Example 20 provides the method according to Example 12, where the first reactive precursor includes a platinum (Pt) diketonate, the second reactive precursor comprises trimethylgallium (GaMe₃) or triethylgallium (GaEt₃), and the structure comprises a single element platinum metal or an alloy or platinum and gallium having porosity of 10% or less.

[00126] Example 21 provides the method according to Example 12, where the first reactive precursor includes a silver (Ag) diketonate phosphine complex, the second reactive

precursor comprises trimethylgallium (GaMe₃) or triethylgallium (GaEt₃), and the structure comprises a single element silver metal or an alloy of silver and gallium having porosity of 10% or less.

[00127] Example 22 provides the method according to any one of Examples 15-21, where reaction of the first reactive precursor with the second reactive precursor on the print surface includes transmetallation followed by spontaneous reductive elimination.

[00128] In various embodiments of Examples 15-22, instead of or in addition to trimethylgallium (GaMe₃) or triethylgallium (GaEt₃), the second reactive precursor may include triethylaluminum (AlEt₃) or/and diethylzinc (ZnEt₂).

[00129] In various embodiments of Examples 15-22, the second reactive precursor may be provided as a vapor or as a concentrated solution.

[00130] Example 23 provides the method according to Example 12, where the first reactive precursor includes a tetrachloroauric(III) acid (HAuCl₄), the second reactive precursor includes a sodium citrate (HOC(COONa)(CH₂COONa)₂), and the structure includes a gold (Au) metal having porosity of 10% or less.

[00131] Example 24 provides the method according to Example 23, where reaction of the first reactive precursor with the second reactive precursor on the print surface includes a reaction resulting from mixing aqueous solutions of the first reactive precursor with the second reactive precursor on the print surface.

[00132] Example 25 provides the method according to Example 12, where the first reactive precursor includes a titanium(IV) chloride (TiCl₄) or tetra-alkoxytitanium(IV) (Ti(OR)₄), where R is one of a methyl (Me) substituent, an ethyl (Et) substituent, a propyl (Pr) substituent, or a butyl (Bu) substituent, the second reactive precursor includes water and one or more acids, and the structure includes a titanium oxide having porosity of 10% or less.

[00133] Example 26 provides the method according to Example 12, where the first reactive precursor includes a zirconium(IV) chloride (ZrCl_4) or tetra-alkoxyzirconium(IV) (Zr(OR)_4), where R is one of a methyl (Me) substituent, an ethyl (Et) substituent, a propyl (Pr) substituent, or a butyl (Bu) substituent, the second reactive precursor includes water and one or more acids, and the structure includes a zirconium oxide having porosity of 10% or less.

[00134] Example 27 provides the method according to Example 12, where the first reactive precursor includes a hafnium(IV) chloride (HfCl_4) or tetra-alkoxyhafnium(IV) (Hf(OR)_4), where R is one of a methyl (Me) substituent, an ethyl (Et) substituent, a propyl (Pr) substituent, or a butyl (Bu) substituent, the second reactive precursor includes water and one or more acids, and the structure includes a hafnium oxide having porosity of 10% or less.

[00135] Example 28 provides the method according to any one of Examples 25-27, where reaction of the first reactive precursor with the second reactive precursor on the print surface includes hydrolysis and cross-linking.

[00136] Example 29 provides the method according to Example 12, where the first reactive precursor includes metal oxide nanoclusters (e.g. hafnia (HfO_2) nanoclusters, titania (TiO_2) nanoclusters, zirconia (ZrO_2) nanoclusters, stannic oxide (SnO_2) nanoclusters, etc) with carboxylate capping ligands, the second reactive precursor includes water, and the structure includes the metal or the metal oxide nanoclusters having porosity of 50% or less.

[00137] Example 30 provides the method according to Example 12, where the first reactive precursor includes 1,3,5-triethoxy-1,3,5-trisilacyclohexane or a formulation of hexaethoxytrisilacyclohexane and 1,3,5-trisilacyclohexane, the second reactive precursor includes tris(perfluorophenyl)borane ($\text{B(C}_6\text{F}_5)_3$), and the structure includes carbon-doped silicon oxide having porosity of 15% or less.

[00138] Example 31 provides the method according to any one of Examples 11-30, where the first reactive precursor and the second reactive precursor are provided onto the print surface in an inert atmosphere.

[00139] Example 32 provides the method according to any one of Examples 11-31, further including providing an excitation to facilitate reaction of the first reactive precursor and the second reactive precursor on the print surface.

[00140] Example 33 provides the method according to Example 32, where the excitation includes heating the print surface at 30 to 300 degrees Celsius for 30 seconds to the duration of the print period plus an additional heat treatment period of up to 24 hours.

[00141] Example 34 provides the method according to Examples 32 or 33, where the excitation includes optical excitation.

[00142] Example 35 provides the method according to any one of the preceding Examples, further including removing volatile by-products from the print surface.

[00143] Example 36 provides a semiconductor device including an alloy of ruthenium and gallium provided as a three-dimensional structure on a print surface.

[00144] Example 37 provides the semiconductor device according to Example 36, where the alloy of ruthenium and gallium has porosity equal to or less than 10%.

[00145] Example 38 provides a semiconductor device including an alloy of palladium and gallium provided as a three-dimensional structure on a print surface.

[00146] Example 39 provides the semiconductor device according to Example 38, where the alloy of palladium and gallium has porosity equal to or less than 10%.

[00147] Example 40 provides a semiconductor device including an alloy of platinum and gallium provided as a three-dimensional structure on a print surface.

[00148] Example 41 provides the semiconductor device according to Example 40, where the alloy of platinum and gallium has porosity equal to or less than 10%.

[00149] Example 42 provides a semiconductor device including an alloy of silver and gallium provided as a three-dimensional structure on a print surface.

[00150] Example 43 provides the semiconductor device according to Example 42, where the alloy of silver and gallium has porosity equal to or less than 10%.

[00151] Example 44 provides a print head for 3D printing of a structure of a semiconductor integrated circuit, the print head including: a first container for holding a first reactive precursor; a second container for holding a second reactive precursor; means for providing the first reactive precursor onto a print surface; and means for providing the second reactive precursor onto the print surface to react with the second reactive precursor on the print surface to form the structure comprising a metal or a dielectric.

[00152] Example 45 provides the print head according to Example 44, where the means for providing the first reactive precursor and/or the means for providing the second reactive precursor onto the print surface include one or more of: a gas jet dispenser, an aerosol dispenser, an ink jet dispenser, and a capillary dispenser.

[00153] The above description of illustrated implementations of the disclosure, including what is described in the Abstract, is not intended to be exhaustive or to limit the disclosure to the precise forms disclosed. While specific implementations of, and examples for, the disclosure are described herein for illustrative purposes, various equivalent modifications are possible within the scope of the disclosure, as those skilled in the relevant art will recognize.

[00154] These modifications may be made to the disclosure in light of the above detailed description. The terms used in the following claims should not be construed to limit the disclosure to the specific implementations disclosed in the specification and the claims. Rather, the scope of the disclosure is to be determined entirely by the following claims, which are to be construed in accordance with established doctrines of claim interpretation.

Claims

1. A method for three-dimensional (3D) printing of a structure of a semiconductor integrated circuit, the method comprising:

providing one or more functional groups on a print surface; and

depositing a first reactive precursor onto the print surface to react with the one or more functional groups to form the structure comprising a metal or a dielectric.
2. The method according to claim 1, wherein the first reactive precursor comprises iron pentacarbonyl ($\text{Fe}(\text{CO})_5$) and the structure comprises an iron (Fe) metal or an iron carbide having porosity of 10% or less.
3. The method according to claim 1, wherein the first reactive precursor comprises dicobalt octacarbonyl ($\text{Co}_2(\text{CO})_8$) and the structure comprises a cobalt (Co) metal having porosity of 10% or less.
4. The method according to claim 1, wherein the first reactive precursor comprises nickel tetracarbonyl ($\text{Ni}(\text{CO})_4$) and the structure comprises a nickel (Ni) metal having porosity of 10% or less.
5. The method according to claim 1, wherein the first reactive precursor comprises triruthenium dodecacarbonyl ($\text{Ru}_3(\text{CO})_{12}$) and the structure comprises a ruthenium (Ru) metal having porosity of 10% or less.
6. The method according to claim 1, wherein the first reactive precursor comprises metal oxide nanoclusters with carboxylate capping ligands, the structure comprises the metal oxide nanoclusters having porosity of 50% or less and the method further comprises providing an optical excitation to facilitate reaction of the first reactive precursor on the print surface.
7. A method for three-dimensional (3D) printing of a structure of a semiconductor integrated circuit, the method comprising:

providing a first reactive precursor onto a print surface; and

providing a second reactive precursor onto the print surface to react with the second reactive precursor on the print surface to form the structure comprising a metal or a dielectric.

8. The method according to claim 7, wherein the first reactive precursor comprises a copper (Cu) based precursor, the second reactive precursor comprises trimethylgallium (GaMe₃) or triethylgallium (GaEt₃), and the structure comprises a single element copper metal or a copper alloy having porosity of 10% or less.

9. The method according to claim 8, wherein reaction of the first reactive precursor with the second reactive precursor on the print surface comprises transmetallation followed by spontaneous reductive elimination to form the structure comprising the single element copper metal or the copper alloy.

10. The method according to claim 7, wherein the first reactive precursor comprises an iron (Fe) diketonate, the second reactive precursor comprises trimethylgallium (GaMe₃) or triethylgallium (GaEt₃), and the structure comprises a single element iron metal or an iron alloy having porosity of 10% or less.

11. The method according to claim 7, wherein the first reactive precursor comprises a cobalt (Co) diketonate, the second reactive precursor comprises trimethylgallium (GaMe₃) or triethylgallium (GaEt₃), and the structure comprises a single element cobalt metal or a cobalt alloy having porosity of 10% or less.

12. The method according to claim 7, wherein the first reactive precursor comprises a nickel (Ni) diketonate, the second reactive precursor comprises trimethylgallium (GaMe₃) or triethylgallium (GaEt₃), and the structure comprises a single element nickel metal or a nickel-gallium alloy having porosity of 10% or less.

13. The method according to claim 7, wherein the first reactive precursor comprises a ruthenium (Ru) diketonate, the second reactive precursor comprises

trimethylgallium (GaMe₃) or triethylgallium (GaEt₃), and the structure comprises a single element ruthenium metal or a ruthenium-gallium alloy having porosity of 10% or less.

14. The method according to claim 7, wherein the first reactive precursor comprises a palladium (Pd) diketonate, the second reactive precursor comprises trimethylgallium (GaMe₃) or triethylgallium (GaEt₃), and the structure comprises a single element palladium metal or a palladium-gallium alloy having porosity of 10% or less.

15. The method according to claim 7, wherein the first reactive precursor comprises a platinum (Pt) diketonate, the second reactive precursor comprises trimethylgallium (GaMe₃) or triethylgallium (GaEt₃), and the structure comprises a single element platinum metal or a platinum-gallium alloy having porosity of 10% or less.

16. The method according to claim 7, wherein the first reactive precursor comprises a silver (Ag) diketonate phosphine complex, the second reactive precursor comprises trimethylgallium (GaMe₃) or triethylgallium (GaEt₃), and the structure comprises a single element silver metal or a silver-gallium alloy having porosity of 10% or less.

17. The method according to claim 7, wherein the first reactive precursor comprises a tetrachloroauric(III) acid (HAuCl₄), the second reactive precursor comprises a sodium citrate (HOC(COONa)(CH₂COONa)₂), and the structure comprises a gold (Au) metal having porosity of 10% or less.

18. The method according to claim 7, wherein the first reactive precursor comprises a titanium(IV) chloride (TiCl₄) or tetra-alkoxytitanium(IV) (Ti(OR)₄), where R is one of a methyl (Me) substituent, an ethyl (Et) substituent, a propyl (Pr) substituent, or a butyl (Bu) substituent, the second reactive precursor comprises water and one or more acids, and the structure comprises a titanium oxide having porosity of 10% or less.

19. The method according to claim 7, wherein the first reactive precursor comprises a zirconium(IV) chloride (ZrCl₄) or tetra-alkoxyzirconium(IV) (Zr(OR)₄), where R is one of a methyl (Me) substituent, an ethyl (Et) substituent, a propyl (Pr) substituent, or a

butyl (Bu) substituent, the second reactive precursor comprises water and one or more acids, and the structure comprises a zirconium oxide having porosity of 10% or less.

20. The method according to claim 7, wherein the first reactive precursor comprises a hafnium(IV) chloride (HfCl_4) or tetra-alkoxyhafnium(IV) ($\text{Hf}(\text{OR})_4$), where R is one of a methyl (Me) substituent, an ethyl (Et) substituent, a propyl (Pr) substituent, or a butyl (Bu) substituent, the second reactive precursor comprises water and one or more acids, and the structure comprises a hafnium oxide having porosity of 10% or less.

21. The method according to claim 7, wherein the first reactive precursor comprises 1,3,5-triethoxy-1,3,5-trisilacyclohexane or a formulation of hexaethoxytrisilacyclohexane and 1,3,5-trisilacyclohexane, the second reactive precursor comprises tris(perfluorophenyl)borane ($\text{B}(\text{C}_6\text{F}_5)_3$), and the structure comprises carbon-doped silicon oxide having porosity of 15% or less.

22. A semiconductor device comprising:

an alloy of ruthenium and gallium provided as a three-dimensional structure on a surface, wherein the alloy of ruthenium and gallium has porosity equal to or less than 10%.

23. A semiconductor device comprising:

an alloy of gallium and either palladium or platinum provided as a three-dimensional structure on a surface, wherein the alloy has porosity equal to or less than 10%.

24. A print head for three-dimensional (3D) printing of a structure of a semiconductor integrated circuit, the print head comprising:

a first container for holding a first reactive precursor;

a second container for holding a second reactive precursor;

means for providing the first reactive precursor onto a print surface; and

means for providing the second reactive precursor onto the print surface to react with the second reactive precursor on the print surface to form the structure comprising a metal or a dielectric.

25. The print head according to claim 24, wherein the means for providing the first reactive precursor and/or the means for providing the second reactive precursor onto the print surface comprise one or more of: a gas jet dispenser, an aerosol dispenser, an ink jet dispenser, and a capillary dispenser.

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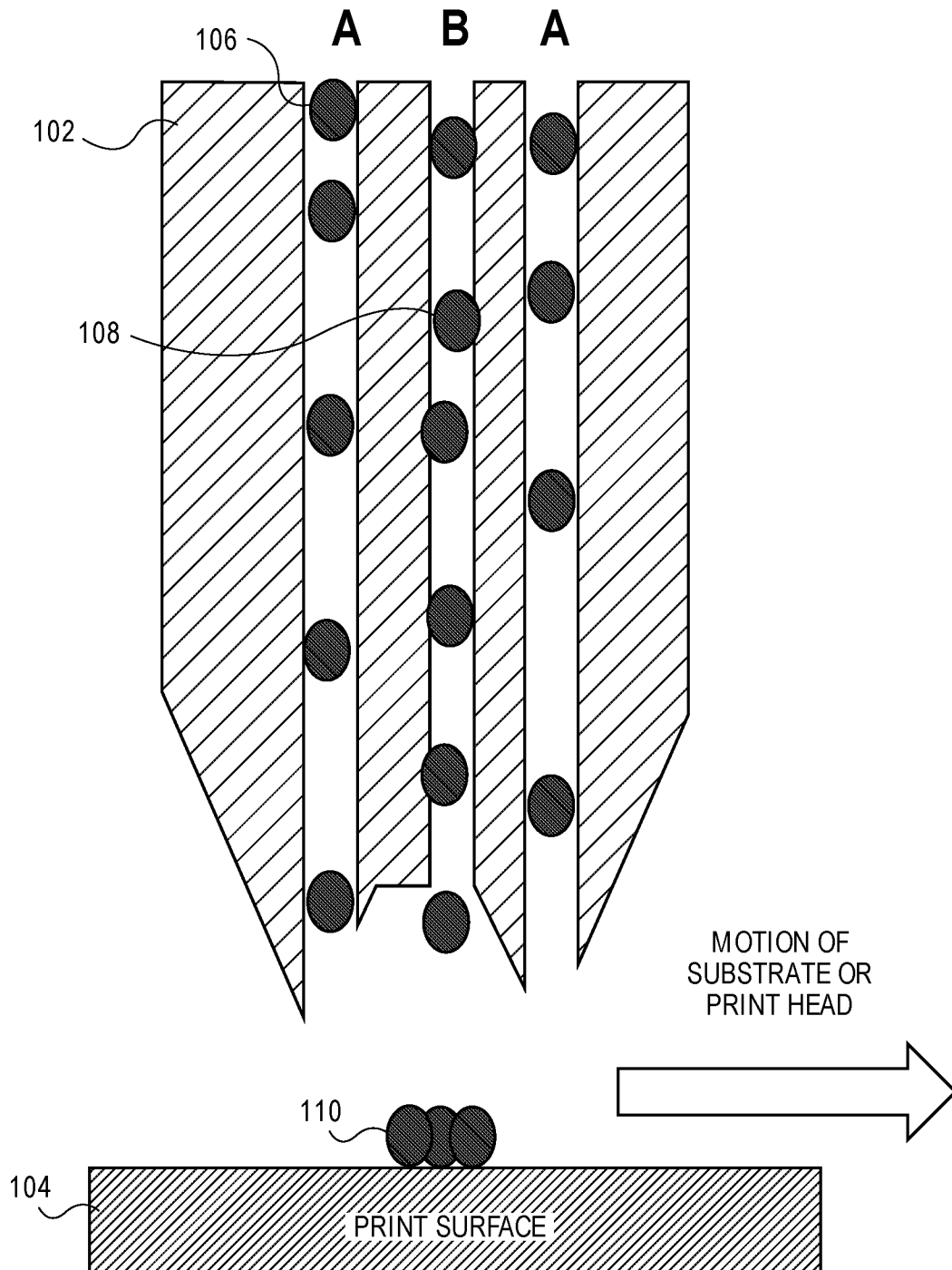
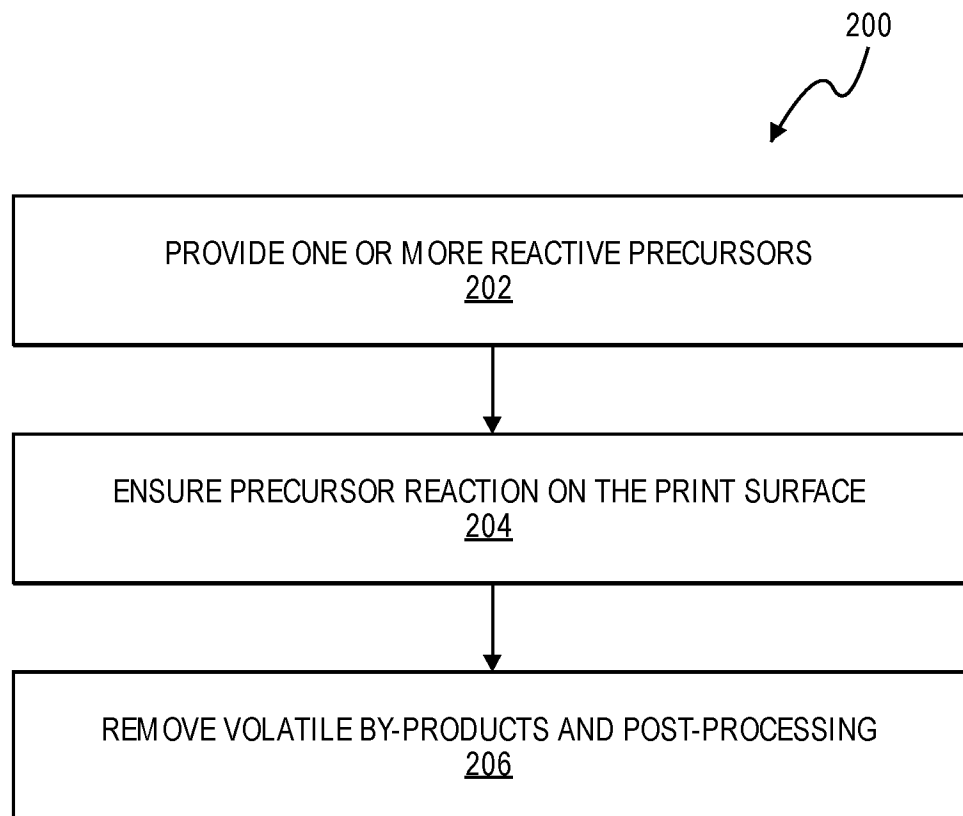
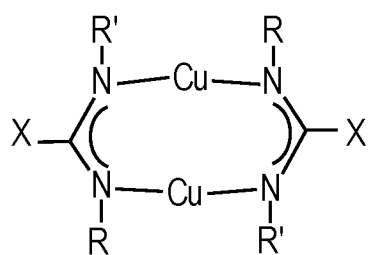
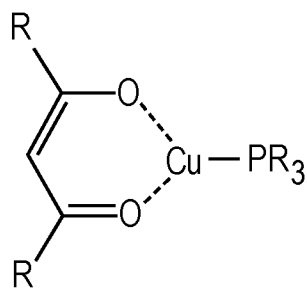
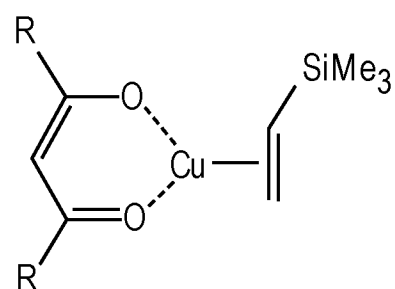
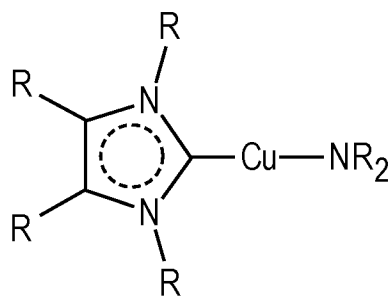
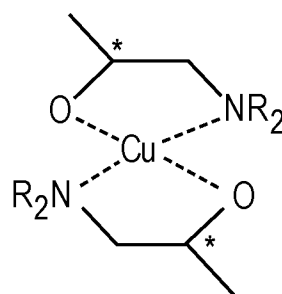
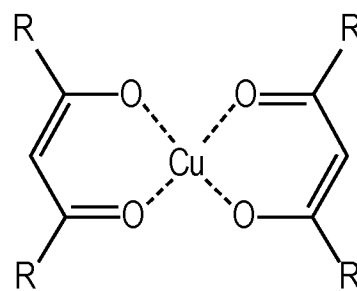
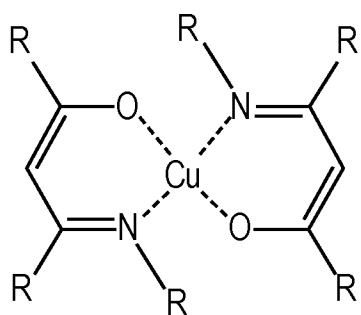
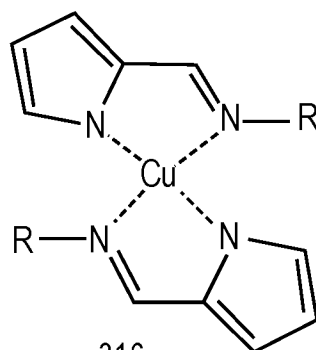


FIG. 1

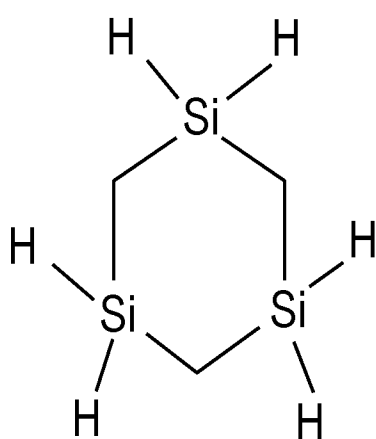
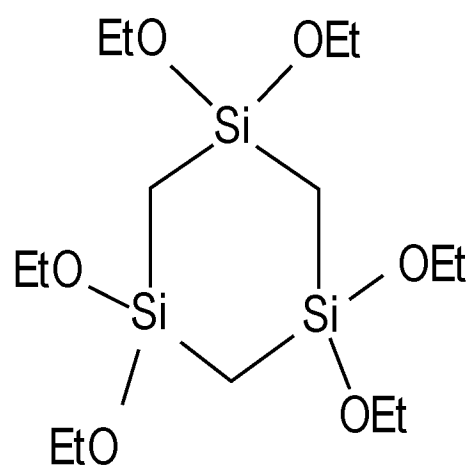
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**FIG. 2**

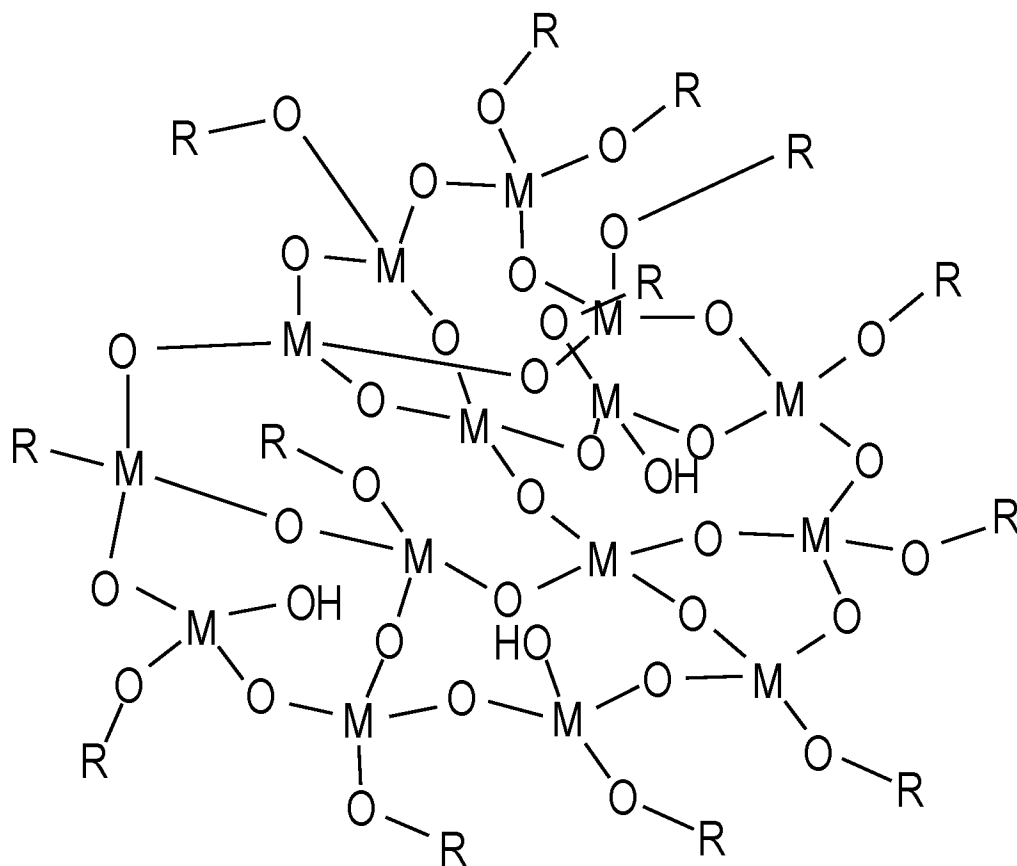
3/9

302304306308310312314316**FIG. 3**

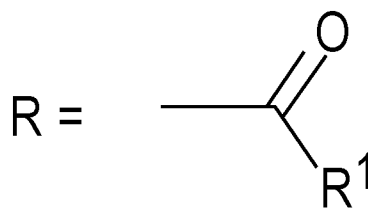
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402404**FIG. 4**

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M = Hf, Zr, Ti, Sn, etc.

504**FIG. 5**

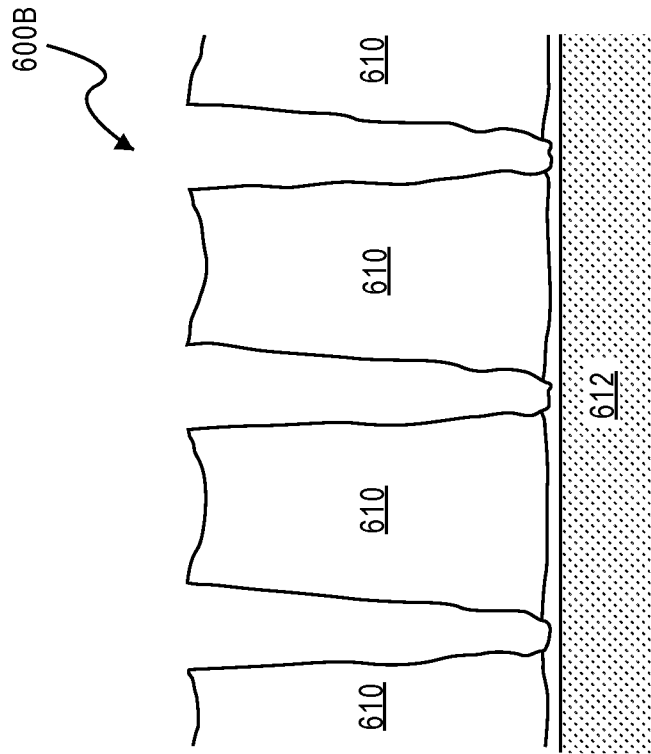


FIG. 6B

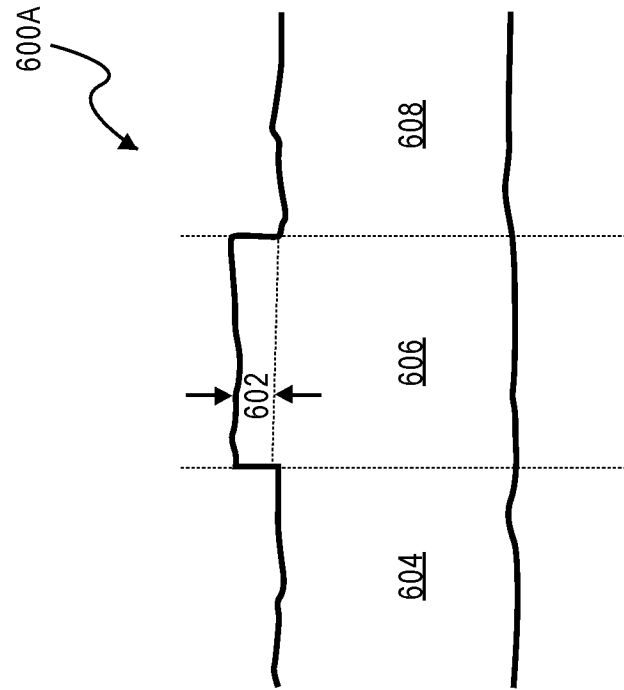


FIG. 6A

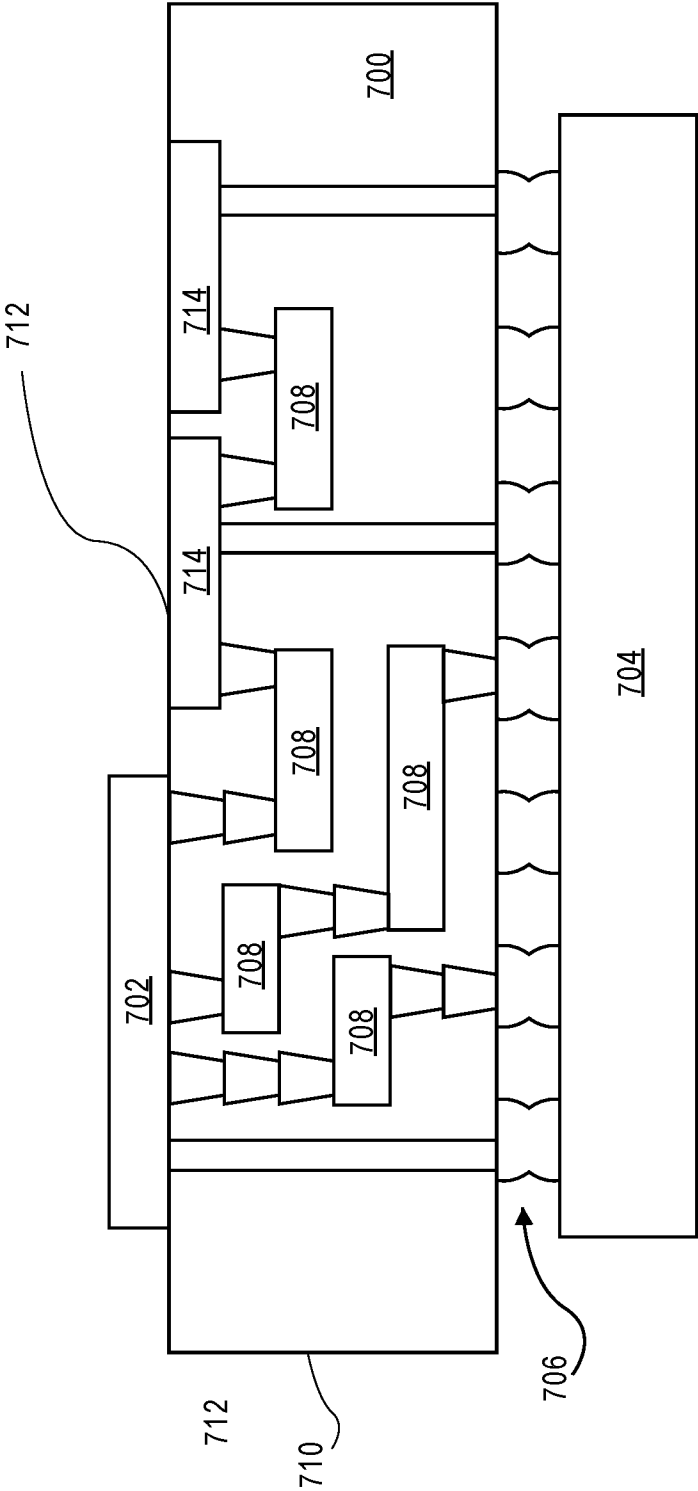
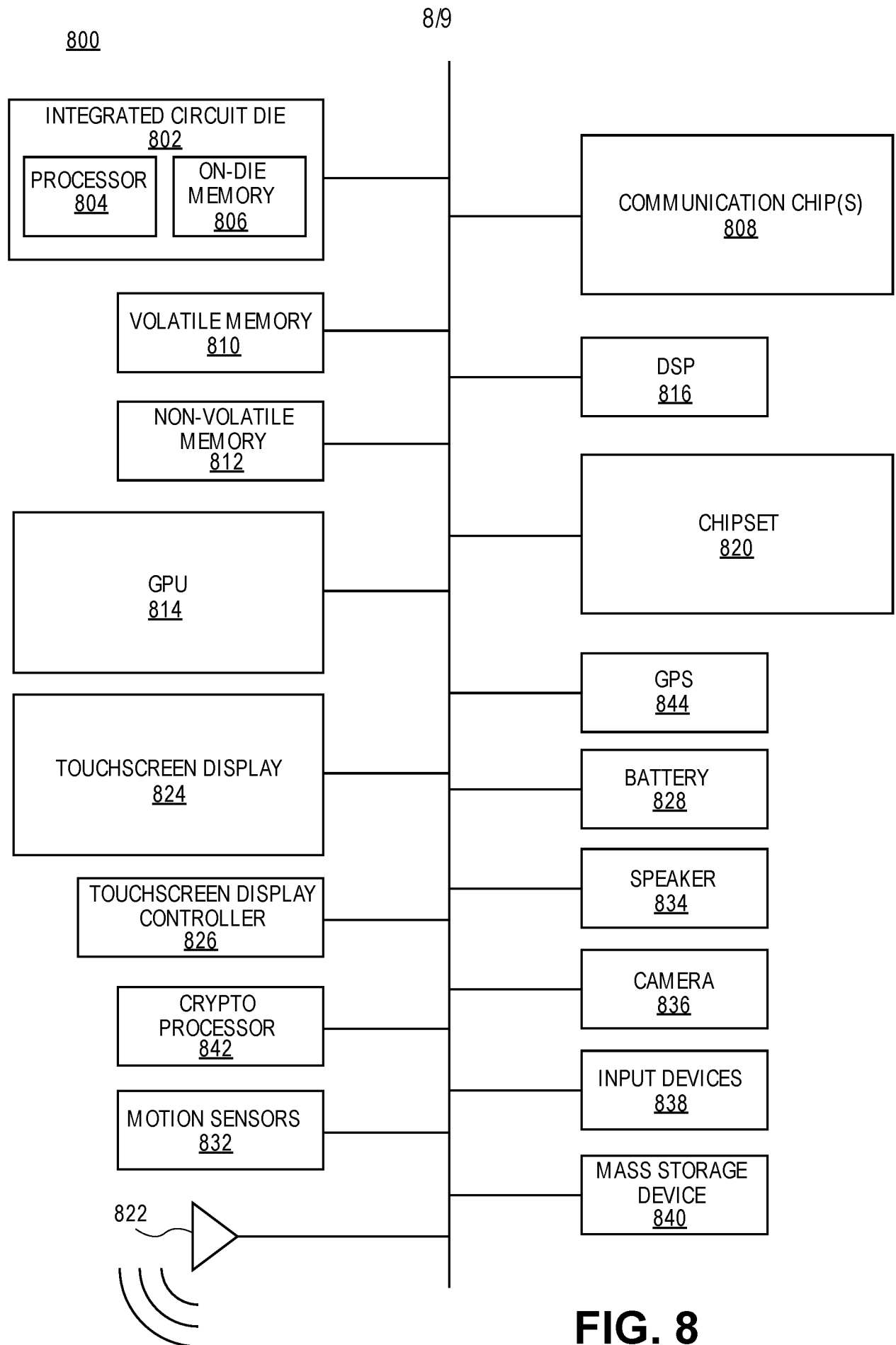
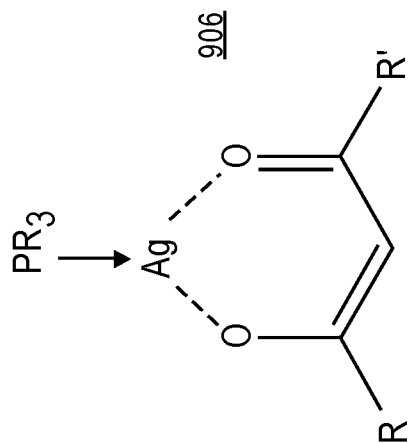
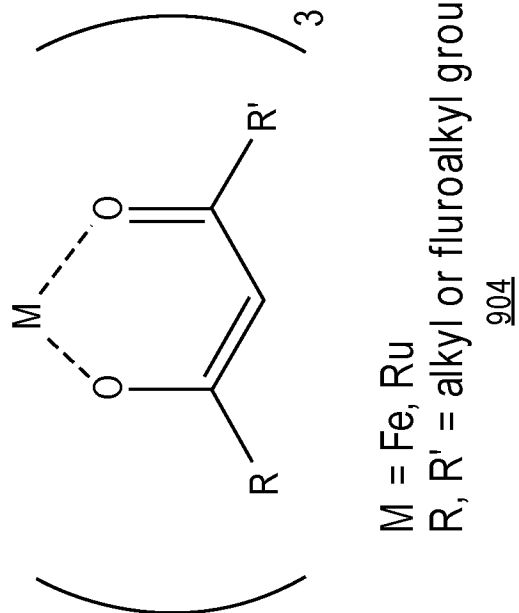
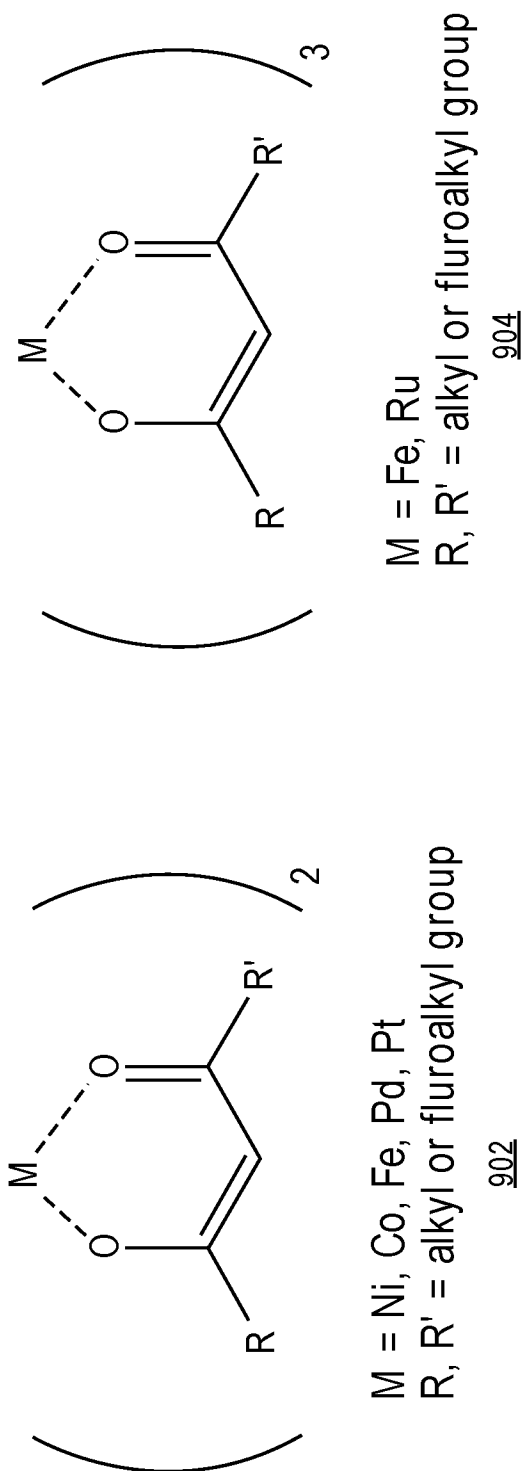


FIG. 7

**FIG. 8**

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$R, R' = \text{alkyl or fluoroalkyl group}$

FIG. 9

A. CLASSIFICATION OF SUBJECT MATTER**H01L 21/283(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 21/283; B05D 3/02; B05D 5/00; B32B 3/00; H01L 51/00; H01L 21/28; C09D 11/00; H01L 21/16

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: substrate, print, 3D, metal, precursor, porous

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2007-0184576 A1 (CHIH-HUNG CHANG et al.) 09 August 2007 See abstract, paragraphs [0030], [0088]-[0099], [0159]-[0169], claims 1-7, 50-53 and figure 1.	1-17, 21-23
Y		18-20
Y	US 2003-0162004 A1 (CHARD A. MIRKIN et al.) 28 August 2003 See abstract, paragraphs [0059]-[0060] and figure 1.	18-20
X	US 2013-0203198 A1 (SUNG YONG MIN et al.) 08 August 2013 See abstract, paragraphs [0053]-[0056] and figures 2A-2B.	24-25
A	US 2010-0022078 A1 (JOERG ROCKENBERGER et al.) 28 January 2010 See abstract, paragraphs [0066]-[0077] and figures 1A-1C.	1-25
A	US 2004-0142106 A1 (CHAD A. MIRKIN et al.) 22 July 2004 See abstract, paragraphs [0075]-[0076] and figure 1.	1-25



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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"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

28 November 2016 (28.11.2016)

Date of mailing of the international search report

28 November 2016 (28.11.2016)

Name and mailing address of the ISA/KR

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2016/020795

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