US 20160314967A1

(19) **United States**

(12) **Patent Application Publication**

Tolle

(10) **Pub. No.: US 2016/0314967 A1**

(43) **Pub. Date: Oct. 27, 2016**

(54) **STRUCTURES AND DEVICES INCLUDING GERMANIUM-TIN FILMS AND METHODS OF FORMING SAME**

(71) Applicant: **ASM IP HOLDING, B.V.**, ALMERE (NL)

(72) Inventor: **John Tolle**, Gilbert, AZ (US)

(21) Appl. No.: **15/203,642**

(22) Filed: **Jul. 6, 2016**

Related U.S. Application Data

(63) Continuation-in-part of application No. 13/966,782, filed on Aug. 14, 2013, now Pat. No. 9,396,934.

Publication Classification

(51) **Int. Cl.**

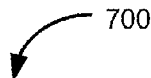
H01L 21/02 (2006.01)
H01L 31/18 (2006.01)
H01L 29/165 (2006.01)
H01L 31/0745 (2006.01)

(52) **U.S. Cl.**

CPC ***H01L 21/02535*** (2013.01); ***H01L 31/0745*** (2013.01); ***H01L 31/1812*** (2013.01); ***H01L 21/0262*** (2013.01); ***H01L 21/02636*** (2013.01); ***H01L 21/02381*** (2013.01); ***H01L 21/02384*** (2013.01); ***H01L 29/165*** (2013.01)

(57) **ABSTRACT**

Methods of forming germanium-tin films using germane as a precursor are disclosed. Exemplary methods include growing films including germanium and tin in an epitaxial chemical vapor deposition reactor, wherein a ratio of a tin precursor to germane is less than 0.1. Also disclosed are structures and devices including germanium-tin films formed using the methods described herein.



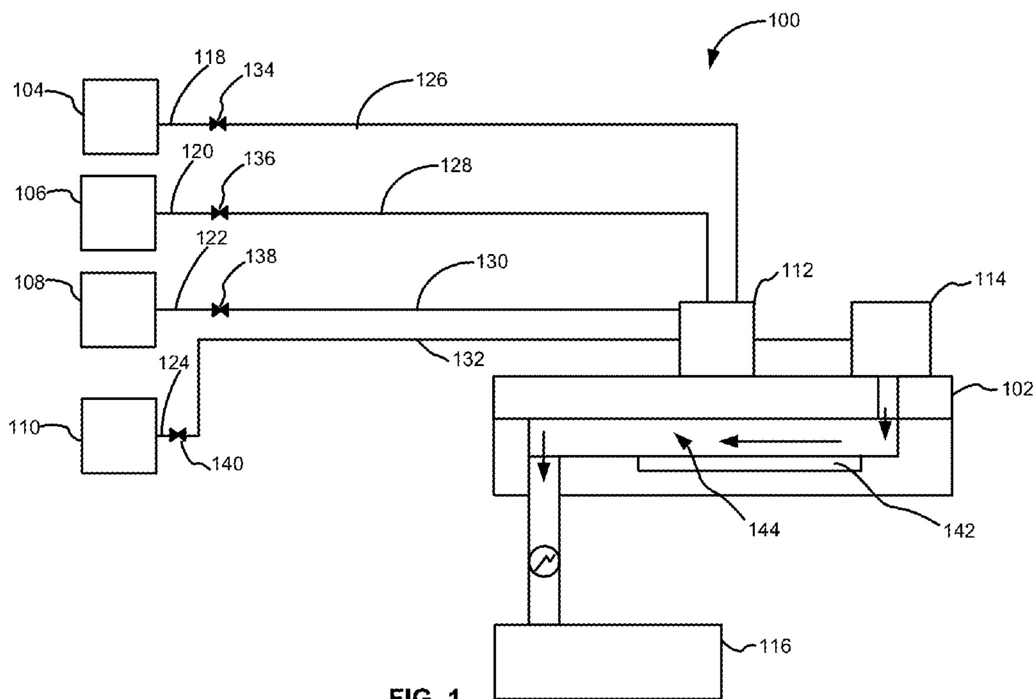


FIG. 1

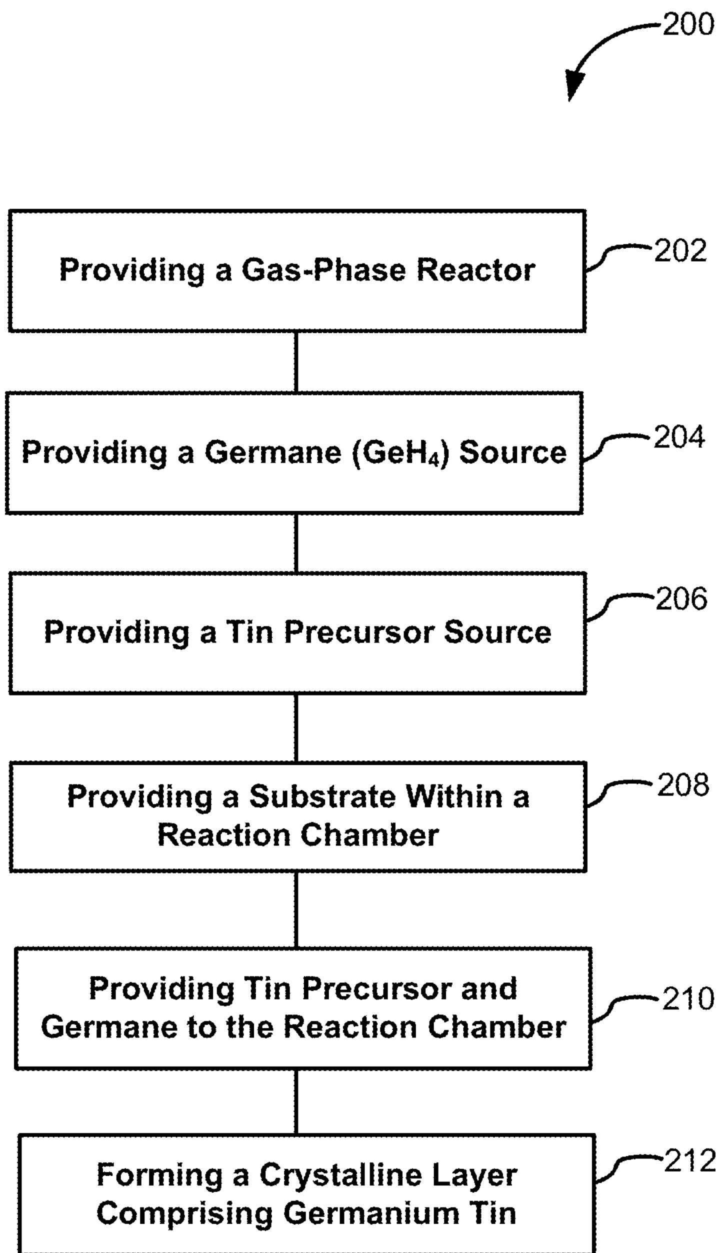


FIG. 2

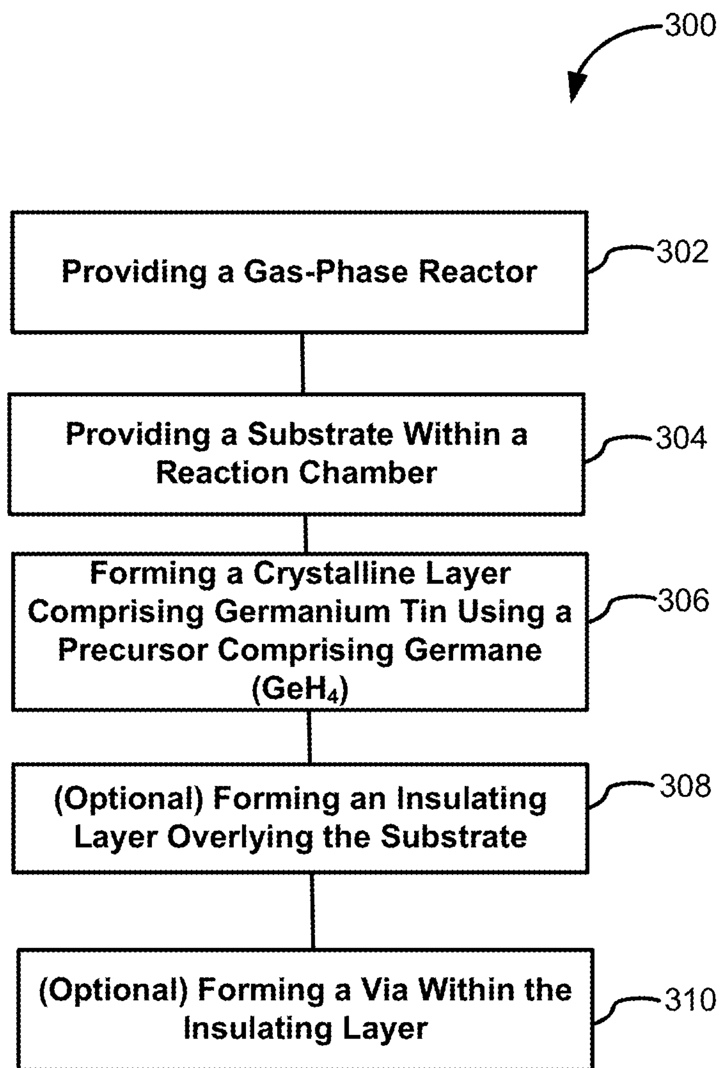


FIG. 3

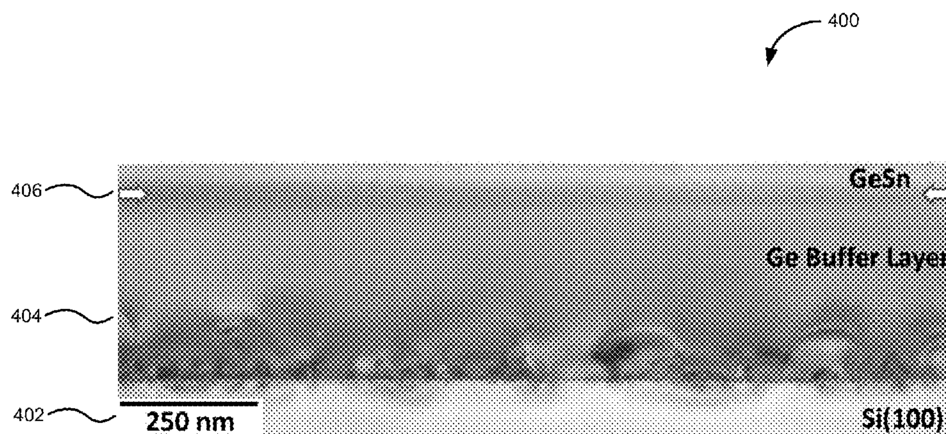


FIG. 4

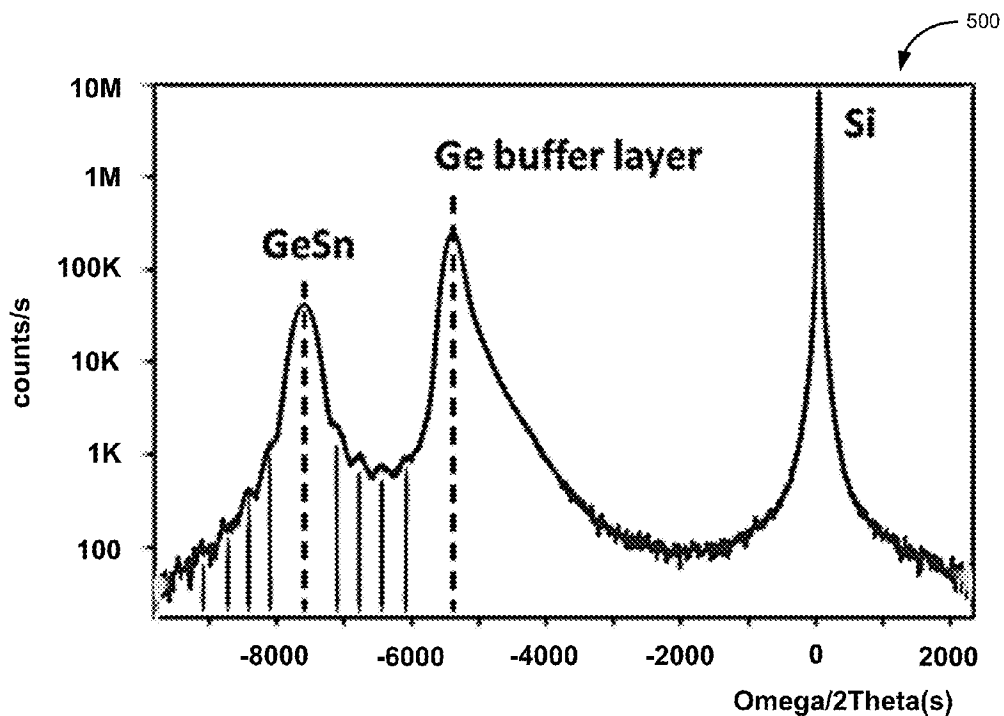


FIG. 5

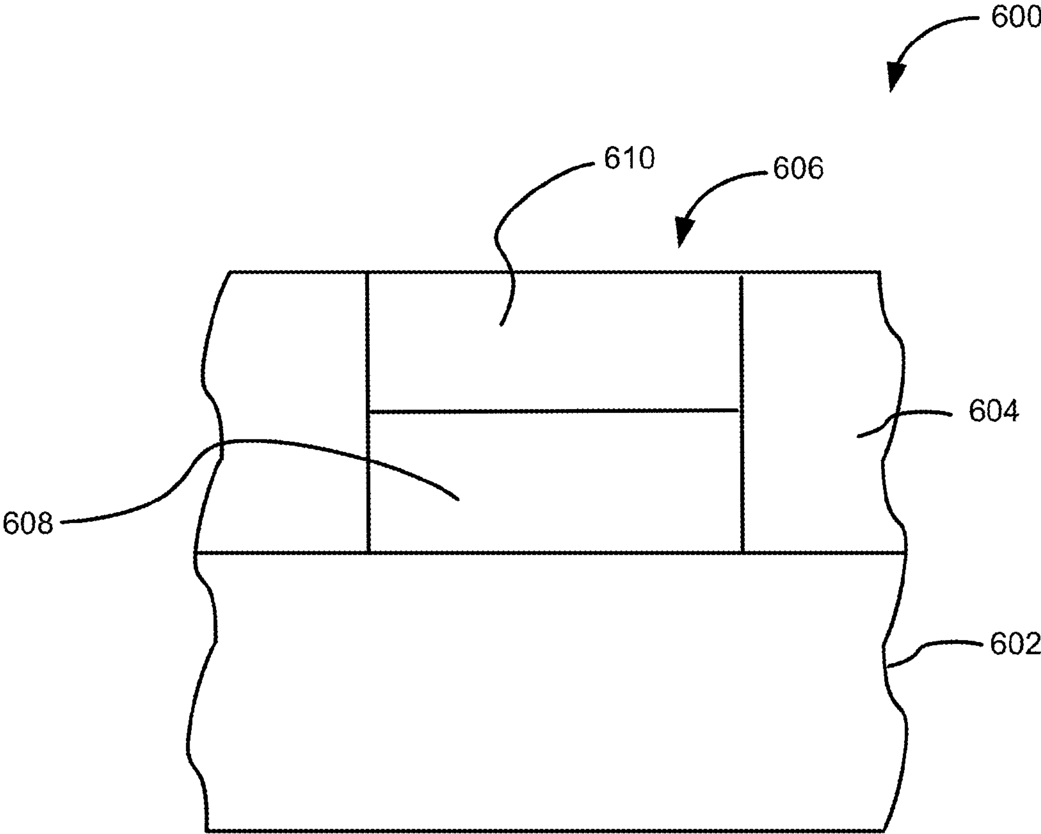


FIG. 6

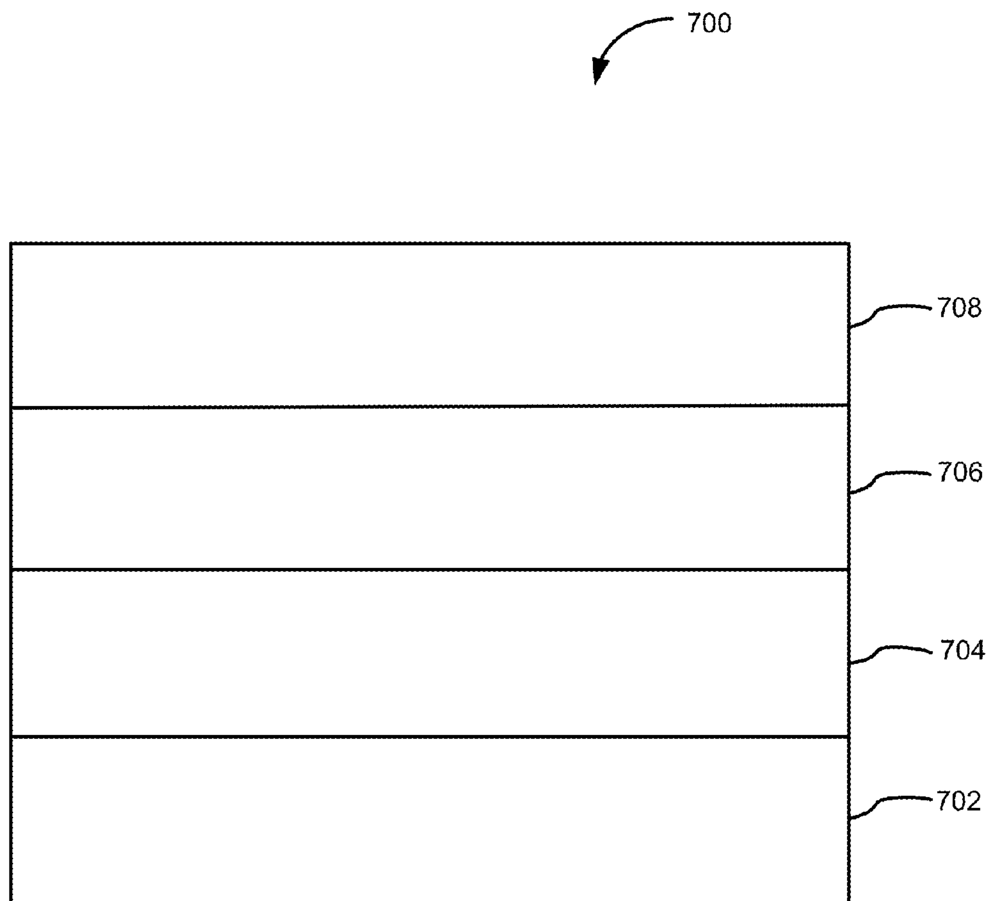


FIG. 7

STRUCTURES AND DEVICES INCLUDING GERMANIUM-TIN FILMS AND METHODS OF FORMING SAME

CROSS REFERENCE TO RELATED APPLICATION

[0001] The present application is a continuation-in-part of U.S. application Ser. No. 13/966,782 titled "Methods of Forming Films Including Germanium Tin and Structures and Devices Including the Films," filed on Aug. 14, 2013. The disclosures of which is incorporated herein by reference.

FIELD OF INVENTION

[0002] The present disclosure generally relates to techniques for depositing films including germanium and tin and to structures and devices including such films. More particularly, the disclosure relates to methods of forming films comprising germanium and tin using germane as a precursor, to methods of forming structures and devices including the films, and to structures and devices including the films.

BACKGROUND OF THE DISCLOSURE

[0003] Various electronic devices, such as semiconductor devices, and photonic devices, such as lasers and solar devices, may include or may desirably include germanium-tin layers, such as GeSn, GeSiSn, and the like. For example, GeSn layers can be used to form direct band gap devices and/or may be used to provide strain in an adjacent germanium layer to increase mobility in the germanium layer. Similarly, GeSiSn layers can be used to form tunable band gap devices as well as optical devices having tunable optical properties. To obtain the desired device properties, the germanium-tin films generally have a crystalline structure, which generally follows the crystalline structure of the underlying layer.

[0004] GeSn layers may be deposited or grown using a variety of techniques. For example, vacuum processes, including molecular beam epitaxy and ultra-high vacuum chemical vapor deposition, have been used to form GeSn films. The germanium precursor for such processes typically includes digermane (Ge_2H_6) or trigermane (Ge_3H_8). When the film includes silicon, the silicon precursor may include a disilane, trisilane, or other higher order silane compounds, or hetero-nuclear Si—Ge compounds with the general formula of $(H_3Ge)_xSiH_{4-x}$(x=1-4), $(H_3Si)_xGeH_{4-x}$(x=1-4).

[0005] Although such processes have been used to deposit or grow crystalline GeSn and GeSiSn layers, use of digermane, trigermane, or higher order germane precursors is problematic in several respects. For example, formation of films or layers including GeSn using digermane or higher order germane precursors, such as trigermane, is not selective when certain carrier gasses (e.g., hydrogen) and/or dopants (e.g., p-type dopants) are used with the precursor. Also, digermane is relatively unstable (explosive) in concentrated form; as a result, an amount of the precursor contained in a vessel may be limited, typically to less than 154 grams, which in turn, causes throughput of processes using such a precursor to be relatively low. In addition, digermane and higher order germanes are relatively expensive. Accordingly, improved processes for forming crystalline films including GeSn are desired.

SUMMARY OF THE DISCLOSURE

[0006] Various embodiments of the present disclosure relate to methods of forming GeSn films and to structures and devices including the films. The films formed using the methods described herein may be used, for example, for semiconductor, direct band gap, photonic, or any device including the film. While the ways in which various embodiments of the disclosure address the drawbacks of the prior art methods are discussed in more detail below, in general, the disclosure provides methods of forming germanium-tin layers (e.g., crystalline), using a germane (GeH_4) precursor, on a surface of a substrate and structures and devices including such films.

[0007] As used herein, germanium-tin (GeSn) layers (also referred to herein as films) or layers including germanium and tin are layers that include the elements germanium and tin. The layers may include additional elements, such as silicon (e.g., GeSnSi) or carbon (e.g., GeSnSiC) or dopants, such as boron, gallium, phosphorus, arsenic, or antimony, for example.

[0008] In accordance with various embodiments of the disclosure, methods of forming a layer including GeSn includes the steps of providing a gas-phase reactor, providing a germane precursor source coupled to the gas-phase reactor, providing a tin precursor source coupled to the gas-phase reactor, providing a substrate within a reaction chamber of the gas-phase reactor, providing a germane precursor and a tin precursor to the reaction chamber, and forming (e.g., epitaxially growing) a crystalline layer of germanium tin on a surface of the substrate. In accordance with various aspects of these embodiments, the step of providing a germane precursor and a tin precursor to the reaction chamber includes providing a mixture of the tin precursor and the germane precursor having a volumetric ratio of tin precursor to germane of about 0.001 to about 0.1, about 0.005 to about 0.05, less than about 0.1, or less than about 0.05. A reaction chamber temperature and pressure during the step of forming a crystalline layer of germanium tin may vary in accordance with various factors. Exemplary reaction chamber temperatures range from about 200° C. to about 500° C., about 250° C. to about 450° C., or about 300° C. to about 420° C. Exemplary reaction chamber pressures during this step range from about 300 Torr to about 850 Torr, about 400 Torr to about 800 Torr, about 500 Torr to about 760 Torr, ambient atmospheric pressure±about 20 Torr, ambient atmospheric pressure±about 10 Torr, or ambient atmospheric pressure±about 5 Torr. In accordance with further aspects of these embodiments, the germanium-tin layer includes silicon. In these cases, the method further comprises a step of providing a silicon source precursor to the reaction chamber. Exemplary silicon source precursors include disilane, trisiliane, tetrasilane, neopentasilane, and higher order silane compounds. An amount of tin incorporated into the crystalline germanium-tin layer may be about greater than 1 at %, greater than 2 at %, or greater than 5 at %, or range from about 0 at % to about 15 at % tin, about 2 at % to about 15 at % tin, about 0.2 at % to about 5 at % tin, or about 0.2 at % to about 15 at % tin. When the layer of crystalline germanium-tin includes silicon, the layer may include greater than 0 at % silicon, greater than about 1 at % silicon, or between about 1 at % silicon and about 20 at % silicon, about 2 at % silicon and about 16 at % silicon, or about 4 at % silicon and about 12 at % silicon. In accordance with further aspects of these embodiments, the substrate

includes silicon. In accordance with other aspects, the substrate includes a layer of germanium—e.g., overlying silicon. Exemplary methods in accordance with these embodiments additionally include the steps of forming an insulating layer overlying the substrate, forming a via within the insulating layer, and forming (e.g., selectively) the (e.g., crystalline) germanium-tin layer within the via and overlying the substrate, which may include one or more previously formed layers.

[0009] In accordance with further exemplary embodiments of the disclosure, a method of forming a structure comprising a germanium-tin (e.g., crystalline) layer includes the steps of providing a gas-phase reactor, providing a substrate within a reaction chamber of the gas-phase reactor, and forming a layer comprising germanium and tin (e.g., crystalline) on a surface of the substrate using one or more precursors comprising germane (GeH_4). In accordance with various aspects of these embodiments, the step of forming a layer comprising germanium and tin includes providing a mixture of a tin precursor and the germane having a volumetric ratio of tin precursor to germane of about 0.001 to about 0.1, about 0.005 to about 0.05, less than about 0.1, or less than about 0.05. In accordance with further aspects, a reaction chamber temperature during the step of forming a crystalline layer comprising germanium tin ranges from about 200° C. to about 500° C., about 250° C. to about 450° C., or about 300° C. to about 420° C. In accordance with yet further aspects, a reaction chamber pressure during the step of forming a layer comprising germanium tin ranges from about 300 Torr to about 850 Torr, about 400 Torr to about 800 Torr, about 500 Torr to about 760 Torr, ambient atmospheric pressure±about 20 Torr, ambient atmospheric pressure±about 10 Torr, or ambient atmospheric pressure±about 5 Torr. In accordance with yet further aspects of these embodiments, the step of forming a layer comprising germanium and tin includes forming a layer comprising silicon germanium tin. In these cases, a silicon precursor is provided to the reaction chamber. Exemplary silicon source precursors include disilane, trisiliane, tetrasilane, neopentasilane, and higher order silane compounds. An amount of tin incorporated into the germanium-tin layer may be about greater than 1 at %, greater than 2 at %, or greater than 5 at %, or range from about 0 at % to about 15 at % tin, about 2 at % to about 15 at % tin, about 0.2 at % to about 5 at % tin, or about 0.2 at % to about 15 at % tin. When the layer of crystalline germanium-tin layer includes silicon, the layer may include greater than 0 at % silicon, greater than about 1 at % silicon, or between about 1 at % silicon and about 20 at % silicon, about 2 at % silicon and about 16 at % silicon, or about 4 at % silicon and about 12 at % silicon. In accordance with various aspects of these embodiments, the substrate includes silicon. In accordance with other aspects, the substrate includes a layer of germanium—e.g., overlying silicon. Exemplary methods in accordance with these embodiments additionally include the steps of forming an insulating layer overlying the substrate, forming a via within the insulating layer, and forming (e.g., selectively) the layer of germanium tin within the via and overlying the substrate.

[0010] In accordance with yet further embodiments of the disclosure, a structure includes a crystalline germanium-tin layer formed in accordance with a method of the present disclosure. The structure may be used to form electronic (e.g., semiconductor) or photonic (e.g., solar or light-emitting) devices.

[0011] And in accordance with yet additional exemplary embodiments of the disclosure, a device includes a crystalline germanium-tin layer formed in accordance with a method of the present disclosure.

BRIEF DESCRIPTION OF THE DRAWING FIGURES

[0012] A more complete understanding of exemplary embodiments of the present disclosure may be derived by referring to the detailed description and claims when considered in connection with the following illustrative figures.

[0013] FIG. **1** illustrates a system for forming a layer of crystalline germanium tin in accordance with exemplary embodiments of the disclosure.

[0014] FIG. **2** illustrates a method of forming a layer comprising germanium tin in accordance with further exemplary embodiments of the disclosure.

[0015] FIG. **3** illustrates another method of forming a layer comprising germanium tin in accordance with exemplary embodiments of the disclosure.

[0016] FIG. **4** illustrates a structure in accordance with exemplary embodiments of the disclosure.

[0017] FIG. **5** illustrates a rocking scan of a structure in accordance with exemplary embodiments of the disclosure.

[0018] FIG. **6** illustrates another structure according to yet additional exemplary embodiments of the present disclosure.

[0019] FIG. **7** illustrates yet another structure according to additional exemplary embodiments of the present disclosure.

[0020] It will be appreciated that elements in the figures are illustrated for simplicity and clarity and have not necessarily been drawn to scale. For example, the dimensions of some of the elements in the figures may be exaggerated relative to other elements to help to improve understanding of illustrated embodiments of the present disclosure

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS OF THE DISCLOSURE

[0021] The description of exemplary embodiments of methods, structures, and devices provided below is merely exemplary and is intended for purposes of illustration only; the following description is not intended to limit the scope of the disclosure or the claims. Moreover, recitation of multiple embodiments having stated features is not intended to exclude other embodiments having additional features or other embodiments incorporating different combinations of the stated features.

[0022] The present disclosure relates, generally, to methods of forming layers, such as a crystalline layer, including germanium and tin, overlying a substrate. The germanium-tin layers may include additional elements, such as silicon and/or carbon, which form part of a crystalline lattice with the germanium-tin layer.

[0023] As used herein, a "substrate" refers to any material having a surface onto which material can be deposited. A substrate may include a bulk material such as silicon (e.g., single crystal silicon, single crystal germanium, or other semiconductor wafer) or may include one or more layers overlying the bulk material. Further, the substrate may

include various topologies, such as trenches, vias, lines, and the like formed within or on at least a portion of a layer of the substrate. Exemplary substrates include a silicon wafer, a layer comprising germanium overlying silicon, and a layer comprising germanium silicon tin overlying silicon.

[0024] FIG. **1** illustrates a system **100** suitable for forming germanium-tin using the methods described herein. In the illustrated example, system **100** includes a reactor **102**, a germane precursor source **104**, a tin precursor source **106**, an optional third precursor source **108** (e.g., for inclusion of silicon or other element(s) in a formed layer), a purge and/or carrier gas source **110**, an optional mixer **112**, an optional intake plenum **114**, and a vacuum source **116**. Sources **104-110** may be coupled to mixer **112** or reactor **102** using lines **118-132** and valves **134-140**. Although not illustrated, a system, such as system **100**, may include additional sources and corresponding delivery lines for dopants (e.g., n-type dopants such as phosphorous or arsenic or p-type dopants such as boron). Additionally or alternatively, the dopants may be included in one or more of the precursor sources **102-108**.

[0025] Reactor **102** may be a standalone reactor or part of a cluster tool. Further, reactor **102** may be dedicated to a particular process, such as a deposition process, or reactor **102** may be used for other processes—e.g., for layer passivation and/or etch processes. For example, reactor **102** may include a reactor typically used for epitaxial chemical vapor deposition (CVD) processing, such as an Epsilon® 2000 Plus or Intrepid™ XP, available from ASM, and may include direct plasma, and/or remote plasma apparatus (not illustrated) and/or various heating systems, such as radiant, inductive, and/or resistive heating systems (also not illustrated). Using a plasma may enhance the reactivity of one or more precursors. The illustrated reactor is a single-substrate, horizontal-flow reactor, which enables laminar flow of reactants over a substrate **142**, with low residence times, which in turn facilitates relatively rapid sequential substrate processing. An exemplary CVD reactor suitable for system **100** is described in U.S. Pat. No. 7,476,627, issued to Pomarede et al. on Jan. 13, 2009, the contents of which are hereby incorporated herein by reference, to the extent such contents do not conflict with the present disclosure. Although illustrated as a horizontal-flow reactor, reactor **102** in accordance with alternative embodiments may include a vertical flow, for example, flow emanating from a showerhead and flowing substantially downward onto a substrate.

[0026] An operating pressure of a reaction chamber **144** of reactor **102** may vary in accordance with various factors. Reactor **102** may be configured to operate at near ambient atmospheric pressure. Operating near ambient atmospheric pressure allows for relatively fast film formation. By way of examples, an operating pressure of reactor **102** during layer formation steps ranges from about 300 Torr to about 850 Torr, about 400 Torr to about 800 Torr, about 500 Torr to about 760 Torr, ambient atmospheric pressure±about 20 Torr, ambient atmospheric pressure±about 10 Torr, or ambient atmospheric pressure±about 5 Torr.

[0027] Source **104** includes germane (GeH_4) and may optionally include one or more dopant compounds, such as compounds typically used to fabricate photonic and/or semiconductor devices. Exemplary p-type dopant compounds include B_2H_6 and exemplary n-type dopant compounds include AsH_3.

[0028] Use of germane is advantageous over other precursors, such as digermane, trigermane, and other higher-order germanes, used to form germanium-tin layers, because germane is relatively selective when mixed with various carrier gasses (e.g., hydrogen, nitrogen, or the like) and can also be relatively selective (e.g., using various process conditions as set forth herein), even when dopants (e.g., p-type dopants) are used with the precursor. Also, germane is relatively safe, compared to higher order digermanes, and thus can be used and/or transported in higher quantities, compared the higher order germanes. Also, germane is used as a precursor for other layers, such as germanium, and is more readily available and is less expensive, compared to higher-order germane compounds.

[0029] Tin precursor source **106** includes any compound suitable for providing tin to a germanium-tin layer. Exemplary tin precursors include tin chloride ($SnCl_4$), deuterated stannane (SnD_4), and methyl and/or halide substituted stannanes, such as compounds having a formula $Sn(CH_3)_{4-n}X_n$, in which X is H, D (deuterium), Cl, or Br and n is 0, 1, 2, or 3; $ZSn(CH_3)_{3-n}X_n$ in which Z is H or D, X is Cl or Br, and n is 0, 1, or 2; $Z_2Sn(CH_3)_{2-n}X_n$ in which Z is H or D, X is Cl or Br, and n is 0 or 1; or $SnBr_4$. Some exemplary tin precursors suitable for use with the present disclosure are discussed in more detail in application Ser. No. 13/783,762, filed Mar. 4, 2013, entitled TIN PRECURSORS FOR VAPOR DEPOSITION AND DEPOSITION PROCESSES, the contents of which are hereby incorporated herein by reference, to the extent such contents do not conflict with the present disclosure.

[0030] Optional third precursor source **108**, when used, includes a precursor for additional elements or compounds that may be included in a deposited layer. For example, precursor source **108** may include a silicon precursor, such as disilane, trisilane, tetrasilane, neopentasilane, and higher order silanes, a carbon precursor, such as H_3SiCH_3, $(H_3Si)_4C$, CH_4, H_3GeCH_3, and $(H_3Ge)_2CH_2$, and/or may include one or more compounds suitable as a dopant precursor/compound. If source **108** includes a silicon precursor, then, as noted above, system **100** may include additional dopant sources and corresponding supply lines.

[0031] Gas source **110** may include any suitable purge or carrier gas. Exemplary gasses suitable as carrier and purge gasses include nitrogen, argon, helium, and hydrogen.

[0032] System **100** may include a gas distribution system. An exemplary gas distribution system, which allows for fast switching between gasses (e.g., from sources **104-110**) is set forth U.S. Pat. No. 8,152,922 to Schmidt et al., issued Apr. 10, 2012, entitled "Gas Mixer and Manifold Assembly for ALD Reactor," the contents of which are hereby incorporated herein by reference, to the extent the contents do not conflict with the present disclosure. The gas distribution system may be used to, for example, mix one or more precursor gasses and a carrier gas (which may be the same or different from a purge gas from gas source **108**) prior to the gasses reaching plenum **114** or reactor **102**.

[0033] Turning now to FIG. **2**, an exemplary method **200** of forming a crystalline germanium-tin layer is illustrated. Method **200** comprises, consists essentially or, or consists of the steps of providing a gas-phase reactor (step **202**), providing a germane source coupled to the gas-phase reactor (step **204**), providing a tin precursor source coupled to the gas-phase reactor (step **206**), providing a substrate within a reaction chamber of the gas-phase reactor (step **208**), pro-

viding germane and a tin precursor to the reaction chamber, wherein a ratio of the tin precursor to the germane is less than 0.1 (step **210**), and forming a crystalline layer of germanium tin on a surface of the substrate (step **212**). Method **200** can be used to form (e.g., selectively grow) germanium-tin films without requiring an etchant during, and/or before the forming a crystalline layer of germanium tin on a surface of the substrate step **212**.

[0034] During step **202**, a gas-phase reactor, such as a CVD reactor suitable for epitaxial growth is provided. The reactor may be a single-substrate, laminar flow reactor. Such reactors are available from ASM, such as the Epsilon® 2000 Plus and the Intrepid™ XP.

[0035] During steps **204** and **206**, suitable germane (GeH_4) and tin precursor sources are coupled to the reactor. As noted above, the germane source may include dopant compounds, such as p-type dopant compounds. Or, dopants may be supplied from additional sources (not illustrated). The tin precursor source may include, for example, tin chloride and/or tin deuteride and/or other tin precursors noted herein.

[0036] During step **208**, a substrate is loaded into a reaction chamber of a reactor. The substrate may be received from a loading load lock of a reactor system and transported to the reaction chamber using a suitable transfer mechanism.

[0037] At step **210**, the tin precursor and germane are provided to a reaction chamber of a reactor. The tin precursor and germane may be mixed (e.g., at mixer **112**) prior to entering the chamber. Additionally, the germane and tin precursor may be individually or in combination mixed with one or more carrier gasses. The germane and/or tin precursor may be mixed with a carrier upstream of the reaction chamber, such as at a mixer, or upstream of a mixer.

[0038] As noted above, use of germane has several advantages over use of typical precursors used to form layers including germanium and tin. It was surprisingly and unexpectedly found that using relatively high partial pressures of germane relative to the tin precursor formed high-quality, crystalline germanium-tin layers. In accordance with various aspects of exemplary embodiments of the disclosure, the step of providing germane and a tin precursor to the reaction chamber includes providing a mixture of a tin precursor and the germane having a volumetric ratio of tin precursor to germane of about 0.001 to about 0.1, about 0.005 to about 0.05, less than about 0.1, or less than about 0.05.

[0039] During step **212**, a crystalline layer (e.g., an epitaxial layer) is formed overlying a substrate. Exemplary reaction chamber temperatures during step **212** may range from about 200° C. to about 500° C., about 250° C. to about 450° C., or about 300° C. to about 420° C. And, exemplary reaction chamber pressures during this step may range from about 300 Torr to about 850 Torr, about 400 Torr to about 800 Torr, about 500 Torr to about 760 Torr, ambient atmospheric pressure±about 20 Torr, ambient atmospheric pressure±about 10 Torr, or ambient atmospheric pressure±about 5 Torr. Operating at relatively high pressures allows rapid throughput of structures including the germanium-tin films.

[0040] Step **212** may include forming a layer comprising germanium silicon tin. In these cases, a silicon precursor is provided to the reaction chamber. Exemplary silicon source precursors include disilane, trisiliane, tetrasilane, neopentasilane, and higher order silane compounds. Additionally or alternatively step **212** includes forming a layer including carbon. In these cases, a carbon source can include one or more of be H_3SiCH_3, $(H_3Si)_4C$, CH_4, H_3GeCH_3, and $(H_3Ge)_2CH_2$. The silicon and/or carbon precursor or other suitable precursor may be mixed with a carrier gas and optionally mixed with one or more other precursors as described herein. Step **212** can include selective deposition without use of an etchant during or before step **212**.

[0041] Method **200** may also include steps of forming an insulating layer overlying a substrate and forming a via within the insulating layer. Exemplary techniques of forming an insulating layer and a via within the insulating layer are described in more detail below. In these cases, the germanium-tin layer may be selectively formed on the substrate within the via, as described below—e.g., without the use of an additional step of exposing the substrate to an etchant to be able to selectively deposit the germanium-tin film.

[0042] FIG. **3** illustrates another method **300** in accordance with additional embodiments of the disclosure. Method **300** comprises, consists essentially of, or consists of the steps of providing a gas-phase reactor (step **302**), providing a substrate within a reaction chamber of the gas-phase reactor (step **304**), and forming a crystalline layer comprising germanium tin on a surface of the substrate using one or more precursors comprising germane (step **306**). Similar to method **200**, method **300** can be used to form (e.g., selectively) germanium-tin layers without requiring an etchant during or before the step of forming a crystalline layer comprising germanium tin.

[0043] During step **302**, a reactor suitable for growing a crystalline layer comprising germanium tin is provided. The reactor may include any reactor described herein, such as a horizontal-flow epitaxial CVD reactor.

[0044] During step **304**, a substrate is provided within a reaction chamber of a reactor. Step **304** may be the same as or similar to step **208** of method **200**.

[0045] At step **308**, a crystalline layer comprising germanium tin is formed. In accordance with various aspects of exemplary embodiments of the disclosure, the step of forming a layer comprising germanium tin includes providing a mixture of a tin precursor and the germane having a volumetric ratio of tin precursor to germane of about 0.001 to about 0.1, about 0.005 to about 0.05, less than about 0.1, or less than about 0.05. In accordance with further aspects, a reaction chamber temperature during the step of forming a crystalline layer comprising germanium tin ranges from about 200° C. to about 500° C., about 250° C. to about 450° C., or about 300° C. to about 420° C. And, in accordance with yet further aspects, a reaction chamber pressure during the step of forming a layer comprising germanium tin ranges from about 300 Torr to about 850 Torr, about 400 Torr to about 800 Torr, about 500 Torr to about 760 Torr, ambient atmospheric pressure±about 20 Torr, ambient atmospheric pressure±about 10 Torr, or ambient atmospheric pressure±about 5 Torr.

[0046] Step **306** may include forming a layer comprising silicon germanium tin. In these cases, a silicon precursor is provided to the reaction chamber. Exemplary silicon source precursors include disilane, trisiliane, tetrasilane, neopentasilane, and higher order silane compounds. Additionally or alternatively, step **306** includes forming a germanium tin layer comprising carbon. Exemplary carbon precursors include one or more of H_3SiCH_3, $(H_3Si)_4C$, CH_4, H_3GeCH_3, and $(H_3Ge)_2CH_2$.

[0047] Method **300** may also include optional steps **308** and **310** of forming an insulating layer overlying a substrate (step **308**) and forming a via within the insulating layer. During step **308**, any suitable insulating layer, such as silicon oxide or silicon nitride may be deposited onto the substrate. Then, during step **310**, one or more vias may be formed within the insulating layer. Reactive ion etching or other suitable technique may be used to form the one or more vias.

[0048] In the cases where steps **308** and **310** are performed, the crystalline layer formed during step **306** may be selectively formed within the vias. As noted above, use of a germane precursor is advantageous because it is relatively selective when using a variety of carrier gasses, such as hydrogen and when the layer includes one or more dopants, such as p-type dopants. As noted above, method **300** can be used to selectively deposit germanium-tin films without requiring use of an etchant.

[0049] The layers formed using method **200** or method **300** (e.g., during steps **212** or **306**) may include, for example, greater than 1 at %, greater than 2 at %, or greater than 5 at %, or between about 0 at % and about 15 at % tin, about 2 at % and about 15 at % tin, about 0.2 at % and about 5 at % tin, or about 0.2 at % and about 15 at % tin. When the layer of crystalline germanium tin includes silicon, the layer may include greater than 0 at % silicon, greater than about 1 at % silicon, or between about 1 at % silicon and about 20 at % silicon, about 2 at % silicon and about 16 at % silicon, or about 4 at % silicon and about 12 at % silicon. When the film includes carbon, the films can include additional tin. Exemplary germanium tin films that include carbon can include from about 0.2 to about 20 at % tin, about 0 to about 20 at % silicon, and about 0 to about 10 at % carbon.

[0050] FIG. **4** illustrates a transmission electron microscope image of a structure **400** formed in accordance with various embodiments of the invention, such as method **200** or method **300**. Structure **400** includes a silicon substrate **402**, a germanium buffer layer **404** overlying substrate **402**, and a germanium-tin layer **406** formed using germane as a precursor. In the illustrated example, layer **406** includes about 8 at % tin. No threading defects were observed in the illustrated structure.

[0051] FIG. **5** illustrates a (004) rocking scan of a structure, such as structure **400**. The scan illustrates discrete peaks associated with the germanium-tin layer, the germanium layer, and the silicon substrate. As illustrated, the germanium-tin peak is associated with Pendellosung fringes, indicating a high degree of crystallinity in the germanium-tin layer.

[0052] Turning now to FIG. **6**, a structure **600** in accordance with additional exemplary embodiments of the disclosure is illustrated. Structure **600** includes a substrate **602**, an insulating layer **604**, a via **606** formed within layer **604**, a germanium layer **608** (e.g., epitaxially formed overlying substrate **602**), and a germanium-tin layer **610** (e.g., epitaxially formed overlying layer **608**). Layers **608** and/or **610** may be selectively formed within via **606**—e.g., using method **200** or method **300**.

[0053] FIG. **7** illustrates yet another structure **700** in accordance with additional embodiments of the disclosure. Structure **700** includes a substrate **702**, a first layer (e.g., one or more of a germanium-silicon-tin layer, a germanium-silicon-carbon-tin layer, a germanium tin layer, a germanium-silicon layer, or a germanium layer) **704**, a germanium-tin layer **706**, and a second layer (e.g., one or more of a germanium-silicon-tin layer, a germanium-silicon-carbon-tin layer, a germanium tin layer, a germanium-silicon layer, or a germanium layer) **708**. In the illustrated example, germanium-tin layer **706** is between first layer **704** and second layer **708**; layers **704** and **708** can comprise the same material (with the same or different compositions) or different materials. Table 1 below illustrates exemplary combinations of layer **704** and layer **708** materials.

TABLE 1

Example	Layer 704	Layer 708
1	GeSiCSn	GeSiCSn
2	$GeSn_x$	$GeSn_y$ $(x \neq y)$
3	$GeSi_x$	$GeSi_y$ $(x \neq y)$
4	Ge	Ge

[0054] Layers **704**-**708** may be formed according to methods described herein. Further, although not illustrated, one or more layers **704**-**708** may be formed within a via of an insulating material, as described above in connection with FIG. **6**. By way of examples, first layer **704** can comprise $GeSn_x$ and second layer **708** can comprise $GeSn_y$, where x and y are not equal.

[0055] It is to be understood that the configurations and/or approaches described herein are exemplary in nature, and that these specific embodiments or examples are not to be considered in a limiting sense. The specific routines or methods described herein may represent one or more of any number of processing strategies. Thus, the various acts illustrated may be performed in the sequence illustrated, performed in other sequences, performed simultaneously, or omitted in some cases.

[0056] The subject matter of the present disclosure includes all novel and nonobvious combinations and subcombinations of the various processes, systems and configurations, and other features, functions, acts, and/or properties disclosed herein, as well as any and all equivalents thereof.

I claim:

1. A method of forming a crystalline germanium-tin layer, the method comprising the steps of:

providing a gas-phase reactor;

providing a germane source coupled to the gas-phase reactor;

providing a tin precursor source coupled to the gas-phase reactor;

providing a substrate within a reaction chamber of the gas-phase reactor;

providing germane and a tin precursor to the reaction chamber, wherein a ratio of the tin precursor to the germane is less than 0.1; and

forming a crystalline layer of germanium tin on a surface of the substrate in a reaction chamber at a pressure between about 300 Torr and about 850 Torr.

2. The method of forming a crystalline germanium-tin layer according to claim **1**, wherein the crystalline layer of germanium tin comprises silicon and the method further comprises:

providing a silicon source precursor.

3. The method of forming a crystalline germanium-tin layer according to claim **2**, wherein the step of providing a silicon source precursor comprises providing a precursor

selected from the group consisting of: disilane, trisiliane, tetrasilane, and neopentasilane.

4. The method of forming a crystalline germanium-tin layer according to claim **1**, wherein, during the step of growing a crystalline layer of germanium tin on a surface of the substrate, an operating pressure of the reaction chamber is about 400 Torr to about 800 Torr.

5. The method of forming a crystalline germanium-tin layer according to claim **1**, wherein, during the step of growing a crystalline layer of germanium tin on a surface of the substrate, an operating pressure of the reaction chamber is about 500 Torr to about 760 Torr.

6. The method of forming a crystalline germanium-tin layer according to claim **1**, wherein, during the step of growing a crystalline layer of germanium tin on a surface of the substrate, an operating pressure of the reaction chamber is ambient atmospheric pressure±about 20 Torr.

7. The method of forming a crystalline germanium-tin layer according to claim **1**, wherein a ratio of the tin precursor to the germane is about 0.001 to about 0.1.

8. The method of forming a crystalline germanium-tin layer according to claim **1**, wherein, during the step of growing a crystalline layer of germanium tin on a surface of the substrate, an operating temperature within the reaction chamber is about 200° C. to about 500° C.

9. The method of forming a crystalline germanium-tin layer according to claim **1**, wherein, during the step of growing a crystalline layer of germanium tin on a surface of the substrate, an operating temperature within the reaction chamber is about 250° C. to about 450° C.

10. The method of forming a crystalline germanium-tin layer according to claim **1**, wherein the step of providing a tin precursor source comprises providing a tin source selected from the group consisting of $SnCl_4$, SnD_4, and a methyl and halide substituted stannate.

11. The method of forming a crystalline germanium-tin layer according to claim **1**, wherein the step of growing a crystalline layer of germanium tin on a surface of the substrate comprises growing a crystalline layer comprising about 2 at % to about 15 at % tin.

12. The method of forming a crystalline germanium-tin layer according to claim **1**, wherein a ratio of the tin precursor to the germane precursor is less than 0.05.

13. A method of forming a structure comprising a germanium-tin layer, the method comprising the steps of:
- providing a gas-phase reactor;
- providing a substrate within a reaction chamber of the gas-phase reactor; and
- forming a crystalline layer comprising germanium tin on a surface of the substrate using one or more precursors comprising germane, wherein a pressure within the reaction chamber is between about 300 Torr and about 850 Torr.

14. The method of forming a structure comprising a germanium-tin layer of claim **13**, wherein the substrate comprises a layer comprising germanium overlying silicon.

15. The method of forming a structure comprising a germanium-tin layer of claim **13**, wherein the germanium-tin layer comprises from about 2 at % tin to about 15 at % tin.

16. The method of forming a structure comprising a germanium-tin layer of claim **13**, wherein the step of forming does not include exposure of the substrate to an etchant.

17. The method of forming a structure comprising a germanium-tin layer of claim **13**, wherein the substrate comprises a layer comprising germanium silicon tin overlying silicon.

18. The method of forming a structure comprising a germanium-tin layer of claim **13**, further comprising the steps of:
- forming an insulating layer overlying the substrate;
- forming a via within the insulating layer, and
- selectively forming the crystalline layer comprising germanium tin within the via.

19. A structure comprising a crystalline layer of germanium tin formed according to the method of claim **13**.

20. The structure comprising a crystalline layer of germanium tin of claim **19**, wherein the structure comprises a germanium tin layer between two layers of germanium silicon tin.

* * * * *