LOW TEMPERATURE DEPOSITION OF PHASE CHANGE MEMORY MATERIALS

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

[0001] The present invention relates to low temperature deposition of phase change memory materials, by deposition techniques such as chemical vapor deposition and atomic layer deposition, to form microelectronic device structures.

DESCRIPTION OF THE RELATED ART

[0002] Phase Change Memory (PCM) refers to a novel memory technology based on chalcogenide materials that undergo a phase change via a heater and are read out as "0" or "1" based on their electrical resistivity, which changes in correspondence to whether the phase change material in the cell is in the crystalline or amorphous phase.

[0003] The chalcogenide materials used in PCM comprise a large number of binary, ternary, and quaternary alloys of a number of metals and metalloids. Examples include GeSbTe, GeSbInTe, and many others. As contained herein, the identification of compounds such as GeSbTe and GeSbInTe without appertaining stoichiometric coefficients or values will be understood as a general representation inclusive of all forms of such compounds containing the specified elements, and inclusive of all appertaining stoichiometric coefficients and values. For example, the reference to GeSbInTe includes $Ge_2Sb_2Te_5$, as well as all other stoichiometric forms of such compound GeSbInTe.

[0004] PCM devices require relatively pure chalconide material alloys, with well controlled composition. Current processes for making PCM devices utilize physical vapor deposition to deposit thin films of these chalconide materials. The thick planar structures of the current generation are well-served by PVD.

[0005] As device geometries shrink, the chalconide material must be deposited into vias in order to control the phase transition and the necessary heat transfer. Such implementation of chalconide materials can also be beneficial in improving reliability of small volume devices.

[0006] A major deficiency in the current art is the requirement of high deposition temperatures needed for conventionally employed alkyl (e.g., Me_3Sb, Me_2Te) or halide sources. These temperatures are typically well in excess of 300°C, and may for example be on the order of 500°C. Such high temperatures substantially exceed the thermal budget for device

integration and can result in the evaporation of the chalcogenide, rendering the product PCM device deficient or even useless for its intended purpose.

[0007] The art continues to seek improvements in the art of PCM devices, including improvements in manufacturing techniques and improved precursors useful for forming memory device structures.

SUMMARY OF THE INVENTION

[0008] The present invention relates to systems and processes for deposition of phase change memory material on substrates, for fabrication of a phase change memory devices.

[0009] The invention relates in one aspect to a method of forming a phase change memory material on a substrate, comprising contacting the substrate with precursors for a phase change memory chalcogenide alloy under conditions producing deposition of the chalcogenide alloy on the substrate, wherein such conditions comprise temperature below 350°C and such contacting comprises chemical vapor deposition or atomic layer deposition.

[0010] In another aspect, the invention relates to a method of forming a germanium-antimony-tellurium phase change memory material on a substrate, comprising contacting the substrate with precursors for a phase change memory germanium-antimony-tellurium alloy under conditions producing deposition of the germanium-antimony-tellurium alloy on the substrate, wherein such conditions comprise temperature below 350°C and such contacting comprises chemical vapor deposition or atomic layer deposition, with the precursors comprising at least one halide precursor.

[0011] Yet another aspect of the invention relates to a system for fabricating a phase change memory device including a phase change memory material on a substrate, such system including a deposition tool adapted to receive precursors from precursor supply packages, and precursor supply packages containing precursors for forming a phase change memory chalcogenide alloy under conditions producing deposition of the chalcogenide alloy on the substrate, wherein such deposition tool is adapted for chemical vapor deposition or atomic layer deposition operation under conditions comprising deposition temperature below 350°C.

[0012] A further aspect of the invention relates to a system for fabricating a germanium-antimony-tellurium phase change memory device including a germanium-antimony-tellurium phase change memory material on a substrate, such system comprising a deposition tool adapted to receive precursors from precursor supply packages, and precursor supply packages containing germanium, antimony and tellurium precursors for forming a germanium-antimony-tellurium phase change memory chalcogenide alloy under conditions producing deposition of the chalcogenide alloy on the substrate, wherein the deposition tool is adapted for chemical vapor deposition or atomic layer deposition operation under conditions comprising deposition

temperature below 350°C, and at least one of the precursor supply packages contains a halide precursor.

[0013] Additional aspects of the invention relate to PCM films formed in accordance with the present invention; corresponding devices; tellurium complexes, germanium complexes, germanium tellurides, and processes utilizing same for forming GST films; compositions including combinations of precursors for forming PCM films; and packaged precursors adapted for coupling to a deposition tool comprising such compositions, as hereinafter more fully described.

[0014] Other aspects, features and embodiments of the invention will be more fully apparent from the ensuing disclosure and appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] FIG. 1 is a schematic representation of a phase change memory device comprising a phase change memory material film formed on a substrate, according to one embodiment of the invention.

[0016] FIG. 2 is a schematic representation of a process installation including a deposition tool for depositing a phase change memory material on a substrate in accordance with one embodiment of the invention, from respective precursor supply packages of germanium precursor, antimony precursor and tellurium precursor.

DETAILED DESCRIPTION OF THE INVENTION, AND PREFERRED EMBODIMENTS THEREOF

[0017] The present invention relates to deposition of phase change memory materials to form PCM devices.

[0018] More specifically, the invention in one aspect relates to chalcogenide alloys, and to their low temperature deposition e.g., by chemical vapor deposition (CVD) or atomic layer deposition (ALD), to form PCM devices. CVD and ALD methods are employed in the practice of the present invention to achieve scalability to large area wafers and for composition control. Preferred chalconide alloys include alloys including two or more of germanium, antimony and tellurium.

[0019] As used herein, the term "low temperature" means a temperature below 350°C. The temperature at which the PCM material is deposited is preferably less than 300°C, more preferably less than 250°C and most preferably less than 225°C.

[0020] In one aspect, the invention relates to a method of forming a phase change memory material on a substrate, comprising contacting the substrate with precursors for a phase change

memory chalcogenide alloy under conditions producing deposition of the chalcogenide alloy on the substrate, wherein such conditions comprise temperature below 350°C and such contacting comprises chemical vapor deposition or atomic layer deposition.

[0021] The advantages of chemical vapor deposition and atomic layer deposition at low deposition temperature in the fabrication of PCM devices include substantial improvement of read/re-write times in small devices, as a result of the high conformality of the deposited PCM material.

[0022] Such method may further include fabricating said phase change memory material is into a phase change memory device.

[0023] The chalcogenide metal and metal alloy precursors that are advantageously used for forming PCM films and devices include:

(i) butyl- and propyl-substituted alkyl hydrides of the formula R_xMH_{y-x} wherein: R is butyl or propyl, with R preferably being t-butyl or isopropyl; M is a metal having an oxidation state y, e.g., Ge, Sb or Te; x> 1; and (y-x) may have a zero value;

(ii) butyl- and propyl-substituted alkyl halides of the formula R_xMX_{y-x} wherein: R is butyl or propyl, with R preferably being t-butyl or isopropyl; X is F, Cl, or Br; M is a metal having an oxidation state y, e.g., Ge, Sb or Te; x> 1; and (y-x) may have a zero value;

(iii) digermanes of the formula $Ge_2(R^1)_6$ wherein the R^1 substituents are the same as or different from one another, and each R^1 is independently selected from among H, C_1-C_8 alkyl, C_1-C_8 fluroalkyl, C_6-C_{12} aryl, C_6-C_{12} fluoroaryl, C_3-C_8 cycloalkyl, and C_3-C_8 cyclo-fluoroalkyl, with illustrative digermanes including Ge_2H_6, Ge_2Me_6, Ge_2Et_6. Ge_2iPr_6, Ge_2tBu_6, $Ge_2(SiMe_3)_6$ and Ge_2Ph_6, wherein Me = methyl, Et = ethyl, iPr = isopropyl, Bu = butyl and Ph = phenyl;

(iv) digermanes of the formula $Ge_2(R^1)_4$ wherein the R^1 substituents are the same as or different from one another, and each R^1 is independently selected from among H, C_1-C_8 alkyl, C_1-C_8 fluroalkyl, C_6-C_{12} aryl, C_6-C_{12} fluoroaryl, C_3-C_8 cycloalkyl, and C_3-C_8 cyclo-fluoroalkyl, with illustrative digermanes including Ge_2Ph, wherein Ph = phenyl;

(v) ring compounds including Ge as a ring constituent, e.g., five-member ring compounds;

(vi) Ge(II) compounds of the formula $Ge(Cp(R^2)_5)_2$ wherein Cp is cyclopentadienyl having R^2 substituents on the cyclopentadienyl ring carbon atoms, wherein the R^2 substituents are the same as or different from one another, and each R^2 is independently selected from among H, C_1-C_8 alkyl, C_1-C_8 fluoroalkyl, C_1-C_8 alkylamino, C_6-C_{12} aryl, C_6-C_{12} fluoroaryl, C_3-C_8 cycloalkyl, and C_3-C_8 cyclo-fluoroalkyl;

(vii) Ge(II) compounds of the formula $Ge(R^3)_2$, wherein the R^3 substituents are the same as or different from one another, and each R^3 is independently selected from among silyl, silylalkyl and substituted silylalkyl, e.g., wherein each R^3 is $-CH(SiMe_3)_2$;

(viii) Sb compounds of the formula $Sb(R^4)_3$ wherein R^4 is phenyl, or substituted phenyl whose substituent(s) on the phenyl ring are independently selected from among H, C_1-C_8 alkyl, and C_1-C_8 fluroalkyl;

(ix) Sb and Te analogs of germanium compounds (iii), (iv), (v), (vi), and (vii);

(x) Ge and Te analogs of antimony compounds (viii); and

(xi) GeI_4, SbI_3 and TeI_2.

It will be appreciated that the component metal species may have different oxidation states in the various above-mentioned compounds.

[0024] The above listing of precursors, in reference to the digermanes, germane ring compounds and Ge(II) compounds identified above, may further include corresponding analogs wherein Ge is replaced by Sb or Te. Likewise, the above listing of precursors, in reference to the Sb compounds identified above, may further include corresponding analogs wherein Sb is replaced by Ge or Te.

[0025] Various of the above compounds, e.g., antimony compounds of group (viii), are light-sensitive in character and amenable to light/UV-activated processes for PCM deposition. Such compounds thus may be exposed to radiation for activation during the deposition, involving visible light exposure or ultraviolet light exposure.

[0026] The deposition may be carried out in a chamber of a deposition reactor, as a deposition tool that is arranged and adapted for production of PCM products. The invention contemplates the provision of doping of the deposited PCM material, with dopant species that improve the character of the deposited material for PCM applications. For example, oxygen doping may be employed, or doping with other implanted species, to provide PCM films of superior character. The invention also contemplates the in situ doping of the PCM material at the time of its formation on the substrate.

[0027] A still further aspect of the invention relates to a system for fabricating a phase change memory device including a phase change memory material on a substrate, such system including a deposition tool adapted to receive precursors from precursor supply packages, and precursor supply packages containing precursors for forming a phase change memory chalcogenide alloy under conditions producing deposition of the chalcogenide alloy on the substrate, wherein such deposition tool is adapted for chemical vapor deposition or atomic layer deposition operation under conditions comprising deposition temperature below 350°C.

[0028] The chalcogenide metal and alloy precursors described above have been discovered to provide superior deposition when utilized in CVD and ALD processes, with lower deposition temperatures employed in the CVD or ALD process than have heretofore been achievable using physical vapor deposition techniques. Such lower temperature deposition capability in CVD and ALD processes is realized as a result of the chalcogenide metal or metal alloy compound undergoing beta hydrogen elimination reaction in the CVD and ALD deposition processes, e.g.,

involving iso-propyl and/or t-butyl groups. The digermane compositions benefit from the low bond energy of Ge-Ge. The Ge(II) compounds are easier to reduce than Ge(IV) compounds.

[0029] The chalcogenide metal or metal alloy precursors for the PCM material deposition may be provided in any suitable form, including solids, liquids and gases, and multiphase compositions, depending on the specific precursors involved. The precursors can be delivered to the deposition chamber, for carrying out CVD or ALD therein, by any suitable delivery techniques, dependent on their phase characteristics, required flow rate, temperature, etc. Co-reactants may be employed with the precursors to effect the CVD or ALD operation.

[0030] The precursor and co-reactant species can be supplied from material storage and dispensing packages of any suitable type, depending on the phase and the material characteristics of the precursor involved. For example, the storage and dispensing packages may include supply vessels of a type commercially available from ATMI, Inc. (Danbury, CT, USA) under the trademarks SDS, VAC, SAGE or ProE-Vap. The storage and dispensing packages in preferred practice can comprise sub-atmospheric pressure systems providing improved safety and cost of ownership character, in relation to conventional high pressure material sources, such as the aforementioned packages available under the SDS, VAC and SAGE trademarks.

[0031] In such system and method, at least one of the precursors can be delivered for the contacting from a storage and dispensing vessel containing at least one of physical adsorbent, a gas low pressure regulator, a heat transfer structure, or an ionic liquid. The storage and dispensing vessel advantageously is adapted to contain precursor at sub-atmospheric pressure.

[0032] For example, the precursor when in a solid or liquid form can be volatilized to form a precursor vapor which then is flowed to the deposition chamber and contacted with the substrate on which the PCM device is to be fabricated. The substrate in such instance can be suitably heated, by a susceptor or other heating arrangement, whereby the contact between the precursor vapor and the substrate results in the deposition of a PCM material, e.g., in a film, on the substrate. As used in such context, the term "film" means a layer of the PCM material that is below 1 micrometer in thickness.

[0033] In the delivery operation associated with the CVD or ALD process, wherein the precursors are in a liquid state, separate bubblers or other delivery equipment can be employed for each precursor. Liquid injection of mixtures of precursors can be advantageously employed to manage disparate volatilities of the different precursors and to deliver precise volumetric flows of precursor medium having a desired composition. In the precursor delivery, the precursors may be utilized in the form of neat liquids, or precursor/solvent mixtures may be employed, in which the precursor is dissolved or suspended in a compatible solvent medium. Suitable solvents for such purpose can be identified by solubility and compatibility data for the

precursor(s) of interest, or by routine solvent screening determinations, within the skill of the art, based on the disclosure herein.

[0034] The PCM material is deposited on the substrate by CVD or ALD techniques, in accordance with the invention.

[0035] When chemical vapor deposition is employed to form the PCM material layer on the substrate, continuous CVD in a thermal mode may be employed, with the CVD operation being conducted in a suitable CVD reactor chamber. The precursor vapor can be delivered in a carrier gas stream including the precursor vapor, and a carrier gas such as hydrogen, or other reducing gas, or an inert gas, or an oxidant, as may be desirable in a specific application.

[0036] When atomic layer deposition or pulsed deposition is used, a dose step involving introduction of the precursor vapor is alternated with injection into the deposition chamber of a co-reactant. The co-reactant can be of any suitable type, as effective to provide a PCM material layer of desired character on the substrate.

[0037] In one embodiment, the alternatingly introduced co-reactant is a hydrogen plasma, or other plasma co-reactant.

[0038] Alternatively, other activation techniques can be employed, such as ultraviolet (UV) radiation or other light source "tuned" to the precursor to effect the deposition of the desired PCM material. Light used for such purpose can be continuous with the precursor introduction, or may be dosed separately into the deposition chamber to avoid gas-phase reactions.

[0039] The pulsed introduction of reagents into the deposition chamber in atomic layer deposition operation can include introduction of a reductive co-reactant in alternation with the introduction of the metal or metal alloy precursor. The reductive co-reactant may for example include GeH_4.

[0040] The invention further contemplates use of a reductive co-reactant that is activatable by radiation exposure. Further, in ALD processes in accordance with the invention, the precursor for formation of the PCM material on the substrate is alternatingly pulsed into the deposition chamber. Thus, in instances in which the PCM material is deposited on a substrate in a pulsed introduction for contacting the substrate, it may be advantageous in some embodiments to utilize radiation to activate the PCM material and/or a co-reactant, e.g., to pulse the radiation source so that the PCM material or co-reactant are activated. Alternatively, if both PCM material and the co-reactant are radiation-activatable, then it may be desirable to maintain radiation generation and exposure throughout the deposition operation. As a still further variation, it may be desirable in some instances to pulse the radiation so that the radiation source is pulsed on when the precursor is not turned on.

[0041] The specific deposition conditions (e.g., temperature, pressure, flow rate, composition, etc.) for the CVD or ALD operation that is employed to form the PCM layer on

the substrate can be readily determined within the skill of the art, based on the disclosure herein. CVD and ALD systems and techniques generally applicable to the present invention are more fully described in U.S. Provisional Patent Application 60/791,299 filed April 12, 2006 for "PRECURSOR COMPOSITIONS FOR ATOMIC LAYER DEPOSITION AND CHEMICAL VAPOR DEPOSITION OF TITANATE DIELECTRIC FILMS," the disclosure of which hereby is incorporated herein by reference, in its entirety.

[0042] In another specific aspect, the invention relates to low temperature deposition of germanium-antimony-tellurium (Ge-Sb-Te, or "GST") material on substrates by a halide precursor approach.

[0043] More specifically, the invention in such aspect relates to a method of forming a germanium-antimony-tellurium phase change memory material on a substrate, comprising contacting the substrate with precursors for a phase change memory germanium-antimony-tellurium alloy under conditions producing deposition of the germanium-antimony-tellurium alloy on the substrate, wherein such conditions comprise temperature below 350°C and such contacting comprises chemical vapor deposition or atomic layer deposition, with the precursors comprising at least one halide precursor.

[0044] Germanium, antimony and tellurium halides are volatile, and usefully employed for depositing GST thin films. In particular, their iodides are volatile and the corresponding metal-iodine bonds are weak. Accordingly, GeI_4, SbI_3 and TeI_2 are preferred halide source reagents for formation of GST films by CVD or ALD, e.g., using solid precursor delivery techniques.

[0045] Alternatively, one or two of the respective (Ge, Sb, Te) metals can be supplied from an iodide or other halide precursor compound(s), and the other one(s) of the metals can be supplied from alkyl metal compound(s). By way of specific illustrative example, the precursors can include GeI_4 and TeI_2 as halide precursors and $Sb(CH_3)_3$ as an alkyl precursor, to form the GST layer on the substrate. In such halide/alkyl precursor scheme, the alkyl(s) function as reducing agent(s) to eliminate iodo-methane, thereby enabling the achievement of clean GST films at low temperature.

[0046] The precursor delivery and deposition conditions can be readily determined, as appropriate for a given application of forming a GST material on a substrate, by simple empirical determination, to identify suitable temperatures, pressures, flow rates and concentrations to be employed for formation of suitable GST deposits on the substrate.

[0047] Thus, the invention contemplates a system for fabricating a germanium-antimony-tellurium phase change memory device including a germanium-antimony-tellurium phase change memory material on a substrate, such system comprising a deposition tool adapted to receive precursors from precursor supply packages, and precursor supply packages containing germanium, antimony and tellurium precursors for forming a germanium-antimony-tellurium phase change memory chalcogenide alloy under conditions producing deposition of the

chalcogenide alloy on the substrate, wherein the deposition tool is adapted for chemical vapor deposition or atomic layer deposition operation under conditions comprising deposition temperature below 350°C, and at least one of the precursor supply packages contains a halide precursor.

[0048] Substrates in the general practice of the present invention can be of any suitable type, and may be doped or undoped, semiconducting, semi-insulating, or of other suitable character for the device structure of the PCM product. Useful substrates in specific applications may include silicon, sapphire, gallium arsenide, gallium nitride, silicon carbide, and the like.

[0049] Referring now to the drawings, FIG. 1 is a schematic representation of a phase change memory device 10 comprising a phase change memory material film 14 formed on a substrate 12, according to one embodiment of the invention. The film 14 may comprise a germanium-antimony-tellurium (GST) film, and the substrate may comprise any suitable substrate compatible with such film.

[0050] FIG. 2 is a schematic representation of a process installation 100 including a deposition tool 120 for depositing a phase change memory material on a substrate in accordance with one embodiment of the invention, from respective precursor supply packages 102, 104 and 106 of germanium precursor (in vessel 102 labeled "Ge")), antimony precursor (in vessel 104 labeled "Sb") and tellurium precursor (in vessel 106 labeled "Te"). Each of the precursor supply packages includes a storage and dispensing vessel equipped with a valve head assembly including a flow control valve that may be manually or automatically operated, to dispense the appertaining precursor on demand at a desired flow rate.

[0051] As illustrated, each of the precursor supply vessels is coupled with flow circuitry for delivery of the dispensed precursor to the tool 120. Thus, the germanium precursor supply package 102 is coupled to the tool by line 110, the antimony precursor supply package 104 is coupled to the tool by line 112, and the tellurium precursors supplied package 106 is coupled to the tool by line 114. The tool can comprise a chemical vapor deposition (CVD) tool, an atomic layer deposition (ALD) tool, or other suitable tool adapted to receive the respective precursors and to form a PCM alloy film on a substrate, in the fabrication of a corresponding PCM device.

[0052] Another aspect of the invention relates to dopants in GeSbTe semiconductors, which can be formed in polycrystalline form and thereby accommodate a wider range of stoichiometries and dopants than typical semiconductors. Doping with nitrogen from levels of a few tenths of 1% to a few percent can be beneficial to properties of such materials in specific applications. Although the following discussion is directed primarily to nitrogen as the dopant species, it will be appreciated that the invention is not thus limited, and extends to the use of other dopant species.

[0053] Doping may be carried out by use of a reactant gas such as ammonia, or a vaporizable liquid such as an amine, to introduce nitrogen into the film. The reaction gas may be introduced separately, as a co-reactant, or it may be used as a carrier for the precursor(s), in which case it may also act as a stabilizing agent for the precursor. If this reactant gas reacts in the gas phase with the precursor(s), it may be necessary to pulse it alternately with the precursor(s), optionally with purge steps between pulses. Such pulsing may also be beneficial if it is desirable to have non-homogeneous layers, in order to achieve different dopant concentrations in contact with one or more electrodes for physical (sticking layer) or electrical (fermi layer adjustment) purposes.

[0054] Doping may also be affected by incorporation of nitrogen from a precursor. Process adjustments, such as conducting the deposition in certain "process windows" of reactor pressure, temperature, and/or gas flow can be employed to control the amount of N incorporated, thereby enabling adjustment of doping parameters. Specific precursors for one or more of Ge, Sb and Te materials may be employed for such purpose.

[0055] In another approach, specific co-reactants are employed to induce reaction pathways with one or more of the precursors that lead to the desired level of N incorporation. By way of example, use of NH_3 as a coreactant can be employed to enable lower temperature deposition and to promote N incorporation into the GST layer, compared to using H_2 as a co-reactant.

[0056] Another aspect of the invention relates to tellurium complexes with beta-diketiminate ligands, which overcome the problems that many tellurium precursors used in deposition applications are very oxygen-sensitive and light-sensitive, and have an unpleasant odor. By base stabilization with beta-diketiminate ligands, a tellurium precursor is obtained of a highly stable character with improved handling and shelf life characteristics, reduced odor, and sufficient volatility for deposition applications.

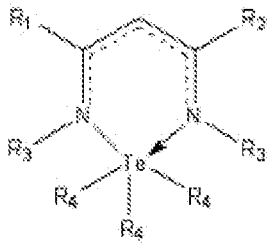
[0057] The tellurium diketiminate complexes of the invention can be used for CVD/ALD to form Te or Te-containing films. These compounds can be used in combination with Ge- and/or Sb-compounds to produce Te-Ge-, Te-Sb- or Ge-Sb-Te films in varied compositions. A general procedure to synthesize diketiminate ligands has been described in the literature, but such procedure is disadvantageous, since very bulky aryl substituents on the coordinating nitrogen atoms are required.

[0058] In contrast, we have discovered that smaller alkyl ligands as iso-propyl, n-butyl, tert-butyl or amine-substituted alkyl groups, as for example ethylene-dimethylamine, can be advantageously used to produce superior tellurium diketiminate precursors for CVD/ALD applications. Smaller substituents on the nitrogen donor atoms provide sufficient volatility to form good films at low temperature.

[0059] The ligands L can be used as the lithium salt or in a free imine form to synthesize the desired Te complexes. The lithium salt of the ligand can be reacted with TeX_4 (wherein X = Cl, Br, I) to generate $LTeX_3$ by salt elimination, which can then be reacted with either a lithium or a Grignard reagent to produce $LTeR_3$ (wherein R = alkyl, aryl, amide, silyl).

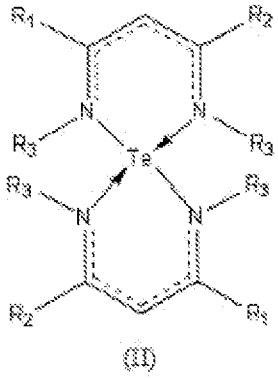
[0060] Alternatively the free imine form of the ligand L can be reacted with a tellurium organic compound such as $TeMe_4$ to produce the desired Te species $LTeMe_3$ by methane elimination. The diketiminate ligands provide very effective base stabilization of the reactive metal center tellurium. The invention therefore provides a new class of Te complexes that provide greater stability and shelf life, while retaining sufficient volatility to form superior Te films via CVD/ALD at low temperatures.

[0061] The tellurium complexes of the invention have the formulae (I) and (II):



(I)

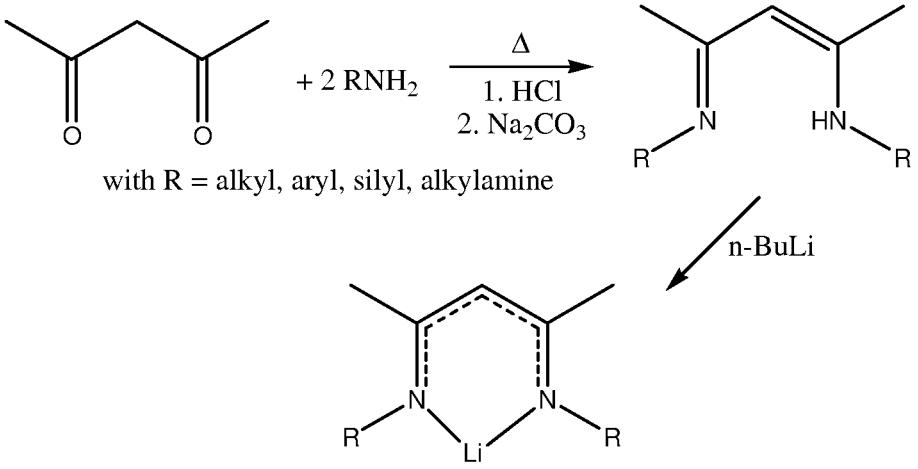
wherein R_1, R_2 and R_3 they be the same as or different from one another, and each is independently selected from C_1-C_6 alkyl, C_6-C_{10} aryl, silyl and C_1-C_{12} alkylamine (which includes both monoalkylamine as well as dialkylamine); and



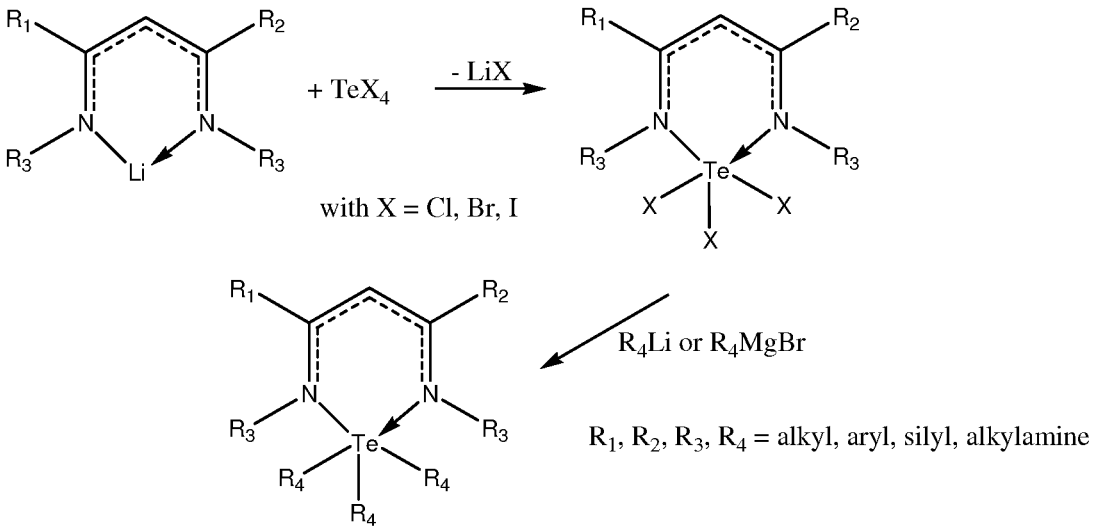
(II)

wherein R_1, R_2 and R_3 they be the same as or different from one another, and each is independently selected from C_1-C_6 alkyl, C_6-C_{10} aryl, silyl and C_1-C_{12} alkylamine (which includes both monoalkylamine as well as dialkylamine).

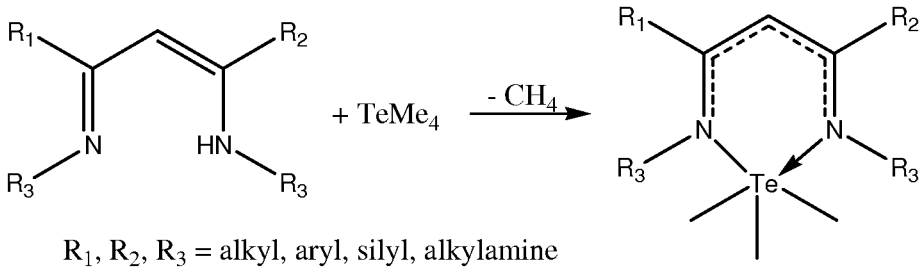
[0062] The beta-diketiminate ligands may for example be synthesized by the following procedure:



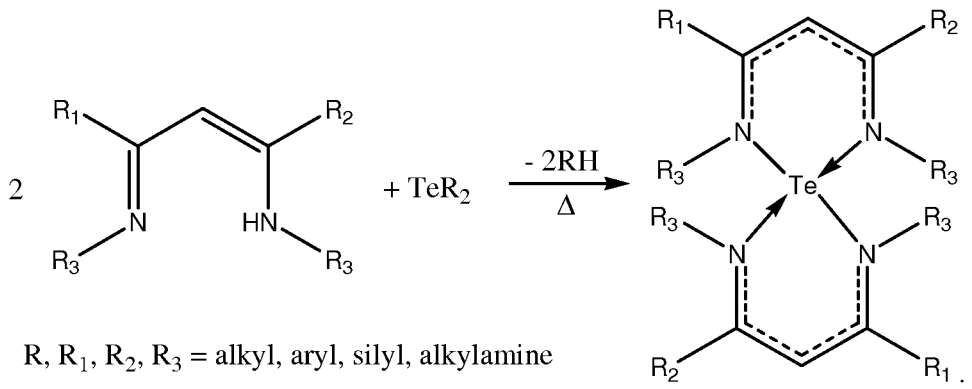
[0063] The tellurium complexes then can be synthesized by the following reaction:



[0064] or alternatively by the following synthesis reaction:



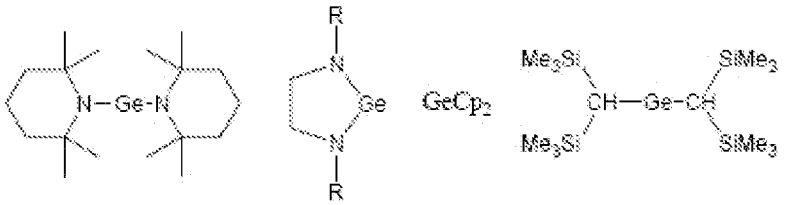
[0065] or by the following synthesis reaction:



R, R_1, R_2, R_3 = alkyl, aryl, silyl, alkylamine

[0066] The tellurium complexes of the invention are usefully employed as CVD/ALD precursors for deposition of tellurium-containing thin films, e.g., by liquid injection of neat precursor material, or in organic solvent or by direct evaporation.

[0067] The invention in another aspect relates to germanium complexes and their use in CVD/ALD for forming germanium-containing films, e.g., GST films, wherein the germanium complexes are selected from among:



wherein the R groups in the second formula may be the same as or different from one another, and each is independently selected from among H, C_1-C_6 alkyl, C_6-C_{10} aryl, C_3-C_8 cycloalkyl, heteroatom groups, and other organo groups.

[0068] Another aspect of the invention relates to digermane and strained ring germanium precursors for CVD/ALD of germanium-containing thin films. Previously employed germanium precursors such as germane that have been used for forming GST (germanium-antimony-tellurium) films for phase change memory devices require very high temperature deposition conditions. This in turn makes it difficult to form a pure $Ge_2Sb_2Te_5$ phase material. The present invention overcomes this deficiency in the provision of precursors having a high vapor pressure at ambient conditions, which are useful to deposit germanium-containing films at temperatures below 300°C.

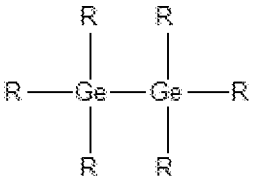
[0069] Germanium-germanium bonds are inherently weak (~ 188 kJ/mole) and become less stable with electron withdrawing substituents such as chlorine or NMe_2. Such bonds can readily dissociate to form R_3Ge radicals under UV photolysis or thermolysis, or by chemical

oxidation using peroxides, ozone, oxygen or plasma. Commercially available digermanes include hydride, methyl, phenyl, or ethyl groups that require high temperatures for decomposition and the resulting films are often contaminated with carbon residues.

[0070] We have overcome such deficiency by the provision of germanium complexes using as ligands isopropyl, isobutyl, benzyl, allyl, alkylamino, nitriles, or isonitriles to achieve complexes that enabled the deposition of pure germanium metal films at low temperatures. In addition, the invention contemplates strained-ring germanium complexes (e.g., germacyclobutane) that can undergo thermal ring opening to generate a diradical intermediate that readily dissociates to germylene fragments. The bond dissociation energy of the strained Ge-C bond (63 kcal/mol) is considerable lower than Ge-CH_3 (83 kcal/mol), thereby enabling lower temperature film deposition of germanium to be achieved, than has been achievable with the aforementioned conventional germanium precursors.

[0071] The germanium complexes of the invention include those of formulae (I) – (III) below:

(I) alkyldigermanes of the formula



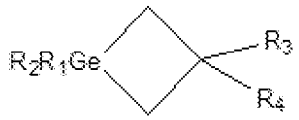
wherein each R may be the same as or different from the others, and each is independently selected from among isopropyl, isobutyl, benzyl, allyl, alkylamino, nitriles, and isonitriles;

(II) alkyl(dialkylamino)germanes of the formula

$_x(R_2R_1N)R_{3-x}Ge\text{-}GeR'_{3-y}(NR_1R_2)_y$

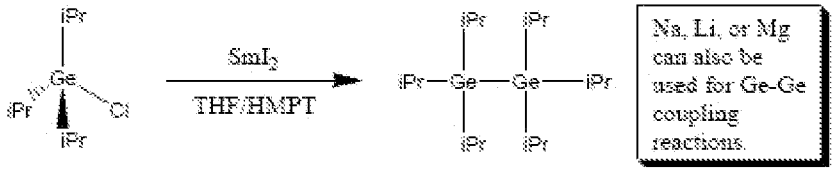
wherein each R may be the same as or different from the others, and each is independently selected from among isopropyl, isobutyl, benzyl, allyl, alkylamino, nitriles, and isonitriles; and

(III) strained-ring germane complexes of the formula:

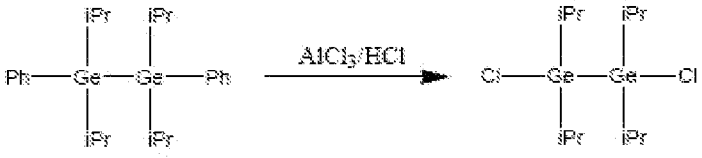


wherein each of R_1, R_2, R_3 and R_4 may be the same as or different from the others, and each is independently selected from among H, C_1-C_6 alkyl, C_6-C_{10} aryl, C_3-C_8 cycloalkyl, or a heteroatom group.

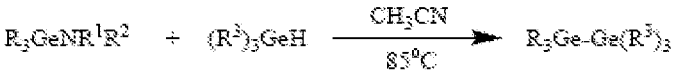
[0072] The complexes (I) can be synthesized, by way of example, according to the following synthesis process:



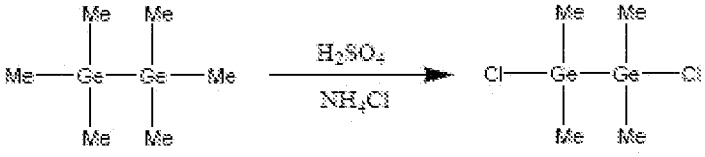
or by the following synthesis:



or by a synthesis such as the following:



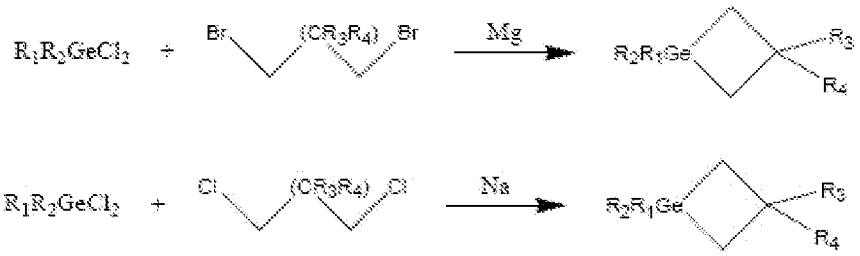
or a synthesis procedure such as:



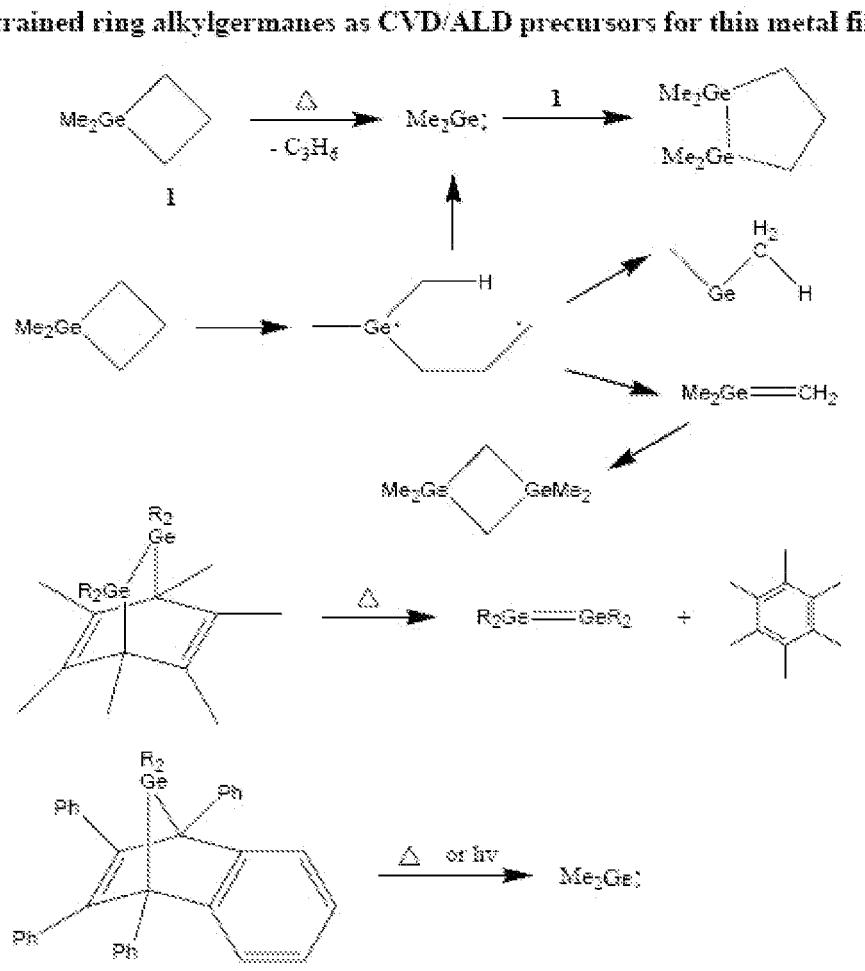
[0073] The germanium complexes of formula (II) can be formed by the following illustrated procedure:



[0074] Illustrative synthesis processes that can be employed for forming germanium complexes of formula (III) includes the following:

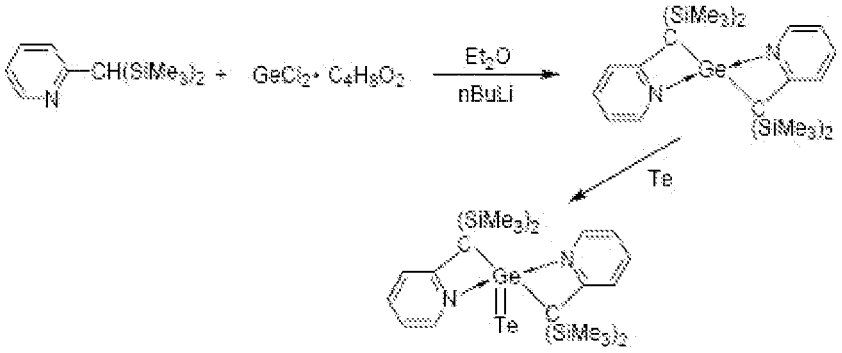


[0075] The strained ring alkylgermanes are usefully employed as CVD/ALD precursors for forming germanium-containing thin films on substrates involving reactions such as those illustratively shown below.



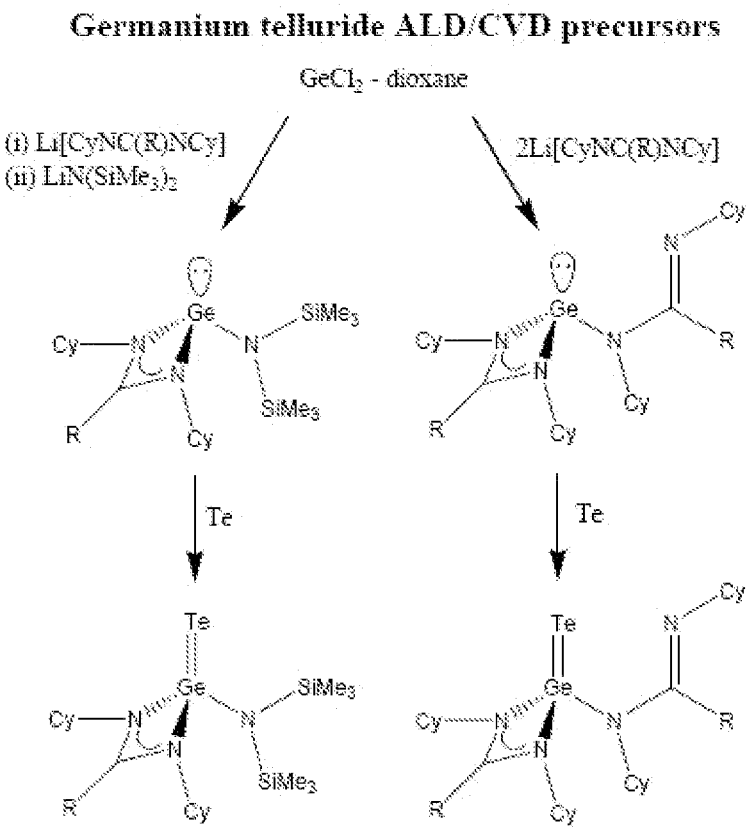
[0076] Another aspect of the invention relates to a single-source precursor for germanium and tellurium, as useful in the formation of GST films. Such single-source of germanium telluride precursors may be used in combination with an antimony precursor for GST film formation, optionally with co-reactants as may be desirable to provide films of appropriate stoichiometry for a given application.

[0077] The germanium telluride complexes of the invention in one aspect include dialkylgermanetellurones. Suitable dialkylgermanetellurones can be synthesized by oxidative addition reaction of germanium (II) dialkyls with elemental tellurium powder in a solvent medium such as tetrahydrofuran (THF). In some instances so it may be desirable to conduct the reaction in the absence of light, depending on the light-sensitivity of the product germanium-tellurium complex. An illustrative synthesis procedure is set out below:

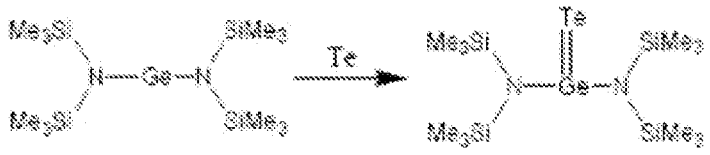


[0078] The single-source Ge-Te precursors of the invention can be advantageously used to facilitate lower temperature deposition processes or to increase GST film growth rates in specific applications.

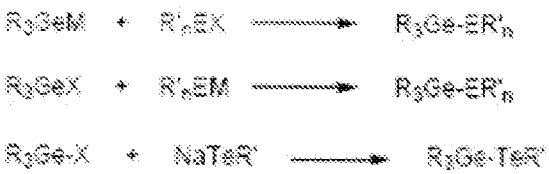
[0079] Germanium tellurides of the invention, in another embodiment, can be formed by the following synthesis procedure:



[0080] Other germanium telluride complexes can be formed by the following synthesis process:



or by the following generalized reactions:



wherein E is tellurium; M is Li, Na, or K, X is chlorine, bromine or iodine; and the R and R' groups may be the same as or different from one another, and each is independently selected from among H, C_1-C_6 alkyl, C_6-C_{10} aryl, C_3-C_8 cycloalkyl, heteroatom groups, and other organo groups.

[0081] One Ge-Te complex of the invention is:



wherein each of the R substituents may be the same as or different from one another, and is independently selected from among H, C_1-C_6 alkyl, C_6-C_{10} aryl, C_3-C_8 cycloalkyl, heteroatom groups, and other organo groups.

[0082] It will therefore be seen that the present invention contemplates a variety of precursors suitable for use in forming phase change memory films, e.g., GST films, and that the various precursors of the invention include precursors enabling deposition of films via CVD/ALD processes at temperatures below 300°C, as well as Ge-Te precursors affording substantial advantage in forming germanium- and tellurium-containing films.

[0083] While the invention has been has been described herein in reference to specific aspects, features and illustrative embodiments of the invention, it will be appreciated that the utility of the invention is not thus limited, but rather extends to and encompasses numerous other variations, modifications and alternative embodiments, as will suggest themselves to those of ordinary skill in the field of the present invention, based on the disclosure herein. Correspondingly, the invention as hereinafter claimed is intended to be broadly construed and interpreted, as including all such variations, modifications and alternative embodiments, within its spirit and scope.

THE CLAIMS

What is claimed is:

1. A method of forming a phase change memory material on a substrate, comprising contacting the substrate with precursors for a phase change memory chalcogenide alloy under conditions producing deposition of the chalcogenide alloy on the substrate, wherein said conditions comprise temperature below 350°C and said contacting comprises chemical vapor deposition or atomic layer deposition.

2. The method of claim 1, further comprising fabricating said phase change memory material is into a phase change memory device.

3. The method of claim 1, wherein said contacting comprises chemical vapor deposition.

4. The method of claim 1, wherein said contacting comprises atomic layer deposition.

5. The method of claim 1, wherein said precursors include at least one precursor selected from the group consisting of:

(i) butyl- and propyl-substituted alkyl hydrides of the formula R_xMH_{y-x} wherein: R is butyl or propyl, with R preferably being t-butyl or isopropyl; M is a metal having an oxidation state y; x> 1; and (y-x) may have a zero value;

(ii) butyl- and propyl-substituted alkyl halides of the formula R_xMX_{y-x} wherein: R is butyl or propyl, with R preferably being t-butyl or isopropyl; X is F, Cl, or Br; M is a metal having an oxidation state y; x> 1; and (y-x) may have a zero value;

(iii) digermanes of the formula $Ge_2(R^1)_6$ wherein the R^1 substituents are the same as or different from one another, and each R^1 is independently selected from among H, C_1-C_8 alkyl, C_1-C_8 fluroalkyl, C_6-C_{12} aryl, C_6-C_{12} fluoroaryl, C_3-C_8 cycloalkyl, and C_3-C_8 cyclo-fluoroalkyl;

(iv) digermanes of the formula $Ge_2(R^1)_4$ wherein the R^1 substituents are the same as or different from one another, and each R^1 is independently selected from among H, C_1-C_8 alkyl, C_1-C_8 fluroalkyl, C_6-C_{12} aryl, C_6-C_{12} fluoroaryl, C_3-C_8 cycloalkyl, and C_3-C_8 cyclo-fluoroalkyl;

(v) ring compounds including Ge as a ring constituent;

(vi) Ge(II) compounds of the formula $Ge(Cp(R^2)_5)_2$ wherein Cp is cyclopentadienyl having R^2 substituents on the cyclopentadienyl ring carbon atoms, wherein the R^2 substituents are the same as or different from one another, and each R^2 is independently selected from among H, C_1-C_8 alkyl, C_1-C_8 fluoroalkyl, C_1-C_8 alkylamino, C_6-C_{12} aryl, C_6-C_{12} fluoroaryl, C_3-C_8 cycloalkyl, and C_3-C_8 cyclo-fluoroalkyl;

(vii) Ge(II) compounds of the formula $Ge(R^3)_2$, wherein the R^3 substituents are the same as or different from one another, and each R^3 is independently selected from among silyl, silylalkyl and substituted silylalkyl;
(viii) Sb compounds of the formula $Sb(R^4)_3$ wherein R^4 is phenyl, or substituted phenyl whose substituent(s) on the phenyl ring are independently selected from among H, C_1-C_8 alkyl, and C_1-C_8 fluroalkyl;
(ix) Sb and Te analogs of germanium compounds (iii), (iv), (v), (vi), and (vii);
(x) Ge and Te analogs of antimony compounds (viii); and
(xi) GeI_4, SbI_3 and TeI_2.

6. The method of claim 1, wherein said precursors comprise a digermane selected from the group consisting of Ge_2H_6, Ge_2Me_6, Ge_2Et_6. Ge_2iPr_6, Ge_2tBu_6, $Ge_2(SiMe_3)_6$, Ge_2Ph and Ge_2Ph_6, wherein Me = methyl, Et = ethyl, iPr = isopropyl, Bu = butyl and Ph = phenyl.

7. The method of claim 1, wherein said precursors comprise a Ge(II) compound of the formula $Ge(R^3)_2$, wherein the R^3 substituents are the same as or different from one another, and each R^3 is independently selected from among, silyl, silylalkyl and substituted silylalkyl.

8. The method of claim 7, wherein each R^3 is $-CH(SiMe_3)_2$.

9. The method of claim 1, wherein said precursors comprise an antimony compound of the formula $Sb(R^4)_3$ wherein R^4 is phenyl, or substituted phenyl whose substituent(s) on the phenyl ring are independently selected from among H, C_1-C_8 alkyl, and C_1-C_8 fluroalkyl.

10. The method of claim 1, wherein said compound is exposed to radiation activation during said deposition.

11. The method of claim 10, wherein said radiation comprises visible light.

12. The method of claim 10, wherein said radiation comprises ultraviolet radiation.

13. The method of claim 1, wherein said deposition is conducted in a chamber into which said precursors are delivered.

14. The method of claim 13, wherein at least one of said precursors is volatilized from a non-vapor initial state and delivered into said chamber.

15. The method of claim 13, wherein at least one of said precursors is delivered into said chamber by a liquid delivery process.

16. The method of claim 13, wherein the substrate is heated in said chamber on a susceptor.

17. The method of claim 13, wherein each of said precursors is delivered to said chamber from a separate bubbler.

18. The method of claim 13, wherein the delivery of said precursors to said chamber comprises liquid injection of at least one of said precursors.

19. The method of claim 13, wherein at least one of said precursors is delivered to said chamber in neat form.

20. The method of claim 13, wherein at least one of said precursors is delivered to said chamber in mixture with a carrier medium.

21. The method of claim 13, wherein at least one of said precursors is provided in a precursor/solvent mixture, and said mixture is volatilized for delivery to said chamber.

22. The method of claim 20, wherein said carrier medium comprises a solvent medium.

23. The method of claim 20, wherein said carrier medium comprises a carrier gas medium.

24. The method of claim 23, wherein said carrier gas medium comprises a reducing gas.

25. The method of claim 23, wherein said carrier gas medium comprises an inert gas.

26. The method of claim 23, wherein said carrier gas medium comprises hydrogen.

27. The method of claim 1, wherein said contacting comprises atomic layer deposition, wherein said precursors are repetitively introduced to said contacting, in alternation with a co-reactant comprising a hydrogen plasma.

28. The method of claim 1, wherein said contacting comprises atomic layer deposition, wherein said precursors are repetitively introduced to said contacting, in alternation with a plasma co-reactant.

29. The method of claim 1, wherein at least one of said precursors is activatable by radiation.

30. The method of claim 29, wherein said radiation is selected from the group consisting of visible light and ultraviolet radiation.

31. The method of claim 30, wherein said radiation is continuous during said contacting of the substrate with said precursors.

32. The method of claim 30, wherein said radiation is introduced during said contacting in a manner that avoids gas-phase reactions resulting therefrom.

33. The method of claim 1, wherein said contacting comprises atomic layer deposition and includes introduction of a reductive co-reactant comprising GeH_4.

34. The method of claim 1, wherein at least one of said precursors is delivered for said contacting from a storage and dispensing vessel containing at least one of physical adsorbent, a gas low pressure regulator, a heat transfer structure, or an ionic liquid.

35. The method of claim 34, wherein said storage and dispensing vessel is adapted to contain precursor at sub-atmospheric pressure.

36. A method of forming a germanium-antimony-tellurium phase change memory material on a substrate, comprising contacting the substrate with precursors for a phase change memory germanium-antimony-tellurium alloy under conditions producing deposition of the germanium-antimony-tellurium alloy on the substrate, wherein said conditions comprise temperature below 350°C and said contacting comprises chemical vapor deposition or atomic layer deposition, with said precursors comprising at least one halide precursor.

37. The method of claim 36, wherein at least two of said precursors comprise a corresponding halide precursor.

38. The method of claim 36, wherein all of said precursors comprise corresponding halide precursors.

39. The method of claim 36, wherein each of the precursors that is not a halide precursor is an alkyl precursor.

40. The method of claim 36, wherein each of said halide precursors comprises an iodide precursor.

41. The method of claim 36, wherein said precursors comprise GeI_4, SbI_3 and TeI_2.

42. The method of claim 41, wherein said precursors are delivered to said contacting by a solid precursor delivery.

43. The method of claim 36, wherein said precursors comprise GeI_4, TeI_2 and $Sb(CH_3)_3$.

44. The method of claim 39, wherein said conditions enable the alkyl precursor to function as a reducing agent to eliminate halo-alkyl species in said contacting.

45. The method of claim 1, wherein said substrate comprises material selected from the group consisting of silicon, sapphire, gallium arsenide, gallium nitride, and silicon carbide.

46. The method of claim 36, wherein said substrate comprises material selected from the group consisting of silicon, sapphire, gallium arsenide, gallium nitride, and silicon carbide.

47. The method of claim 1, including pulsed radiation exposure.

48. The method of claim 47, wherein said pulsed radiation exposure includes radiation exposure of at least one of said precursors for activation thereof.

49. The method of claim 47, wherein said pulsed radiation exposure includes radiation exposure of a co-reactant of at least one of said precursors.

50. The method of claim 47, wherein said pulsed radiation exposure is carried out between successive contacting steps.

51. The method of claim 1, further including contacting of the substrate with a co-reactant of at least one of said precursors, including radiation exposure of said at least one of said precursors and said co-reactant during said contacting.

52. The method of claim 1, further including radiation exposure of deposited material on the substrate, when said precursors are not being contacted with the substrate.

53. A system for fabricating a phase change memory device including a phase change memory material on a substrate, said system comprising a deposition tool adapted to receive precursors from precursor supply packages, and precursor supply packages containing precursors for forming a phase change memory chalcogenide alloy under conditions producing deposition of the chalcogenide alloy on the substrate, wherein said deposition tool is adapted for chemical vapor deposition or atomic layer deposition operation under conditions comprising deposition temperature below 350°C.

54. The system of claim 53, wherein said deposition tool is adapted for chemical vapor deposition.

55. The system of claim 53, wherein said deposition tool is adapted for atomic layer deposition.

56. The system of claim 53, wherein said precursors include at least one precursor selected from the group consisting of:

(i) butyl- and propyl-substituted alkyl hydrides of the formula R_xMH_{y-x} wherein: R is butyl or propyl, with R preferably being t-butyl or isopropyl; M is a metal having an oxidation state y; x> 1; and (y-x) may have a zero value;

(ii) butyl- and propyl-substituted alkyl halides of the formula R_xMX_{y-x} wherein: R is butyl or propyl, with R preferably being t-butyl or isopropyl; X is F, Cl, or Br; M is a metal having an oxidation state y; x> 1; and (y-x) may have a zero value;

(iii) digermanes of the formula $Ge_2(R^1)_6$ wherein the R^1 substituents are the same as or different from one another, and each R^1 is independently selected from among H, C_1-C_8 alkyl, C_1-C_8 fluroalkyl, C_6-C_{12} aryl, C_6-C_{12} fluoroaryl, C_3-C_8 cycloalkyl, and C_3-C_8 cyclo-fluoroalkyl;

(iv) digermanes of the formula $Ge_2(R^1)_4$ wherein the R^1 substituents are the same as or different from one another, and each R^1 is independently selected from among H, C_1-C_8 alkyl, C_1-C_8 fluroalkyl, C_6-C_{12} aryl, C_6-C_{12} fluoroaryl, C_3-C_8 cycloalkyl, and C_3-C_8 cyclo-fluoroalkyl;

(v) ring compounds including Ge as a ring constituent;

(vi) Ge(II) compounds of the formula $Ge(Cp(R^2)_5)_2$ wherein Cp is cyclopentadienyl having R^2 substituents on the cyclopentadienyl ring carbon atoms, wherein the R^2 substituents are the same as or different from one another, and each R^2 is independently selected from among H, C_1-C_8 alkyl, C_1-C_8 fluoroalkyl, C_1-C_8 alkylamino, C_6-C_{12} aryl, C_6-C_{12} fluoroaryl, C_3-C_8 cycloalkyl, and C_3-C_8 cyclo-fluoroalkyl;

(vii) Ge(II) compounds of the formula $Ge(R^3)_2$, wherein the R^3 substituents are the same as or different from one another, and each R^3 is independently selected from among silyl, silylalkyl and substituted silylalkyl;

(viii) Sb compounds of the formula $Sb(R^4)_3$ wherein R^4 is phenyl, or substituted phenyl whose substituent(s) on the phenyl ring are independently selected from among H, C_1-C_8 alkyl, and C_1-C_8 fluroalkyl;
(ix) Sb and Te analogs of germanium compounds (iii), (iv), (v), (vi), and (vii);
(x) Ge and Te analogs of antimony compounds (viii); and
(xi) GeI_4, SbI_3 and TeI_2.

57. A system for fabricating a germanium-antimony-tellurium phase change memory device including a germanium-antimony-tellurium phase change memory material on a substrate, said system comprising a deposition tool adapted to receive precursors from precursor supply packages, and precursor supply packages containing germanium, antimony and tellurium precursors for forming a germanium-antimony-tellurium phase change memory chalcogenide alloy under conditions producing deposition of the chalcogenide alloy on the substrate, wherein said deposition tool is adapted for chemical vapor deposition or atomic layer deposition operation under conditions comprising deposition temperature below 350°C, and at least one of said precursor supply packages contains a halide precursor.

58. The system of claim 57, wherein at least two of said precursors comprise a corresponding halide precursor.

59. The system of claim 57, wherein all of said precursors comprise corresponding halide precursors.

60. The system of claim 57, wherein each of the precursors that is not a halide precursor is an alkyl precursor.

61. The system of claim 57, wherein each of said halide precursors comprises an iodide precursor.

62. The system of claim 57, wherein said precursors comprise GeI_4, SbI_3 and TeI_2.

63. The system of claim 57, wherein said precursors comprise GeI_4, TeI_2 and $Sb(CH_3)_3$.

64. The system of claim 57, including a radiation source adapted for pulsed radiation exposure of deposited material on the substrate.

65. The system of claim 57, wherein said radiation source is adapted for radiation exposure of at least one of said precursors for activation thereof.

66. The system of claim 57, wherein said radiation source is adapted for radiation exposure of a co-reactant of at least one of said precursors.

67. The system of claim 57, wherein said radiation source is adapted for pulsed radiation exposure between successive contacting of the precursors with the substrate

68. The system of claim 57, wherein said radiation source is adapted for contacting of the substrate with a co-reactant of at least one of said precursors, including radiation exposure of said at least one of said precursors and said co-reactant.

69. The system of claim 57, wherein said radiation source is adapted for radiation exposure of deposited material on the substrate, when said precursors are not being contacted with the substrate.

70. A phase change memory material, comprising a phase change memory chalcogenide alloy formed at temperature below 350°C.

71. The phase change memory material of claim 70, as formed by chemical vapor deposition.

72. The phase change memory material claim 70, as formed by atomic layer deposition.

73. A packaged composition for forming a phase change memory chalcogenide alloy, comprising a precursor supply package adapted for coupling to a deposition tool, said precursor supply package containing at least one precursors selected from the group consisting of:
(i) butyl- and propyl-substituted alkyl hydrides of the formula R_xMH_{y-x} wherein: R is butyl or propyl, with R preferably being t-butyl or isopropyl; M is a metal having an oxidation state y; x> 1; and (y-x) may have a zero value;
(ii) butyl- and propyl-substituted alkyl halides of the formula R_xMX_{y-x} wherein: R is butyl or propyl, with R preferably being t-butyl or isopropyl; X is F, Cl, or Br; M is a metal having an oxidation state y; x> 1; and (y-x) may have a zero value;
(iii) digermanes of the formula $Ge_2(R^1)_6$ wherein the R^1 substituents are the same as or different from one another, and each R^1 is independently selected from among H, C_1-C_8 alkyl, C_1-C_8 fluroalkyl, C_6-C_{12} aryl, C_6-C_{12} fluoroaryl, C_3-C_8 cycloalkyl, and C_3-C_8 cyclo-fluoroalkyl;

(iv) digermanes of the formula $Ge_2(R^1)_4$ wherein the R^1 substituents are the same as or different from one another, and each R^1 is independently selected from among H, C_1-C_8 alkyl, C_1-C_8 fluroalkyl, C_6-C_{12} aryl, C_6-C_{12} fluoroaryl, C_3-C_8 cycloalkyl, and C_3-C_8 cyclo-fluoroalkyl;
(v) ring compounds including Ge as a ring constituent;
(vi) Ge(II) compounds of the formula $Ge(Cp(R^2)_5)_2$ wherein Cp is cyclopentadienyl having R^2 substituents on the cyclopentadienyl ring carbon atoms, wherein the R^2 substituents are the same as or different from one another, and each R^2 is independently selected from among H, C_1-C_8 alkyl, C_1-C_8 fluoroalkyl, C_1-C_8 alkylamino, C_6-C_{12} aryl, C_6-C_{12} fluoroaryl, C_3-C_8 cycloalkyl, and C_3-C_8 cyclo-fluoroalkyl;
(vii) Ge(II) compounds of the formula $Ge(R^3)_2$, wherein the R^3 substituents are the same as or different from one another, and each R^3 is independently selected from among silyl, silylalkyl and substituted silylalkyl;
(viii) Sb compounds of the formula $Sb(R^4)_3$ wherein R^4 is phenyl, or substituted phenyl whose substituent(s) on the phenyl ring are independently selected from among H, C_1-C_8 alkyl, and C_1-C_8 fluroalkyl;
(ix) Sb and Te analogs of germanium compounds (iii), (iv), (v), (vi), and (vii);
(x) Ge and Te analogs of antimony compounds (viii); and
(xi) GeI_4, SbI_3 and TeI_2.

74. A composition for forming a PCM material, such composition comprising at least two precursors selected from the group consisting of:
(i) butyl- and propyl-substituted alkyl hydrides of the formula R_xMH_{y-x} wherein: R is butyl or propyl, with R preferably being t-butyl or isopropyl; M is a metal having an oxidation state y; x> 1; and (y-x) may have a zero value;
(ii) butyl- and propyl-substituted alkyl halides of the formula R_xMX_{y-x} wherein: R is butyl or propyl, with R preferably being t-butyl or isopropyl; X is F, Cl, or Br; M is a metal having an oxidation state y; x> 1; and (y-x) may have a zero value;
(iii) digermanes of the formula $Ge_2(R^1)_6$ wherein the R^1 substituents are the same as or different from one another, and each R^1 is independently selected from among H, C_1-C_8 alkyl, C_1-C_8 fluroalkyl, C_6-C_{12} aryl, C_6-C_{12} fluoroaryl, C_3-C_8 cycloalkyl, and C_3-C_8 cyclo-fluoroalkyl;
(iv) digermanes of the formula $Ge_2(R^1)_4$ wherein the R^1 substituents are the same as or different from one another, and each R^1 is independently selected from among H, C_1-C_8 alkyl, C_1-C_8 fluroalkyl, C_6-C_{12} aryl, C_6-C_{12} fluoroaryl, C_3-C_8 cycloalkyl, and C_3-C_8 cyclo-fluoroalkyl;
(v) ring compounds including Ge as a ring constituent;
(vi) Ge(II) compounds of the formula $Ge(Cp(R^2)_5)_2$ wherein Cp is cyclopentadienyl having R^2 substituents on the cyclopentadienyl ring carbon atoms, wherein the R^2 substituents are the same as or different from one another, and each R^2 is independently selected from among H,

C_1-C_8 alkyl, C_1-C_8 fluoroalkyl, C_1-C_8 alkylamino, C_6-C_{12} aryl, C_6-C_{12} fluoroaryl, C_3-C_8 cycloalkyl, and C_3-C_8 cyclo-fluoroalkyl;

(vii) Ge(II) compounds of the formula $Ge(R^3)_2$, wherein the R^3 substituents are the same as or different from one another, and each R^3 is independently selected from among silyl, silylalkyl and substituted silylalkyl;

(viii) Sb compounds of the formula $Sb(R^4)_3$ wherein R^4 is phenyl, or substituted phenyl whose substituent(s) on the phenyl ring are independently selected from among H, C_1-C_8 alkyl, and C_1-C_8 fluroalkyl;

(ix) Sb and Te analogs of germanium compounds (iii), (iv), (v), (vi), and (vii);

(x) Ge and Te analogs of antimony compounds (viii); and

(xi) GeI_4, SbI_3 and TeI_2.

75. A method of forming a GeSbTe semiconductor, comprising depositing a film of GeSbTe semiconductor material, and doping same with nitrogen.

76. The method of claim 75, wherein said doping comprises use of a reactant gas.

77. The method of claim 76, wherein said reactant gas comprises ammonia.

78. The method of claim 75, wherein said doping comprises use of a vaporizable liquid.

79. The method of claim 78, wherein said vaporizable liquid comprises an amine liquid.

80. The method of claim 76, wherein the reactant gas is introduced as a co-reactant with precursors during formation of said film.

81. The method of claim 76, wherein the reactant gas is introduced as a carrier gas for precursors during formation of said film.

82. The method of claim 75, wherein the doping comprises pulsing of nitrogen dopant, optionally with purging between pulses.

83. The method of claim 75, where the doping comprises incorporation of nitrogen from a nitrogen-containing precursor in the formation of the film.

84. The method of claim 75, wherein said doping comprises use of ammonia.

85. A tellurium complex comprising tellurium having beta-diketiminate ligands coordinated therewith.

86. A method of forming a tellurium-containing film, comprising use of a tellurium complex as claimed in claim 85.

87. The method of claim 86, comprising CVD or ALD with said tellurium complex as a precursor therefor.

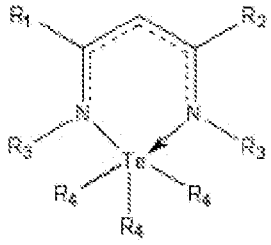
88. The method of claim 86, wherein said tellurium-containing film comprises at least one of germanium and antimony.

89. A method of synthesizing a tellurium diketiminate precursor, comprising use of a lithium salt or free imine of a ligand L in reaction with TeX_4 wherein X = Cl, Br, or I, to generate $LTeX_3$ by salt elimination, followed by a reaction with either a lithium or a Grignard reagent to produce $LTeR_3$ wherein R = alkyl, aryl, amide, or silyl.

90. The method of claim 89, wherein the ligand is selected from the group consisting of iso-propyl, n-butyl, tert-butyl and amine-substituted alkyl groups.

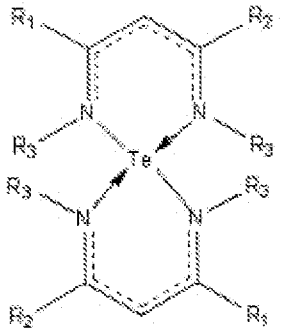
91. The method of claim 89, wherein the ligand is ethylene-dimethylamine.

92. A tellurium complex selected from among complexes having the formulae (I) and (II):



(I)

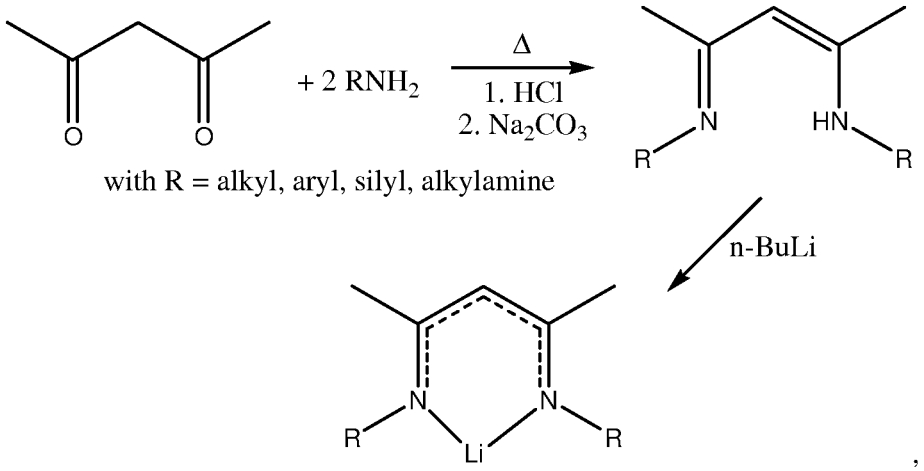
wherein R_1, R_2 and R_3 they be the same as or different from one another, and each is independently selected from C_1-C_6 alkyl, C_6-C_{10} aryl, silyl and C_1-C_{12} alkylamine; and



(II)

wherein R_1, R_2 and R_3 they be the same as or different from one another, and each is independently selected from C_1-C_6 alkyl, C_6-C_{10} aryl, silyl and C_1-C_{12} alkylamine.

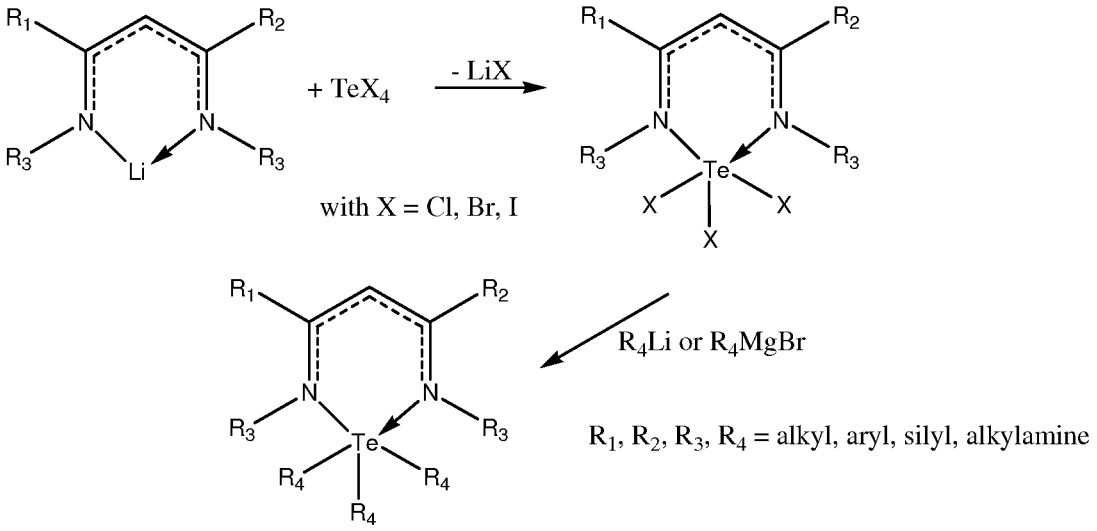
93. A method of making a tellurium complex, comprising synthesizing a beta-diketiminate ligand by the following procedure:



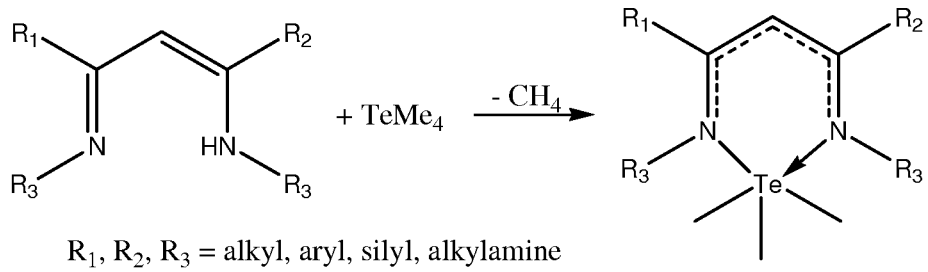
with R = alkyl, aryl, silyl, alkylamine

,

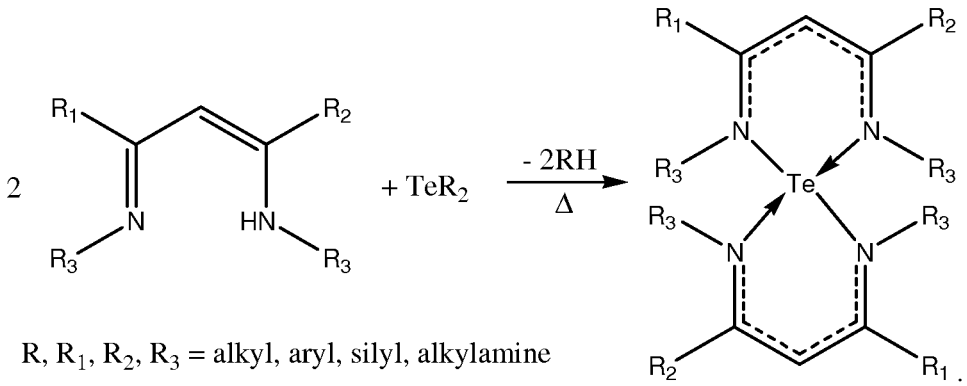
and synthesizing said tellurium complex by the following reaction:



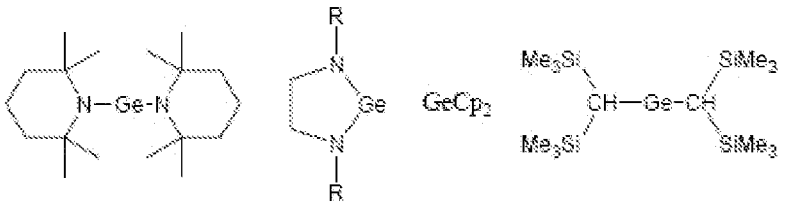
or alternatively by the following synthesis reaction:



or by the following synthesis reaction:



94. A germanium complex selected from among:



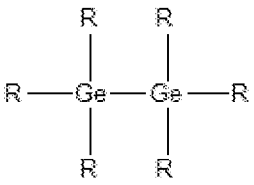
wherein the R groups in the second formula may be the same as or different from one another, and each is independently selected from among H, C_1-C_6 alkyl, C_6-C_{10} aryl, C_3-C_8 cycloalkyl, heteroatom groups, and other organo groups.

95. A method of forming a germanium-containing film on a substrate, comprising use of a digermane or a strained ring germanium precursor in a chemical vapor deposition or atomic layer deposition process, wherein said deposition process is carried out at temperature below 300°C.

96. A method of forming a germanium-containing film on a substrate, comprising use of a germanium complex comprising ligand selected from the group consisting of isopropyl, isobutyl, benzyl, allyl, alkylamino, nitriles, and isonitriles, in chemical vapor deposition or atomic layer deposition conducted at temperature below 300°C.

97. A germanium complex selected from among complexes of formulae (I) – (III):

(I) alkyldigermanes of the formula



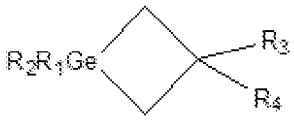
wherein each R may be the same as or different from the others, and each is independently selected from among isopropyl, isobutyl, benzyl, allyl, alkylamino, nitriles, and isonitriles;

(II) alkyl(dialkylamino)germanes of the formula

$_x(R_2R_1N)R_{3-x}Ge\text{-}GeR'_{3-y}(NR_1R_2)_y$

wherein each R may be the same as or different from the others, and each is independently selected from among isopropyl, isobutyl, benzyl, allyl, alkylamino, nitriles, and isonitriles; and

(III) strained-ring germane complexes of the formula:



wherein each of R_1, R_2, R_3 and R_4 may be the same as or different from the others, and each is independently selected from among H, C_1-C_6 alkyl, C_6-C_{10} aryl, C_3-C_8 cycloalkyl, or a heteroatom group.

98. A single-source germanium-tellurium precursor, comprising a dialkylgermanetellurone.

99. A method of making a dialkylgermanetellurone, comprising conducting an oxidative addition reaction of germanium (II) dialkyls with elemental tellurium powder.

100. The method of claim 99, wherein said oxidative addition reaction is conducted in a solvent medium comprising tetrahydrofuran.

101. A method of forming a GST film, comprising conducting a chemical vapor deposition or atomic layer deposition process using a germanium telluride precursor.

102. The method of claim 101, wherein said germanium telluride precursor comprises:



wherein each of the R substituents may be the same as or different from one another, and is independently selected from among H, C_1-C_6 alkyl, C_6-C_{10} aryl, C_3-C_8 cycloalkyl, heteroatom groups, and other organo groups.

103. The method of claim 101, wherein said chemical vapor deposition or atomic layer deposition process is conducted at temperature below 300°C.

104. A germanium telluride complex having the formula:



wherein each of the R substituents may be the same as or different from one another, and is independently selected from among H, C_1-C_6 alkyl, C_6-C_{10} aryl, C_3-C_8 cycloalkyl, heteroatom groups, and other organo groups.