

**ANTIMONY AND GERMANIUM COMPLEXES USEFUL FOR CVD/ALD OF
METAL THIN FILMS**

FIELD OF THE INVENTION

[0001] The present invention relates to antimony and germanium complexes useful for CVD/ALD of metal thin films, to compositions including such complexes and to processes for depositing metal films on substrates using such complexes and compositions.

DESCRIPTION OF THE RELATED ART

[0002] Antimonides have been utilized in infrared detectors, high-speed digital circuits, quantum well structures and recently as a critical component together with germanium (Ge) and tellurium (Te) in phase change chalcogenide nonvolatile memory technology utilizing germanium-antimony-tellurium ($\text{Ge}_2\text{Sb}_2\text{Te}_5$) films.

[0003] Phase-change random access memory (PRAM) devices based on Ge-Sb-Te (GST) thin films utilize a reversible transition from a crystalline state to an amorphous state associated with changes in resistivity of the film material. The film material itself for high-speed commercial manufacturing and performance reasons is desirably formed using techniques such as chemical vapor deposition (CVD) and atomic layer deposition (ALD).

[0004] Despite their promise, there are substantial challenges facing the efforts being made to grow reproducible, high-quality antimonide, Sb_2Te_3 and GST films by CVD and atomic layer deposition ALD at low temperature. These challenges include the following:

(1) a very limited number of antimony CVD/ALD precursors is currently available, most being alkyl-based compounds such as Me_3Sb , Et_3Sb , $(i\text{Pr})_3\text{Sb}$ and Ph_3Sb or hydride-based compounds such as SbH_3 , and these precursors suffer from various deficiencies including low thermal stability, low volatility, synthetic difficulties and high delivery temperatures;

(2) the compatibility of such currently available antimony precursors with germanium or tellurium precursors is undetermined as far as their ability to reproducibly grow microelectronic device quality GST films, and the growth of antimonide films has associated process difficulties, including sensitivity to the V/III ratio and decomposition temperature; and

(3) the deposited metal films formed from such precursors are susceptible to carbon or heteroatom contamination deriving from the precursor that can result in low growth rates, poor morphology and compositional variations in the films.

[0005] Similar issues are encountered in the availability and selection of suitable germanium precursors for deposition of GST films, and in the use of germanium precursors for forming epitaxially grown strained silicon films, e.g., SiGe films.

[0006] Germane (GeH₄) is conventionally used to form germanium films but requires deposition temperatures above 500°C as well as rigorous safety controls and equipment. Other available Ge precursors require temperatures above 350°C for deposition of Ge films, or otherwise exhibit insufficient vapor pressures for transport or produce low film growth rates. Ideally, the germanium precursor can be used in CVD/ALD processes at low temperatures, on the order of 300°C and below, to form GST alloy thin films at high deposition rates, and with low carbon impurity levels in the resulting films.

[0007] In consequence, the art continues to seek new antimony and germanium precursors for use in deposition of corresponding metal and metal alloy films by CVD and ALD techniques.

SUMMARY OF THE INVENTION

[0008] The present invention relates to antimony and germanium precursors useful for CVD/ALD of corresponding metal-containing thin films, to compositions including such precursors, methods of making such precursors, and films and microelectronic device products manufactured using such precursors, as well as corresponding manufacturing methods.

[0009] In one aspect, the invention relates to a metal complex selected from among complexes of formulae (A), (B), (C), (D) and (E)(I)-(E)(XVI):

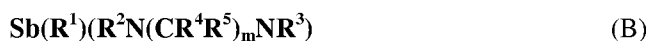


wherein:

R¹, R², R³, and R⁴ may be the same as or different from one another, and are independently selected from C₁-C₆ alkyl, C₃-C₆ cycloalkyl, C₂-C₆ alkenyl (e.g., vinyl, allyl, etc.), C₃-C₆ alkylsilyl, C₆-C₁₀ aryl,

each of R⁵ and R⁶ may be the same as or different from one another and are independently selected from hydrogen, C₁-C₆ alkyl, C₃-C₆ cycloalkyl, C₂-C₆ alkenyl (e.g., vinyl, allyl, etc.), C₃-C₆ alkylsilyl, and C₆-C₁₀ aryl; and

m is an integer from 1 to 4 inclusive;



wherein:

R^1 , R^2 , and R^3 may be the same as or different from one another, and are independently selected from C_1 - C_6 alkyl, C_3 - C_6 cycloalkyl, C_2 - C_6 alkenyl (e.g., vinyl, allyl, etc.), C_3 - C_6 alkylsilyl, and C_6 - C_{10} aryl;

each of R^4 and R^5 may be the same as or different from one another and is independently selected from hydrogen, C_1 - C_6 alkyl, C_3 - C_6 cycloalkyl, C_2 - C_6 alkenyl (e.g., vinyl, allyl, etc.), C_3 - C_6 alkylsilyl, and C_6 - C_{10} aryl; and

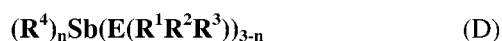
m is an integer from 1 to 4 inclusive;



wherein:

R^1 , R^2 and R^3 may be the same as or different from one another and are independently selected from hydrogen, C_1 - C_6 alkyl, C_3 - C_6 cycloalkyl, C_2 - C_6 alkenyl (e.g., vinyl, allyl, etc.), silyl, C_3 - C_6 alkylsilyl, C_6 - C_{10} aryl and $-\text{NR}^4\text{R}^5$, wherein each of R^4 and R^5 is selected from among H and C_1 - C_4 ; and

n is an integer from 0 to 3 inclusive;



wherein:

R^1 , R^2 , R^3 , and R^4 may be the same as or different from one another, and are independently selected from C_1 - C_6 alkyl, C_3 - C_6 cycloalkyl, C_3 - C_6 alkylsilyl, C_6 - C_{10} aryl, and alkylamino of the formula $-\text{NR}^5\text{R}^6$ wherein each of R^5 and R^6 is independently selected from H and C_1 - C_4 alkyl;

E is silicon (Si) or germanium (Ge); and

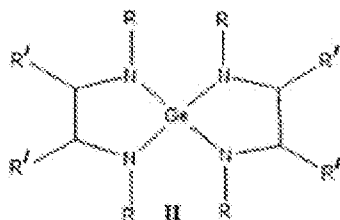
n is an integer from 0 to 3 inclusive;

(E) germanium precursors of the following formulae I-XVI:

**I**

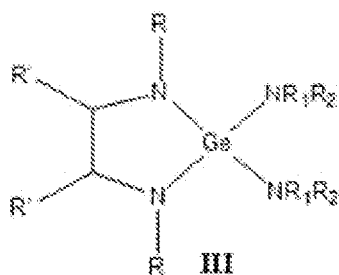
wherein:

R_1 and R_2 may be the same as or different from one another, and are independently selected from H, C_1 - C_6 alkyl, C_2 - C_5 alkenyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}_3)_3$ wherein each R_3 is independently selected from C_1 - C_6 alkyl;

**II**

wherein:

R and R' may be the same as or different from one another, and each R and R' is independently selected from H, C_1 - C_6 alkyl, C_2 - C_5 alkenyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}_3)_3$ wherein each R_3 is independently selected from C_1 - C_6 alkyl;

**III**

wherein:

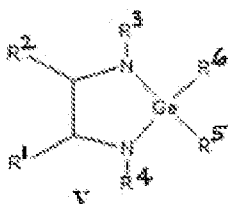
R , R' , R_1 and R_2 may be the same as or different from one another, and each is independently selected from H, C_1 - C_6 alkyl, C_2 - C_5 alkenyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}_3)_3$ wherein each R_3 is independently selected from C_1 - C_6 alkyl;

**IV**

wherein:

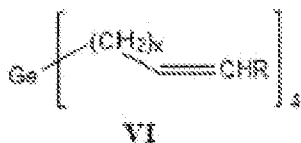
R , R_1 and R_2 may be the same as or different from one another, and each is independently selected from H, C_1 - C_6 alkyl, C_2 - C_5 alkenyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}_3)_3$ wherein each R_3 is independently selected from C_1 - C_6 alkyl; and

n is an integer from 0 to 4 inclusive;



wherein:

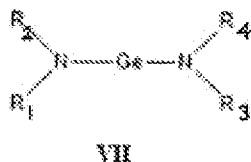
R^1 , R^2 , R^3 , R^4 , R^5 and R^6 may be the same as or different from one another, and each is independently selected from H, C_1 - C_6 alkyl, C_2 - C_5 alkenyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}_3)_3$ wherein each R_3 is independently selected from C_1 - C_6 alkyl;



wherein:

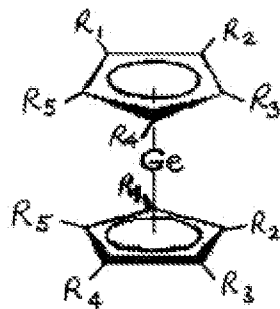
R is selected from H, C_1 - C_6 alkyl, and C_6 - C_{10} aryl; and

x is 0, 1 or 2;



wherein:

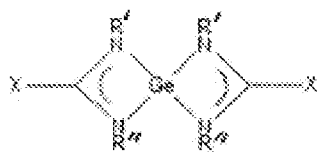
R_1 , R_2 , R_3 and R_4 may be the same as or different from the others, and each is independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}_3)_3$ wherein each R_3 is independently selected from C_1 - C_6 alkyl;



VIII

wherein:

R_1 , R_2 , R_3 , R_4 , and R_5 may be the same as or different from one another, and each is independently selected from among H, C_1 - C_6 alkyl, silyl, $-\text{Si}(\text{R}')_3$, C_6 - C_{10} cycloalkyl, C_6 - C_{10} aryl, $-(\text{CH}_2)_x\text{NR}'\text{R}''$, and $-(\text{CH}_2)_x\text{OR}'''$, wherein $x = 1, 2$ or 3 , and R' , R'' and R''' may be the same as or different from one another, and each is independently selected from C_1 - C_6 alkyl;

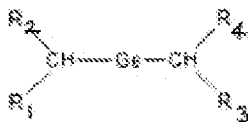


IX

wherein:

R' and R'' may be the same as or different from one another, and are independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl; and

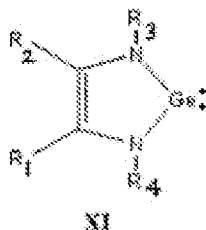
each X is independently selected from among C_1 - C_6 alkyl, C_1 - C_6 alkoxy, $-\text{NR}^1\text{R}^2$, and $-\text{C}(\text{R}^3)_3$, wherein each of R^1 , R^2 and R^3 is independently selected from H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}^4)_3$ wherein each R^4 is independently selected from C_1 - C_6 alkyl;



X

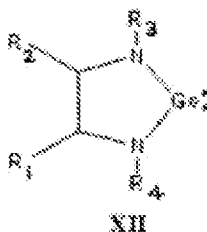
wherein:

R_1 , R_2 , R_3 and R_4 may be same as or different from one another, and are independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl;



wherein:

R_1 , R_2 , R_3 and R_4 may be the same as or different from one another, and are independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl;



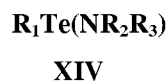
wherein:

R_1 , R_2 , R_3 and R_4 may be the same as or different from one another, and are independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl;



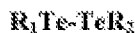
wherein:

R_1 and R_2 may be the same as or different from one another, and are independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl;



wherein:

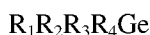
R_1 , R_2 and R_3 may be the same as or different from one another, and are independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}_3)_3$ wherein each R_3 is independently selected from C_1 - C_6 alkyl;



XV

wherein:

R_1 and R_2 may be the same as or different from one another, and are independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl; and



XVI

wherein:

R_1 , R_2 , R_3 , and R_4 may be the same as or different from one another, and are independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl.

[0010] In another aspect, the invention relates to a vapor of an above-described metal complex.

[0011] In another aspect, the invention relates to a precursor mixture including germanium precursor, antimony precursor and tellurium precursor, wherein at least one of the germanium precursor and antimony precursor includes a precursor selected from among the metal complexes of formulae (A), (B), (C), (D) and (E)(I)-(XVI) above.

[0012] In a further aspect, the invention relates to precursor composition comprising a metal complex of the invention, in a solvent medium.

[0013] A further aspect of the invention relates to method of depositing metal on a substrate, comprising contacting the substrate with precursor vapor comprising vapor of a metal complex of the invention.

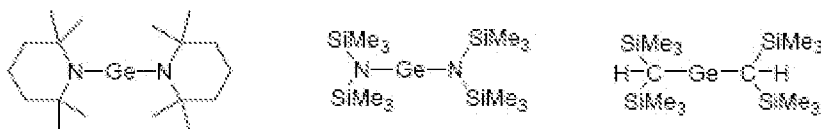
[0014] Additional aspects of the invention relate to methods of making the precursors of the invention.

[0015] A further aspect of the invention relates to $\text{Sb}(\text{NMeEt})_3$, $\text{Sb}(\text{CH}=\text{CMe}_2)_3$ and $\text{Sb}(\text{CH}_2\text{CH}=\text{CH}_2)_3$.

[0016] In another aspect, the invention relates to a packaged precursor supply system comprising a package containing a metal complex of the invention.

[0017] Yet another aspect of the invention relates to a germanium complex whose structure and properties are more fully discussed hereinafter.

[0018] In another aspect, the invention relates to a method of depositing germanium on a substrate, comprising contacting the substrate with precursor vapor comprising vapor of a germanium (II) complex selected from among the following:



[0019] Another aspect of the invention relates to a method of method of depositing germanium on a substrate, comprising contacting the substrate with precursor vapor comprising vapor of dialkylaminotriisopropylgermane.

[0020] The invention also contemplates a precursor vapor comprising vapor of dialkylaminotriisopropylgermane, in another aspect of the invention.

[0021] One aspect of the invention relates to a method of depositing germanium on a substrate, comprising contacting the substrate with a precursor vapor comprising vapor of a germanium complex including ligands selected from among allyl, benzyl, t-butyl, cyclopentadienyl, hydride, phenyl, alkyl, bidentate amines and N, N-dialkylethylenediamine.

[0022] Another aspect of the invention relates to forming a GST film on a substrate, comprising contacting the substrate with a precursor vapor comprising vapor of a germanium complex of the invention, vapor of an antimony complex, and vapor of a tellurium complex.

[0023] Another aspect of the invention relates to a dialkylaminotriisopropylgermane complex, e.g., diethylaminotriisopropylgermane and ethylmethylaminotriisopropylgermane.

[0024] A still further aspect of the invention relates to a method of forming a germanium-containing film on a substrate, comprising contacting the substrate with a precursor vapor comprising vapor of diethylaminotriisopropylgermane or ethylmethylaminotriisopropylgermane.

[0025] A still further aspect of the invention relates to a method of making a microelectronic device, comprising chemical vapor deposition or atomic layer deposition of a metal-containing film on a substrate from a precursor vapor comprising vapor of at least one precursor as described herein.

[0026] Where a range of carbon numbers is provided herein, in description of a corresponding chemical moiety, it is understood that each intervening carbon number and any other stated or intervening carbon number value in that stated range, is encompassed within the invention, e.g., C₁-C₆ alkyl is understood as including methyl (C₁), ethyl (C₂), propyl (C₃), butyl

(C₄), pentyl (C₅) and hexyl (C₆), and the chemical moiety may be of any conformation, e.g., straight-chain or branched, it being further understood that sub-ranges of carbon number within specified carbon number ranges may independently be included in smaller carbon number ranges, within the scope of the invention, and that ranges of carbon numbers specifically excluding a carbon number or numbers are included in the invention, and sub-ranges excluding either or both of carbon number limits of specified ranges are also included in the invention.

[0027] As used herein, the term "film" refers to a layer of deposited material having a thickness below 1000 micrometers, e.g., from such value down to atomic monolayer thickness values. In various embodiments, film thicknesses of deposited material layers in the practice of the invention may for example be below 100, 10, or 1 micrometers, or in various thin film regimes below 200, 100, or 50 nanometers, depending on the specific application involved.

[0028] It is noted that as used herein and in the appended claims, the singular forms "a", "and", and "the" include plural referents unless the context clearly dictates otherwise.

[0029] 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

[0030] FIG. 1 shows the nuclear magnetic resonance spectrum of Sb(NMeEt)₃.

[0031] FIG. 2 shows the nuclear magnetic resonance spectrum of Sb(NMe₂)₃.

[0032] FIG. 3 is a simultaneous thermal analysis (STA) graph for Sb(NMeEt)₃ and Sb(NMe₂)₃, in which percentage thermogravimetry (TG) is plotted as a function of temperature, in degrees Centigrade.

[0033] FIG. 4(a) is a gas chromatography (GC) spectrum for such ethylmethylaminotriisopropylgermane product, and FIG. 4(b) is a corresponding tabulation of peak data for such GC spectrum. FIG. 4(c) is a mass spectrum for the ethylmethylaminotriisopropylgermane product. FIG. 4(d) shows the nuclear magnetic resonance spectrum of *i*Pr₃GeNEtMe.

[0034] FIG. 5 is an STA spectrum of the ethylmethylaminotriisopropylgermane product, showing differential scanning calorimetry (DSC) data and thermogravimetric (TG) data, as a function of temperature.

[0035] FIG. 6 is an Arrhenius plot of deposition rate, in Å/min, as a function of inverse Kelvin temperature, showing the improvement in Ge deposition with ammonia co-reactant.

[0036] FIG. 7 is a plot of deposition rate, in Å/min, as a function of volume percent ammonia introduced in the deposition operation.

[0037] FIG. 8 is a schematic representation of a schematic of a GST device structure.

**DETAILED DESCRIPTION OF THE INVENTION, AND PREFERRED
EMBODIMENTS THEREOF**

[0038] The present invention relates to antimony and germanium precursors useful for CVD/ALD of corresponding metal-containing thin films, to compositions including such precursors, methods of making such precursors, and films and microelectronic device products manufactured using such precursors, as well as corresponding manufacturing methods.

[0039] The invention relates in one aspect to new classes of antimony precursors, of the following formulae (A), (B) and (C):

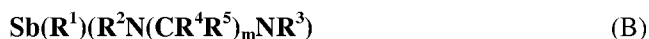


wherein:

R^1 , R^2 , R^3 , and R^4 may be the same as or different from one another, and are independently selected from C_1 - C_6 alkyl, C_3 - C_6 cycloalkyl, C_2 - C_6 alkenyl (e.g., vinyl, allyl, etc.), C_3 - C_6 alkylsilyl, C_6 - C_{10} aryl,

each of R^5 and R^6 may be the same as or different from one another and are independently selected from hydrogen, C_1 - C_6 alkyl, C_3 - C_6 cycloalkyl, C_2 - C_6 alkenyl (e.g., vinyl, allyl, etc.), C_3 - C_6 alkylsilyl, and C_6 - C_{10} aryl; and

m is an integer from 1 to 4 inclusive;



wherein:

R^1 , R^2 , and R^3 may be the same as or different from one another, and are independently selected from C_1 - C_6 alkyl, C_3 - C_6 cycloalkyl, C_2 - C_6 alkenyl (e.g., vinyl, allyl, etc.), C_3 - C_6 alkylsilyl, and C_6 - C_{10} aryl;

each of R^4 and R^5 may be the same as or different from one another and is independently selected from hydrogen, C_1 - C_6 alkyl, C_3 - C_6 cycloalkyl, C_2 - C_6 alkenyl (e.g., vinyl, allyl, etc.), C_3 - C_6 alkylsilyl, and C_6 - C_{10} aryl; and

m is an integer from 1 to 4 inclusive;

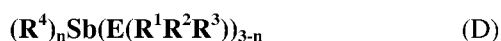


wherein:

R^1 , R^2 and R^3 may be the same as or different from one another and are independently selected from hydrogen, C_1 - C_6 alkyl, C_3 - C_6 cycloalkyl, C_2 - C_6 alkenyl (e.g., vinyl, allyl, etc.), silyl, C_3 - C_6 alkylsilyl, C_6 - C_{10} aryl and $-NR^4R^5$, wherein each of R^4 and R^5 is selected from among H and C_1 - C_4 ; and

n is an integer from 0 to 3 inclusive.

[0040] The invention in another aspect relates to germanyl and silyl antimony precursors of formula (D):



wherein:

R^1 , R^2 , R^3 , and R^4 may be the same as or different from one another, and are independently selected from C_1 - C_6 alkyl, C_3 - C_6 cycloalkyl, C_3 - C_6 alkylsilyl, C_6 - C_{10} aryl, and alkylamino of the formula $-NR^5R^6$ wherein each of R^5 and R^6 is independently selected from H and C_1 - C_4 alkyl;

E is silicon (Si) or germanium (Ge); and

n is an integer from 0 to 3 inclusive.

[0041] The foregoing precursors may be usefully employed for CVD and ALD of Sb, Sb/Ge, Sb/Te and GST films.

[0042] Such precursors may also be used in low temperature deposition applications with reducing co-reactants such as hydrogen, hydrogen plasma, amines, imines, hydrazines, silanes, silyl chalcogenides (e.g., $(Me_3Si)_2Te$), germanes (e.g., GeH_4), ammonia, alkanes, alkenes and alkynes.

[0043] When specific precursors are in a liquid state, they may be used for liquid delivery in neat liquid form.

[0044] Alternatively, when such precursors are in a liquid or solid state, they may be employed in suitable solvents, as a solution or suspension of the precursor. In specific applications, suitable solvents for such purpose include alkanes (e.g., hexane, heptane, octane

and pentane), aryl solvents (e.g., benzene, toluene), amines (e.g., triethylamine, tert-butylamine), imines, hydrazines and ethers.

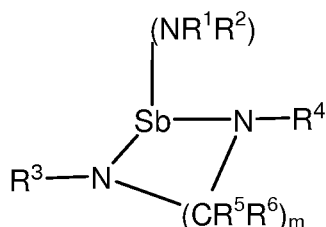
[0045] The choice of a specific solvent composition for a particular antimony precursor or for a specific antimony precursor in combination with other germanium and tellurium precursors, may be readily determined, within the skill of the art based on the disclosure herein, to select an appropriate single component or multiple component solvent medium for liquid delivery vaporization and transport of the specific precursor component(s) involved.

[0046] In various embodiments, where the antimony precursor is in a solid state, a solid delivery system may be utilized for delivery of the antimony precursor, such as for example the ProE-Vap® solid delivery and vaporizer system commercially available from ATMI, Inc., Danbury, Connecticut, USA.

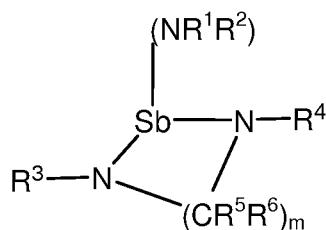
[0047] The antimony precursors of the invention can be "fine-tuned" by choice of appropriate substituents, within the broad formulae set out hereinabove, to provide desired characteristics of thermal stability, volatility and compatibility with other co-reagents or components in a multi-component precursor system.

[0048] The antimony precursors of the invention are readily synthesized, by synthetic routes including those described below.

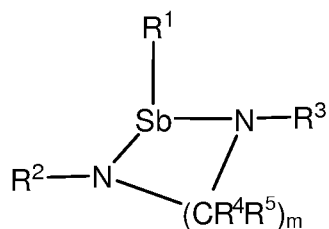
[0049] The antimony precursor of the general formula (A):



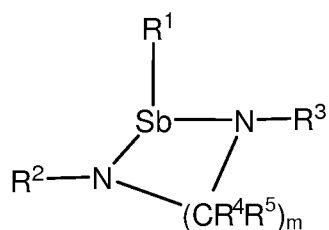
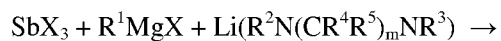
can for example be synthesized according to the following reaction scheme (A):



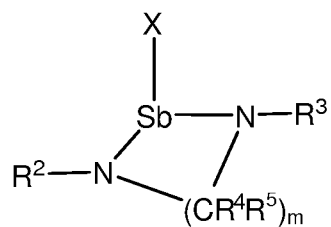
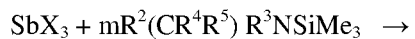
and the antimony precursor of the general formula (B):

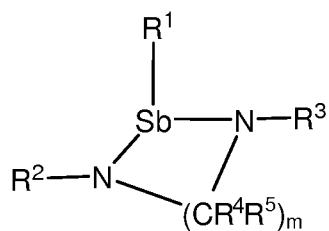


can be synthesized according to the following reaction scheme (B):



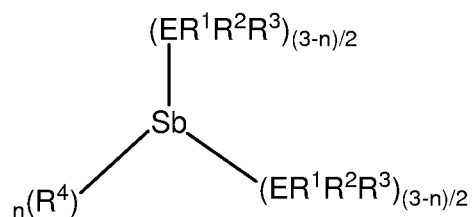
or by the following reaction scheme (C):





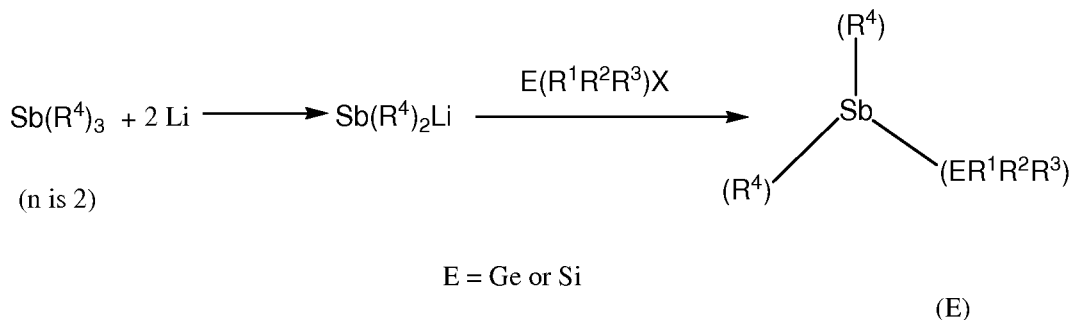
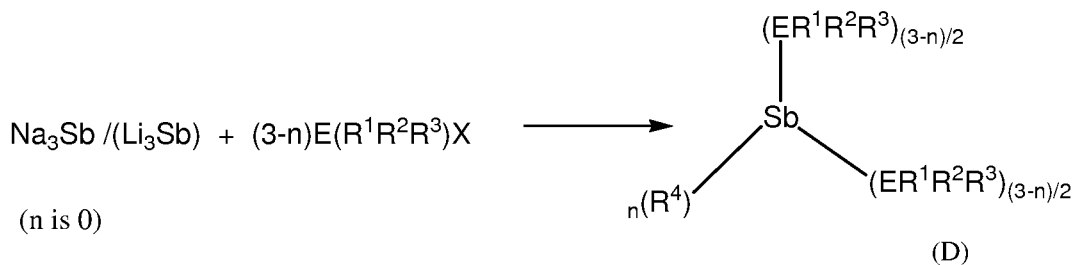
[0050] The antimony precursor of the general formula (C) can be formed by synthesis in a corresponding manner.

[0051] The antimony precursor of the general formula (D), having the following structure:



E = Ge or Si

can for example be synthesized according to the following reaction schemes (D), when n is zero, or (E), when n is 2:



wherein X is halo (fluorine, bromine, chlorine, iodine).

[0052] In the foregoing synthetic examples, RMgX and RLi can be used as alternative synthesis reagents.

[0053] As specific examples illustrative of precursors of the invention, the precursors $\text{Sb}(\text{NMeEt})_3$, $\text{Sb}(\text{CH}=\text{CMe}_2)_3$, $\text{Sb}(\text{CH}_2\text{CH}=\text{CH}_2)_3$ and $\text{Sb}(\text{NMe}_2)_3$ were synthesized and characterized. The precursors $\text{Sb}(\text{NMe}_2)_3$ and $\text{Sb}(\text{NMeEt})_3$ were determined to exhibit photo-sensitivity and therefore to require storage in a container protected from light exposure or in other photo-resistant packaging, to avoid light-induced decomposition thereof. Similar considerations are applicable to $\text{Sb}(\text{CH}=\text{CMe}_2)_3$ and $\text{Sb}(\text{CH}_2\text{CH}=\text{CH}_2)_3$.

[0054] FIG. 1 shows the nuclear magnetic resonance spectrum of $\text{Sb}(\text{NMeEt})_3$ and FIG. 2 shows the nuclear magnetic resonance spectrum of $\text{Sb}(\text{NMe}_2)_3$.

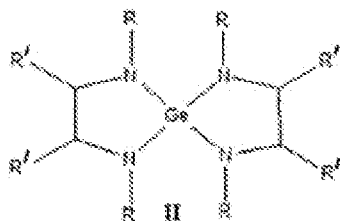
[0055] FIG. 3 is a simultaneous thermal analysis (STA) graph for these two precursors, $\text{Sb}(\text{NMeEt})_3$ and $\text{Sb}(\text{NMe}_2)_3$, in which percentage thermogravimetry (TG) is plotted as a function of temperature, in degrees Centigrade.

[0056] The invention in another aspect relates to germanium precursors useful for CVD and ALD deposition of germanium films on substrates, of the following formulae I-XVI:



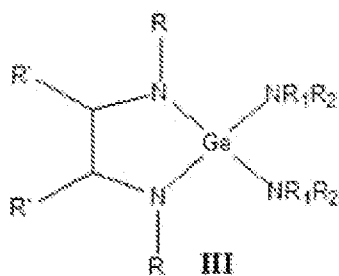
wherein:

R_1 and R_2 may be the same as or different from one another, and are independently selected from H, C_1 - C_6 alkyl, C_2 - C_5 alkenyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}_3)_3$ wherein each R_3 is independently selected from C_1 - C_6 alkyl;



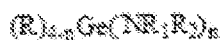
wherein:

R and R' may be the same as or different from one another, and each R and R' is independently selected from H, C_1 - C_6 alkyl, C_2 - C_5 alkenyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}_3)_3$ wherein each R_3 is independently selected from C_1 - C_6 alkyl;



wherein:

R, R', R₁ and R₂ may be the same as or different from one another, and each is independently selected from H, C₁-C₆ alkyl, C₂-C₅ alkenyl, C₅-C₁₀ cycloalkyl, C₆-C₁₀ aryl, and -Si(R₃)₃ wherein each R₃ is independently selected from C₁-C₆ alkyl;

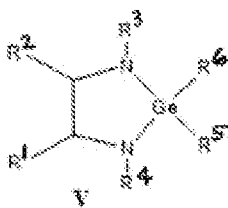


IV

wherein:

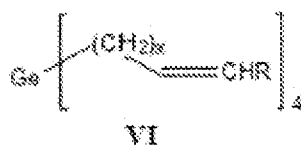
R, R₁ and R₂ may be the same as or different from one another, and each is independently selected from H, C₁-C₆ alkyl, C₂-C₅ alkenyl, C₅-C₁₀ cycloalkyl, C₆-C₁₀ aryl, and -Si(R₃)₃ wherein each R₃ is independently selected from C₁-C₆ alkyl; and

n is an integer from 0 to 4 inclusive;



wherein:

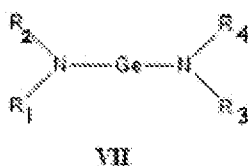
R¹, R², R³, R⁴, R⁵ and R⁶ may be the same as or different from one another, and each is independently selected from H, C₁-C₆ alkyl, C₂-C₅ alkenyl, C₅-C₁₀ cycloalkyl, C₆-C₁₀ aryl, and -Si(R₃)₃ wherein each R₃ is independently selected from C₁-C₆ alkyl;



wherein:

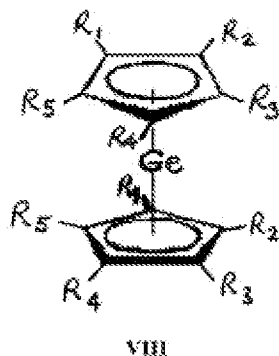
R is selected from H, C₁-C₆ alkyl, and C₆-C₁₀ aryl; and

x is 0, 1 or 2;



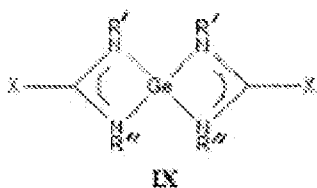
wherein:

R₁, R₂, R₃ and R₄ may be the same as or different from the others, and each is independently selected from among H, C₁-C₆ alkyl, C₅-C₁₀ cycloalkyl, C₆-C₁₀ aryl, and -Si(R₃)₃ wherein each R₃ is independently selected from C₁-C₆ alkyl;



wherein:

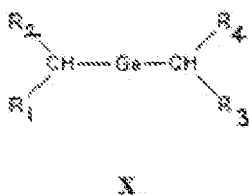
R₁, R₂, R₃, R₄, and R₅ may be the same as or different from one another, and each is independently selected from among H, C₁-C₆ alkyl, silyl, -Si(R')₃, C₆-C₁₀ cycloalkyl, C₆-C₁₀ aryl, -(CH₂)_xNR'R'', and -(CH₂)_xOR''', wherein x = 1, 2 or 3, and R', R'' and R''' may be the same as or different from one another, and each is independently selected from C₁-C₆ alkyl;



wherein:

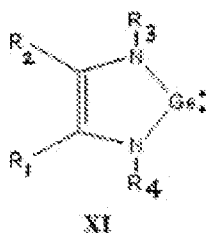
R' and R'' may be the same as or different from one another, and are independently selected from among H, C₁-C₆ alkyl, C₅-C₁₀ cycloalkyl, C₆-C₁₀ aryl, and -Si(R³)₃ wherein each R³ is independently selected from C₁-C₆ alkyl; and

each X is independently selected from among C₁-C₆ alkyl, C₁-C₆ alkoxy, -NR¹R², and -C(R³)₃, wherein each of R¹, R² and R³ is independently selected from H, C₁-C₆ alkyl, C₅-C₁₀ cycloalkyl, C₆-C₁₀ aryl, and -Si(R⁴)₃ wherein each R⁴ is independently selected from C₁-C₆ alkyl;



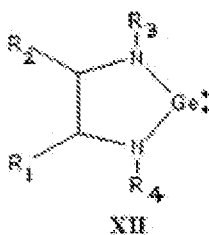
wherein:

R₁, R₂, R₃ and R₄ may be same as or different from one another, and are independently selected from among H, C₁-C₆ alkyl, C₅-C₁₀ cycloalkyl, C₆-C₁₀ aryl, and -Si(R³)₃ wherein each R³ is independently selected from C₁-C₆ alkyl;



wherein:

R₁, R₂, R₃ and R₄ may be the same as or different from one another, and are independently selected from among H, C₁-C₆ alkyl, C₅-C₁₀ cycloalkyl, C₆-C₁₀ aryl, and -Si(R³)₃ wherein each R³ is independently selected from C₁-C₆ alkyl;



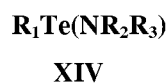
wherein:

R_1 , R_2 , R_3 and R_4 may be the same as or different from one another, and are independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl;



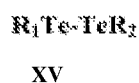
wherein:

R_1 and R_2 may be the same as or different from one another, and are independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl;



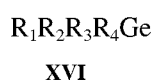
wherein:

R_1 , R_2 and R_3 may be the same as or different from one another, and are independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl;



wherein:

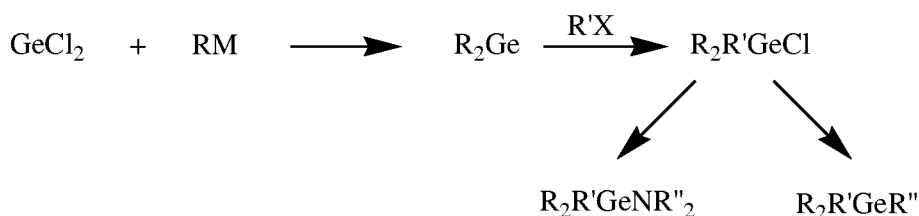
R_1 and R_2 may be the same as or different from one another, and are independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl; and



wherein:

R_1 , R_2 , R_3 , and R_4 may be the same as or different from one another, and are independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl.

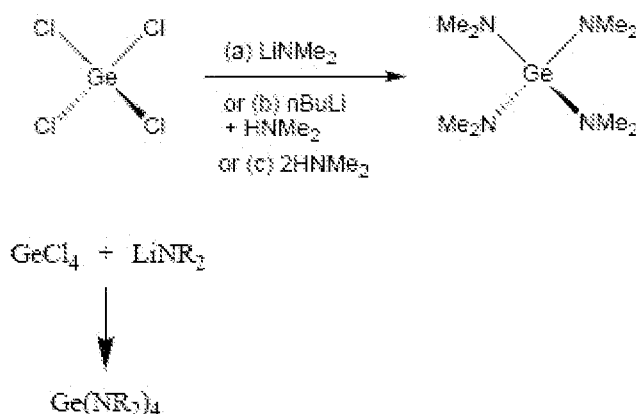
[0057] The synthesis of the above-described germanium precursors can variously be carried out in a ready manner, utilizing synthetic preparations of the types variously shown below. In each instance RMgCl , RMgBr , RMgI , RLi , and RNa can be used as alternative reagents. Further, GeBr_4 can be used in place of GeCl_4 ; LiNR_2 can be replaced by NaNR_2 or KNR_2 ; and $\text{Na}(\text{C}_5\text{R}_5)$ can be used as an alternative to $\text{K}(\text{C}_5\text{R}_5)$. Moreover, a multi-step synthetic approach may be employed to generate mixed alkyl species through oxidative addition to a $\text{Ge}(\text{II})$ complex to generate $\text{Ge}(\text{IV})$ precursors, as shown below:



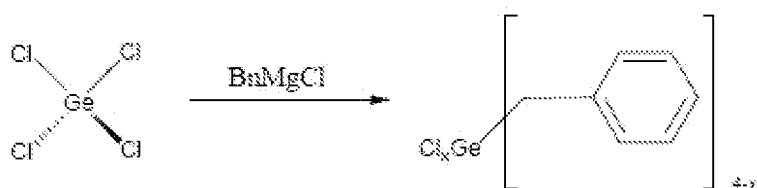
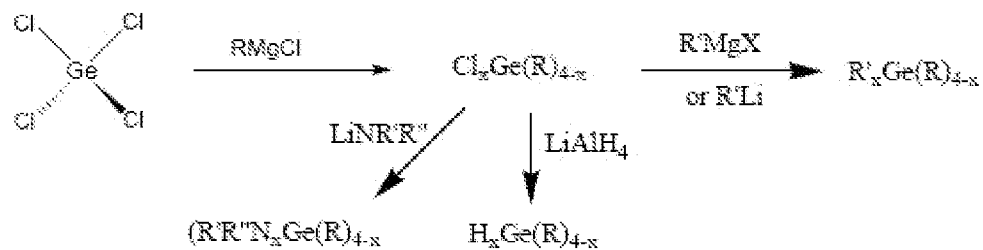
wherein:

R , R' , and R'' may be the same as or different from one another, and each is independently selected from H, C_1 - C_6 alkyl, C_2 - C_6 alkenyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}_3)_3$ wherein each R_3 is independently selected from C_1 - C_6 alkyl, and M is Li, Na, MgCl , MgBr , or MgI .

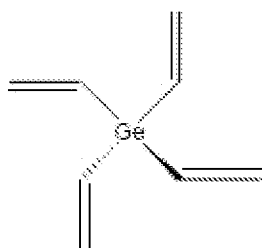
Germanium (IV) Precursors for GST Films



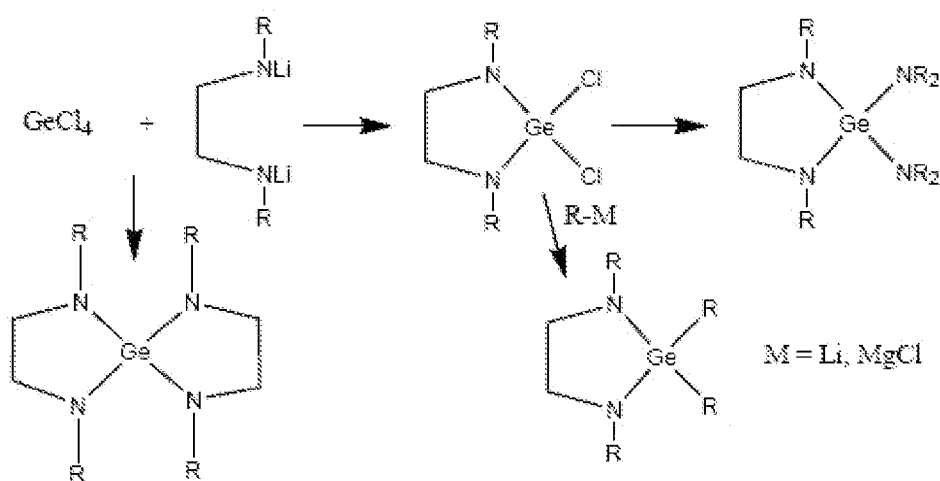
R = Me, Et, iPr, t-Bu or combinations

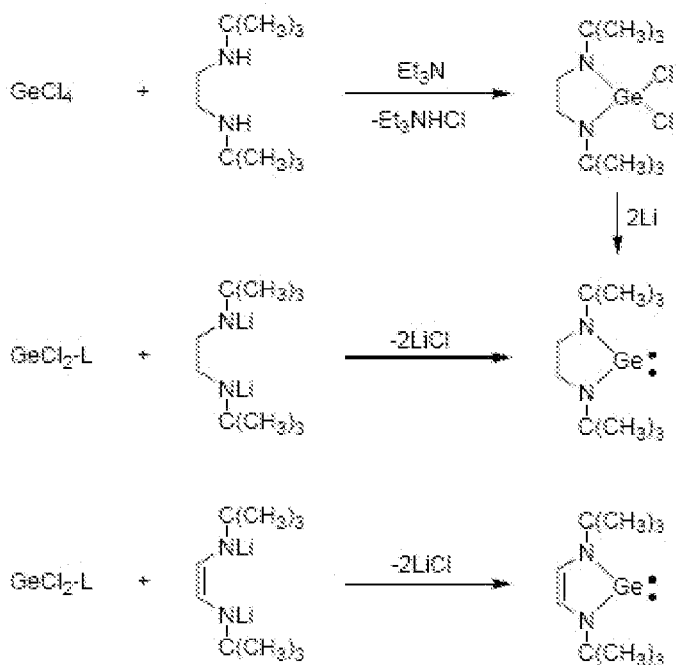
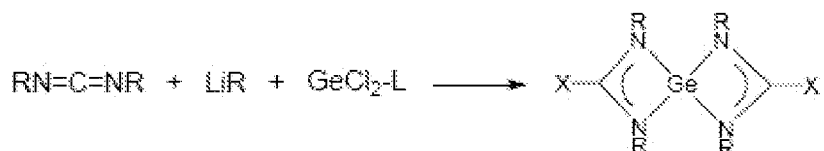
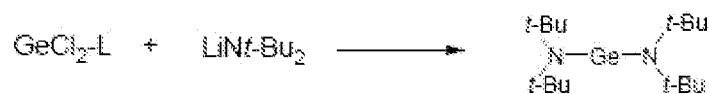


and correspondingly a tetraallylgermanium complex

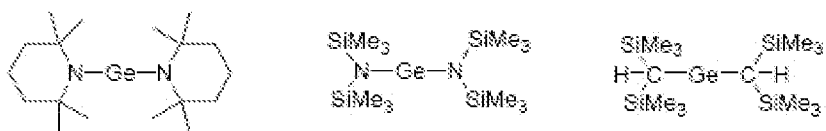


can be formed from such tetrachlorogermanium starting material using a corresponding allyl Grignard reagent R^*MgCl , wherein R^* is allyl

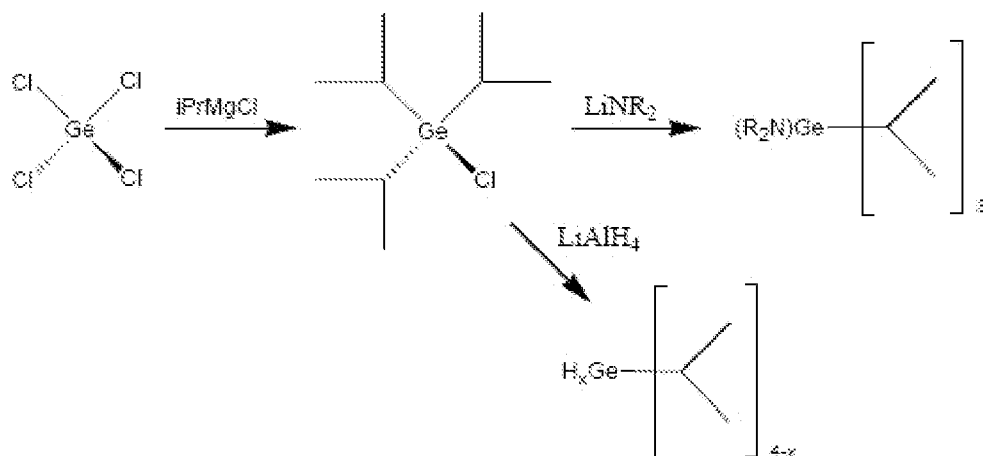


Ge Precursors for GST Films

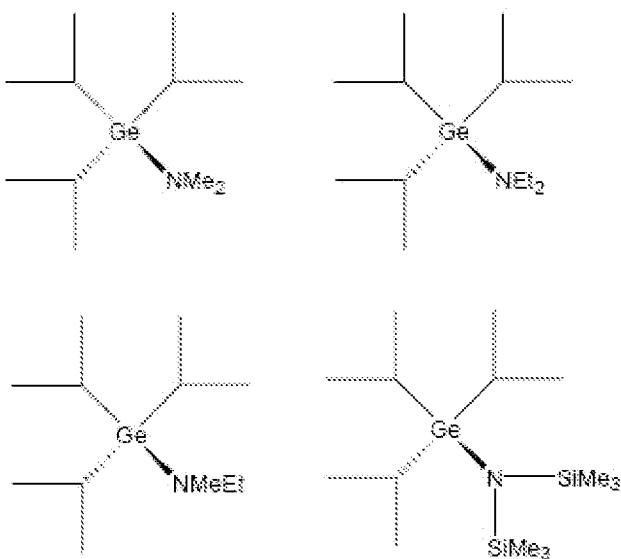
[0058] Illustrative Ge(II) compounds that may be usefully employed for CVD or ALD of germanium-containing films include the following:



[0059] In various embodiments of the invention, dialkylaminoisopropylgermane precursors are used for CVD/ALD formation of GST thin films. Such precursors may be synthesized by a reaction scheme such as that shown below:



to form germanium complexes such as:



[0060] The above-described germanium precursors are useful for CVD and ALD applications, to deposit germanium-containing films on substrates. Tetrakisamidogermanes and triisopropylamines useful for such applications and amenable to transport with a heated bubbler include, for example, $\text{Ge}(\text{NMe}_2)_4$, $\text{Ge}(\text{NEtMe})_4$, $\text{Ge}(\text{NEt}_2)_4$, $i\text{Pr}_3\text{GeCl}$, $i\text{Pr}_3\text{GeNMe}_2$, $i\text{Pr}_3\text{GeNEtMe}$, and $i\text{Pr}_3\text{GeNEt}_2$. The volatility of the germanium precursors of the invention can be readily measured by STA thermogravimetric technique (e.g., by determining material transport under atmospheric pressure in argon) and GC analysis.

[0061] In specific embodiments of germanium precursors of the present invention containing alkyl substituents, isopropyl substituents are in many cases preferred over methyl groups due to the ability of the isopropyl substituents to undergo beta-hydrogen elimination, thereby facilitating low temperature decomposition processing of the germanium precursor, without producing significant carbon residue.

[0062] Nitrogen containing germanium precursors of the invention have the intrinsic benefit in many applications of mediating some incorporation of nitrogen in final films. In this respect, Si- and N-doped GST materials have lower reset currents, thereby enabling a lower temperature phase-change to occur.

[0063] As an additional advantage, various germane precursors of the invention undergo hydrogermolysis coupling reactions to form Ge-Ge bonds, via the reaction



to yield digermane CVD precursors enabling highly efficient Ge-containing film deposition to be achieved, in relation to mono-germane precursors.

[0064] The germanium precursors of the invention can contain a wide variety of ligand species as moieties thereof. Such ligands may for example include, without limitation, allyl, benzyl, t-butyl, cyclopentadienyl, hydride, phenyl, and alkyl. Bidentate amines (e.g. N, N-dialkylethylenediamine) can also be used.

[0065] The germanium precursors can be delivered in solution or suspension in a liquid delivery technique, using suitable solvent media, or may be delivered for vapor phase desposition of Ge-containing films by solid delivery techniques, e.g., as described hereinabove in respect of the antimony precursors of the invention.

[0066] In use as CVD/ALD precursors, the Ge precursor may be deposited separately or in combination with other precursors, e.g., with Sb and Te complexes such as iPr_3Sb , $Sb(NR_2)_3$, iPr_2Te and $Te(NR_2)_2$ to form GST films.

[0067] One illustrative germanium precursor of the invention is Ge(trisopropyl)(methylethylamide), referred to sometimes hereinafter as GePNEM. This precursor can be employed to deposit germanium on a substrate at suitable deposition process conditions, e.g., deposition temperature in a range of from 300°C to 450°C, and at pressure ranging from subatmospheric to superatmospheric (e.g., in a range of from about 0.5 torr to 15 atmospheres or more). Set out in Table I below is a listing of film deposition rate, in Angstroms/minute, at varying temperature and pressure conditions, for deposition of germanium on substrates from the GePNEM precursor, delivered to the substrate in a carrier gas flow of hydrogen gas at 200 standard cubic centimeters per minute.

[0068] Table I.

Film Deposition Rate of Germanium Deposited at Varying Temperature and Pressure Conditions

Temperature (°C)	Temperature 1/T (K)	Pressure 0.8 torr	Pressure 8 torr
300	0.001745201	0.14 Å/min	0.35 Å/min
320	0.001686341	0.45 Å/min	
340	0.001631321	1.32 Å/min	0.8 Å/min
360	0.001579779	1.48 Å/min	1.28 Å/min
380	0.001531394	2.4 Å/min	2.7 Å/min
400	0.001485884	3.4 Å/min	2.3 Å/min
420	0.001443001	6.8 Å/min	10.5 Å/min
440	0.001403	6.5 Å/min	

GePNEM deposition with 200 SCCM H₂

[0069] In another determination of film thicknesses of germanium achieved by deposition from the GePNEM precursor, deposition carried out for a period of 16 minutes gave the following results: (i) temperature = 400°C, pressure = 800 millitorr, reactant gas H₂, film thickness = 57 Å; (ii) temperature = 400°C, pressure = 800 millitorr, reactant gas NH₃, film thickness = 94 Å; and (iii) temperature = 400°C, pressure = 8000 millitorr, reactant gas H₂, film thickness = 36 Å. These results evidence the suitability of GePNEM for forming germanium or germanium-containing thin films on substrates by vapor deposition techniques.

[0070] In various specific embodiments, the invention contemplates a precursor mixture including germanium precursor, antimony precursor and tellurium precursor, wherein at least one of the germanium precursor and antimony precursor includes a precursor selected from among the metal complexes of formulae (A), (B), (C), (D) and (E)(I)-(XVI) described hereinabove.

[0071] In another aspect, the invention contemplates additional classes of antimony precursors. Such antimony precursors are suitable for use in forming GST films, in conjunction with the use of suitable germanium and tellurium precursors.

[0072] Such additional classes of antimony precursors include those of formulae (F), (G), (H), (I), (J), (K), (L) and (M), as defined below:

(F) aminidates, guanidates and isoureates of the formula:



wherein:

where each R^1 and R^2 is independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(R^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl;

each X is independently selected from among C_1 - C_6 alkoxy, $-\text{NR}^4\text{R}^5$, and $-\text{C}(\text{R}^6)_3$, wherein each of R^4 , R^5 and R^6 is independently selected from H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(R^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl;

each R^7 is independently selected from among C_1 - C_6 alkoxy, $-\text{NR}^8\text{R}^9$, and $-\text{C}(\text{R}^{10})_3$, wherein each of R^8 , R^9 and R^{10} is independently selected from H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, $-\text{Si}(R^3)_3$, and $-\text{Ge}(R^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl; and

n is an integer from 0 to 3;

(G) tetra-alkyl guanidates of the formula:



wherein:

each of R^1 and R^2 is independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(R^9)_3$ wherein each R^9 is independently selected from C_1 - C_6 alkyl;

each of R^3 and R^4 is independently selected from H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(R^9)_3$ wherein each R^9 is independently selected from C_1 - C_6 alkyl;

each R^5 is independently selected from among C_1 - C_6 alkoxy, $-\text{NR}^6\text{R}^7$, and $-\text{C}(\text{R}^8)_3$, wherein each of R^6 , R^7 and R^8 is independently selected from H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, $-\text{Si}(R^9)_3$, and $-\text{Ge}(R^9)_3$ wherein each R^9 is independently selected from C_1 - C_6 alkyl; and

n is an integer from 0 to 3.

(H) carbamates and thiocarbamates of the formula:



wherein:

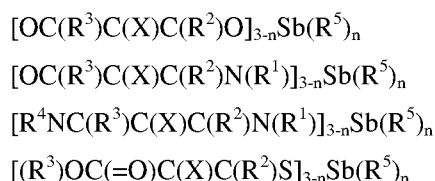
each X is independently selected from among C₁-C₆ alkoxy, -NR¹R², and -C(R³)₃, wherein each of R¹, R² and R³ is independently selected from H, C₁-C₆ alkyl, C₅-C₁₀ cycloalkyl, C₆-C₁₀ aryl, and -Si(R⁵)₃ wherein each R⁵ is independently selected from C₁-C₆ alkyl;

each R⁴ is independently selected from among C₁-C₆ alkoxy, -NR¹R², and -C(R³)₃, wherein each of R¹, R² and R³ is independently selected from H, C₁-C₆ alkyl, C₅-C₁₀ cycloalkyl, C₆-C₁₀ aryl, and -Si(R⁵)₃, -Ge(R⁵)₃ wherein each R⁵ is independently selected from C₁-C₆ alkyl;

E is either O or S; and

n is an integer from 0 to 3;

(I) beta-diketonates, diketoiminates, and diketiminates, of the formulae:



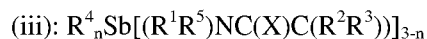
where each of R¹, R², R³ and R⁴ is independently selected from among H, C₁-C₆ alkyl, C₅-C₁₀ cycloalkyl, C₆-C₁₀ aryl, and -Si(R⁶)₃ wherein each R⁶ is independently selected from C₁-C₆ alkyl;

each X is independently selected from among C₁-C₆ alkoxy, -NR⁶R⁷, and -C(R⁸)₃, wherein each of R⁶, R⁷ and R⁸ is independently selected from H, C₁-C₆ alkyl, C₅-C₁₀ cycloalkyl, C₆-C₁₀ aryl, and -Si(R⁶)₃ wherein each R⁶ is independently selected from C₁-C₆ alkyl;

each R⁵ is independently selected from among guanidinate, aminidate, isoureate, allyl, C₁-C₆ alkoxy, -NR⁹R¹⁰, and -C(R¹¹)₃, wherein each of R⁹, R¹⁰ and R¹¹ is independently selected from H, C₁-C₆ alkyl, C₅-C₁₀ cycloalkyl, C₆-C₁₀ aryl, -Si(R⁶)₃, and -Ge(R⁶)₃ wherein each R⁶ is independently selected from C₁-C₆ alkyl; and

n is an integer from 0 to 3.

(J) allyls of the formulae:



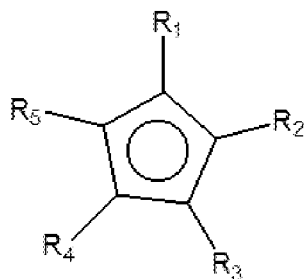
where each R^1, R^2, R^3 and R^5 is independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-Si(R^6)_3$ wherein each R^6 is independently selected from C_1 - C_6 alkyl;

each X is independently selected from among C_1 - C_6 alkoxy, $-NR^1 R^2$, and $-C(R^3)_3$, wherein each of R^1, R^2 and R^3 is independently selected from H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-Si(R^6)_3$ wherein each R^6 is independently selected from C_1 - C_6 alkyl;

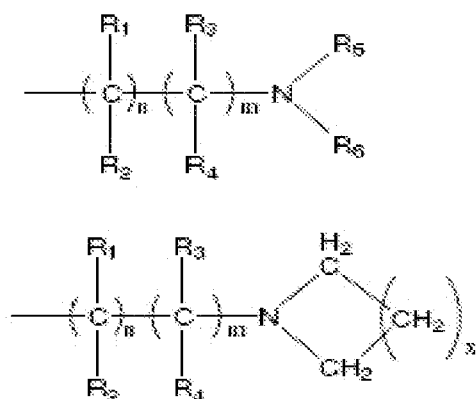
each R^4 is independently selected from among guanidates, aminidates, isoureates, beta-diketonates, diketiminates, diketiminates, C_1 - C_6 alkoxy, $-NR^7 R^8$, and $-C(R^9)_3$, wherein each of R^7, R^8 and R^9 is independently selected from H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, $-Si(R^6)_3$, and $-Ge(R^6)_3$ wherein each R^6 is independently selected from C_1 - C_6 alkyl; and

n is an integer from 0 to 3.

(L) cyclopentadienyl (Cp) antimony compounds wherein the Cp moiety is of the formulae:

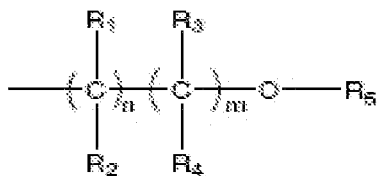


wherein each of R_1 , R_2 , R_3 , R_4 and R_5 can be the same as or different from the others, and each is independently selected from among hydrogen, C_1 - C_{12} alkyl, C_1 - C_{12} alkylamino, C_6 - C_{10} aryl, C_1 - C_{12} alkoxy, C_3 - C_6 alkylsilyl, C_2 - C_{12} alkenyl, $R^1R^2NNR^3$, wherein R^1 , R^2 and R^3 may be the same as or different from one another and each is independently selected from C_1 - C_6 alkyl, and pendant ligands including functional group(s) providing further coordination to the antimony central atom, and selected from among aminoalkyl, alkoxyalkyl, aryloxyalkyl, imidoalkyl, and acetylalkyl, having the following formulae:



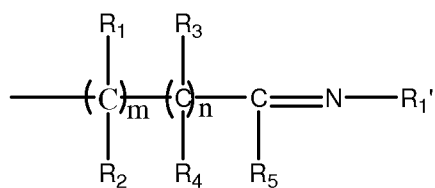
aminoalkyls

wherein: the methylene ($-CH_2-$) moiety could alternatively be another divalent hydrocarbyl moiety; each of R_1 - R_4 is the same as or different from one another, with each being independently selected from among hydrogen, C_1 - C_6 alkyl and C_6 - C_{10} aryl; each of R_5 and R_6 is the same as or different from the other, with each being independently selected from among C_1 - C_6 alkyl; n and m are each selected independently as having a value of from 0 to 4, with the proviso that m and n cannot be 0 at the same time, and x is selected from 1 to 5;

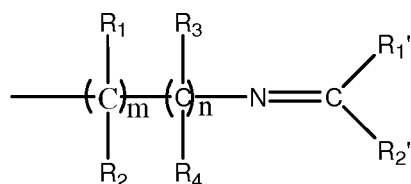


alkoxyalkyls and aryloxyalkyls

wherein each of R_1 - R_4 is the same as or different from one another, with each being independently selected from among hydrogen, C_1 - C_6 alkyl, and C_6 - C_{10} aryl; R_5 is selected from among C_1 - C_6 alkyl, and C_6 - C_{10} aryl; and n and m are selected independently as having a value of from 0 to 4, with the proviso that m and n cannot be 0 at the same time;

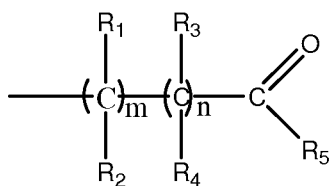


and



imidoalkyl

wherein each of R_1 , R_2 , R_3 , R_4 , R_5 is the same as or different from one another, with each being independently selected from among hydrogen, C_1 - C_6 alkyl, and C_6 - C_{10} aryl; each of R_1' , R_2' is the same as or different from one another, with each being independently selected from C_1 - C_6 alkyl, and C_6 - C_{10} aryl; and n and m are selected independently from 0 to 4, with the proviso that m and n cannot be 0 at the same time;

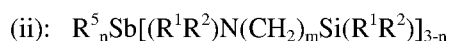


acetylalkyls

wherein each of R_1 - R_4 is the same as or different from one another, with each being independently selected from among hydrogen, C_1 - C_6 alkyl, and C_6 - C_{10} aryl; R_5 is selected from among C_1 - C_6 alkyl, C_6 - C_{10} aryl, and C_1 - C_5 alkoxy; and n and m are selected independently from 0 to 4, with the proviso that m and n cannot be 0 at the same time;

wherein non-Cp ligand(s) of the antimony Cp compound can optionally include ligands selected from the group consisting of guanidates, aminidates, isoureates, allyls, beta-diketonates, diketoiminates, and diketiminates; and

(M) alkyls, alkoxides and silyls with pendent ligands, of the formulae:



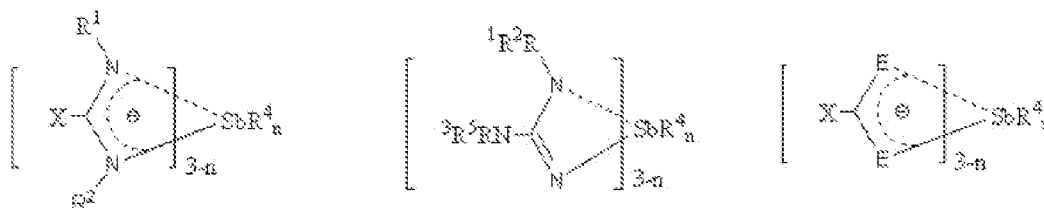
where each of R^1 and R^2 is independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-Si(R^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl;

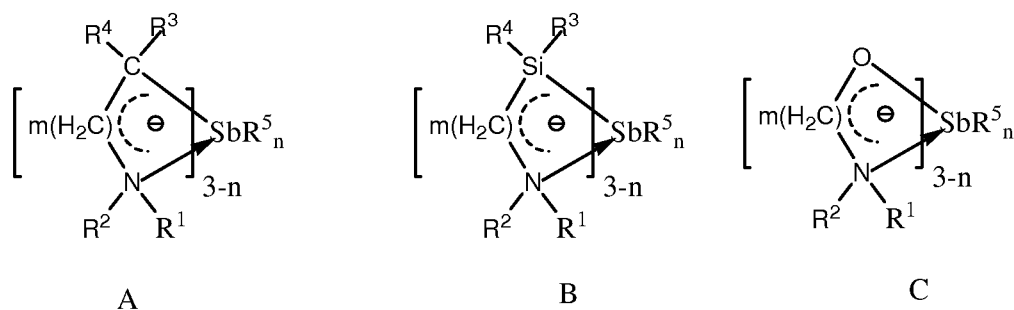
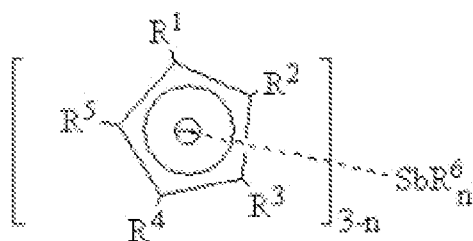
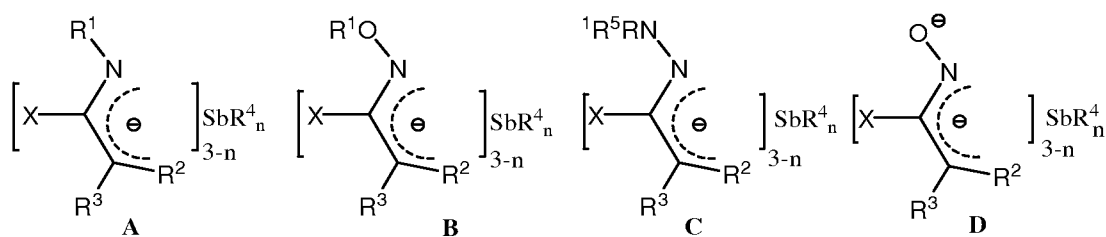
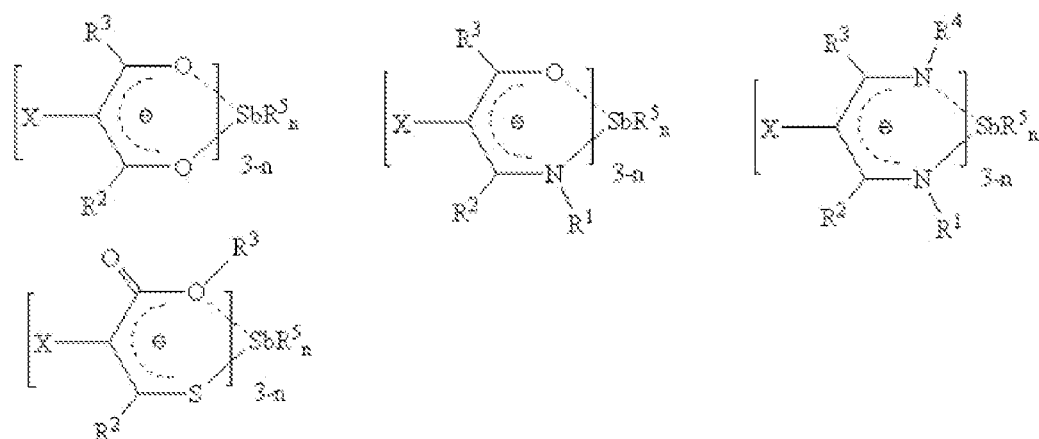
each R^5 is independently selected from among guanidates, aminidates, isoureates, beta-diketonates, diketoiminates, diketiminates, C_1 - C_6 alkoxy, $-NR^6 R^7$, and $-C(R^8)_3$, wherein each of R^6 , R^7 and R^8 is independently selected from H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, $-Si(R^3)_3$, and $-Ge(R^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl;

n is an integer from 0 to 3;

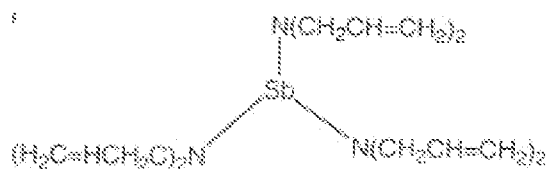
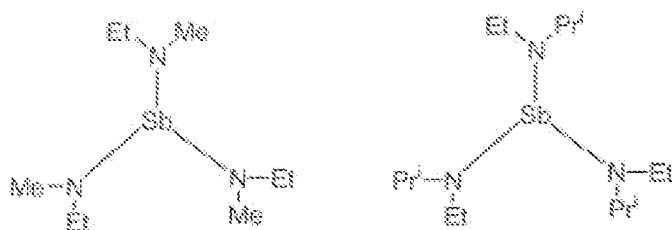
m is integer from 0 to 4.

[0073] Antimony precursors of a general type within the foregoing classes (F)-(M) include precursors having the following structures, wherein the various "R" groups in these structures are not necessarily numbered in exact correspondence with the substituent numberings in the above formulae, but nonetheless reflect the substituted positions in general fashion, which will be understood in reference to the above definitions of the substituents at the various positions of the associated molecules.

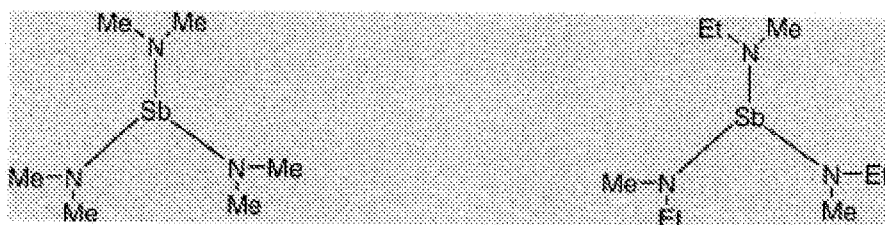




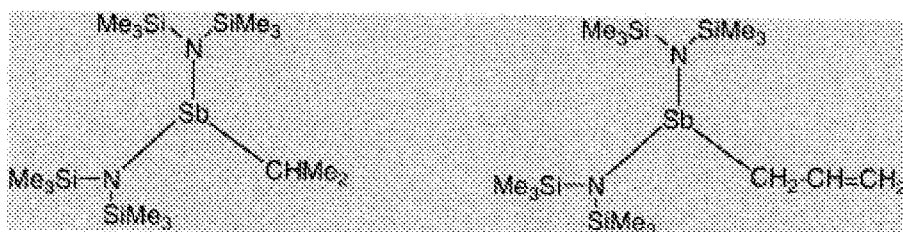
including the following illustrative complexes:



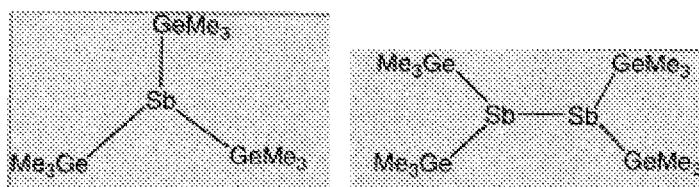
antimony amides of the formulae

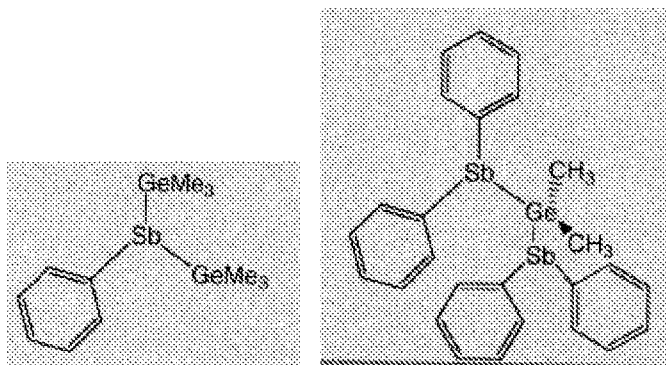


antimony (III) alkyl/amino precursors of the formulae:



and stibenes with germanium anions, of the formulae:





[0074] The antimony precursors of classes (F)-(M) are usefully employed for deposition of antimony at low temperature with reducing co-reactants, e.g., reactants such as hydrogen, H_2 /plasma, amines, imines, hydrazines, silanes, silyl chalcogenides such as $(Me_3Si)_2Te$, germanes such as GeH_4 , ammonia, alkanes, alkenes, and alkynes.

[0075] The antimony precursors may be delivered for such deposition via liquid delivery techniques, in which precursors that are liquids may be used in neat liquid form, and precursors that are solids or liquids may be delivered in solutions or suspensions, in combination with suitable solvents, such as alkane solvents (e.g., hexane, heptane, octane, and pentane), aryl solvents (e.g., benzene or toluene), amines (e.g., triethylamine, tert-butylamine), imines and hydrazines. The utility of specific solvent compositions for particular antimony precursors can be readily empirically determined, to select an appropriate single component or multicomponent solvent medium for liquid delivery vaporization and transport of the specific antimony precursor that is employed.

[0076] In another aspect of the invention, solid delivery techniques may be employed, in which the solid precursor is volatilized, to form a precursor vapor that is delivered to the deposition chamber for forming an antimony or antimony-containing film on the substrate. The solid precursor may be packaged for such use in a storage and dispensing package of suitable character, such as the ProE-Vap solid delivery and vaporizer unit commercially available from ATMI, Inc. (Danbury, CT, USA).

[0077] The invention also contemplates the use of antimony, germanium and tellurium precursors of the present invention separately for deposition of antimony-containing films, germanium-containing films, and tellurium-containing films, respectively. Thus, an antimony precursor of the invention may be employed to deposit an antimony-containing film. In another embodiment, a germanium precursor of the invention may be employed to form a germanium-containing film. In another embodiment, a tellurium precursor of the invention may be employed to form a tellurium-containing film. In still another embodiment, an antimony precursor of the invention and a germanium precursor of the invention may be utilized to form

an antimony/germanium film. In yet another embodiment, an antimony precursor of the invention can be utilized in combination with a tellurium precursor, to form an antimony/tellurium film. Another embodiment of the invention involves use of a germanium precursor of the invention in combination with a tellurium precursor, to form a germanium/tellurium film.

[0078] The antimony and/or germanium precursors of the invention can be used to deposit $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films on suitable microelectronic device substrates in the fabrication of phase change memory devices.

[0079] Such GST films can be fabricated using continuous CVD or ALD techniques using suitable germanium, antimony and tellurium precursors, with at least one of the germanium and antimony precursors comprising a metal complex of the present invention. The precursors may be supplied in appropriate ratios to yield the GST film of desired character. For example, ALD may be performed with the precursors (Ge, Sb, Te) being pulsed in a manner to control composition of the resulting film, e.g., with a pulse cycle including a sequential introduction of precursor species in the sequence Te-Ge-Te-Sb-Te-Ge-Te-Sb-Te, repetitively conducted until a desired film thickness has been achieved.

[0080] As another variant of deposition techniques that may advantageously be employed to form films containing antimony and/or germanium, by use of precursors of the present invention, other co-reactant species may be added in the deposition operation, to compositionally modify the resulting film. Examples include use of co-reactants to compositionally modify the film for oxygen and/or nitrogen incorporation, e.g., with very small amounts of N_2O , O_2 and NO .

[0081] In other embodiments, atomic layer deposition (ALD) and rapid vapor deposition (RVD) techniques may be employed to deposit films containing antimony and/or germanium using precursors of the present invention. For example, a rapid surface catalyzed vapor deposition may be employed using ALD, in which a first precursor vapor is contacted with the substrate to form a saturated surface layer of the precursor, followed by exposure to a second precursor vapor, and thereafter by exposure to a third precursor vapor, with inert gas purges being carried out between the respective precursor vapor contacting steps, in which at least one of the first, second and third precursors comprises an antimony and/or germanium precursor of the invention and, and in which the precursor contacting and intervening purge steps are repetitively conducted until a predetermined thickness of deposited film material has been achieved.

[0082] More generally, the present invention contemplates a wide variety of antimony and germanium complexes that can be utilized to form corresponding Sb- and Ge-containing films. The precursor complexes and compositions of the invention accordingly can be varied in specific usage, and can comprise, consist, or consist essentially of specific metal source

reagents, or such specific reagents and other precursor species. Further, it may be desirable in some applications to employ multiple precursor species of the invention, in combination with one another and/or together with other precursor species.

[0083] The invention also contemplates specific structural definitions and/or specifications of precursor complexes in specific embodiments, and the exclusion of specific moieties, ligands and elemental species in specific embodiments. As an illustrative example, in homoleptic tris(dialkylamido)antimony complexes and tetrakis(dialkylamido)germanium complexes of the invention, the alkyl substituents may exclude methyl. As another example, tetrakisdialkylamidogermenes may be excluded in certain embodiments of the invention. As a still further example, in germanyl and silyl antimony complexes of the invention, trimethylgermanyl and trimethylsilyl species may for example be excluded. It will therefore be appreciated that the invention admits of delimited complexes and compositional features of complexes in various particularized embodiments of the invention, for purposes of identifying precursor complexes and classes of same that are preferred implementations of the invention in certain applications thereof.

[0084] The synthesis of ethylmethyaminotriisopropylgermane is now described to show the details of making an illustrative germanium precursor of the invention.

[0085] Example 1. Synthesis of ethylmethyaminotriisopropylgermane

A solution of nBuLi (2M in hexanes, 26.34mL, 42.14mmol) was slowly added to an ice-cooled solution of ethylmethanamine (3.98mL, 46.35mmol) in ether (100mL). The resulting white mixture was stirred for 2 hours. Triisopropylchlorogermane (9.16mL, 42.14mmol) was added dropwise and the reaction mixture slowly warmed to room temperature. The mixture was stirred overnight, the solvent evaporated under vacuum, and the residue washed with pentane (100mL). The mixture was filtered through a medium glass frit under nitrogen and the solvent evaporated under vacuum to give 10.7g, 98% of a colorless liquid. The product was purified by fractional distillation (40°C, 75mtorr). ¹H NMR (C₆D₆): δ 2.87 (q, 2H, ³J = 6.9Hz, NCH₂CH₃), 2.62 (s, 3H, NCH₃), 1.36 (m, CH(CH₃)₂), 1.18 (d, 18H, ³J = 7.2Hz, CH(CH₃)₂), 1.11 (t, 3H, ³J = 6.9Hz, NCH₂CH₃). ¹³C NMR (C₆D₆): δ 48.42, 38.22 (NCH₂CH₃, NCH₃), 20.19 (CH(CH₃)₂), 16.20, 15.79 (NCH₂CH₃, CH(CH₃)₂).

[0086] FIG. 4(a) is a gas chromatography (GC) spectrum for such ethylmethyaminotriisopropylgermane product, and FIG. 4(b) is a corresponding tabulation of peak data for such GC spectrum. FIG. 4(c) is a mass spectrum for the ethylmethyaminotriisopropylgermane product. FIG. 4(d) shows the nuclear magnetic resonance spectrum of the ethylmethyaminotriisopropylgermane product.

[0087] FIG. 5 is an STA spectrum of the ethylmethyaminotriisopropylgermane product, showing differential scanning calorimetry (DSC) data and thermogravimetric (TG) data, as a function of temperature.

[0088] Another aspect of the invention relates to tellurium complexes with beta-diketiminato 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-diketiminato 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.

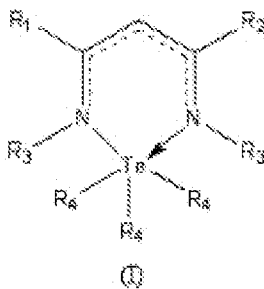
[0089] The tellurium diketiminato complexes of the invention can be used for CVD/ALD to form Te or Te-containing films. These compounds can be used in combination with Ge- and/or Sb-compounds to produce Te-Ge-, Te-Sb- or Ge-Sb-Te films in varied compositions. A general procedure to synthesize diketiminato ligands has been described in the literature, but such procedure is disadvantageous, since very bulky aryl substituents on the coordinating nitrogen atoms are required.

[0090] 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 diketiminato precursors for CVD/ALD applications. Smaller substituents on the nitrogen donor atoms provide sufficient volatility to form good films at low temperature.

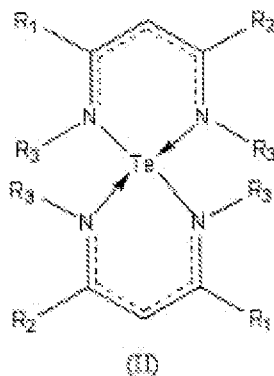
[0091] The ligands L can be used as the lithium salt or in a free imine form to synthesize the desired Te complexes. The lithium salt of the ligand can be reacted with TeX_4 (wherein $X = \text{Cl, Br, I}$) to generate LTeX_3 by salt elimination, which can then be reacted with either a lithium or a Grignard reagent to produce LTeR_3 (wherein $R = \text{alkyl, aryl, amide, silyl}$).

[0092] 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 diketiminato 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.

[0093] The tellurium complexes of the invention have the formulae (I) and (II):

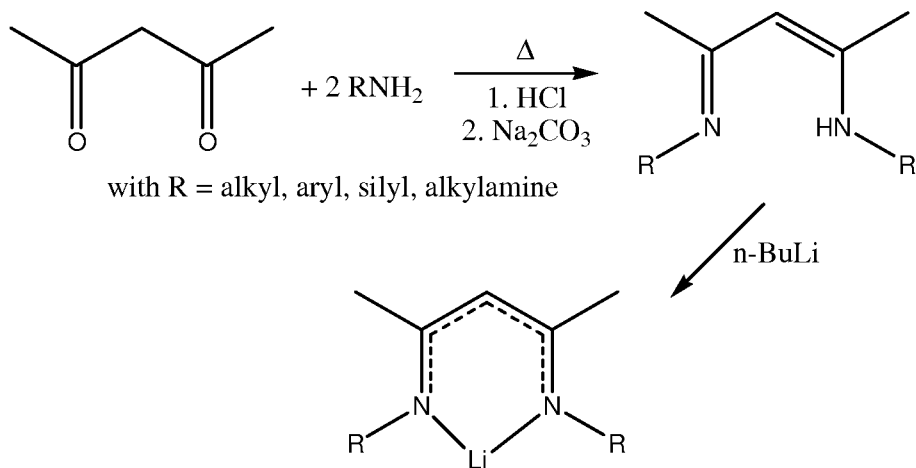


wherein R_1 , R_2 and R_3 they be the same as or different from one another, and each is independently selected from C_1 - C_6 alkyl, C_6 - C_{10} aryl, silyl and C_1 - C_{12} alkylamine (which includes both monoalkylamine as well as dialkylamine); and

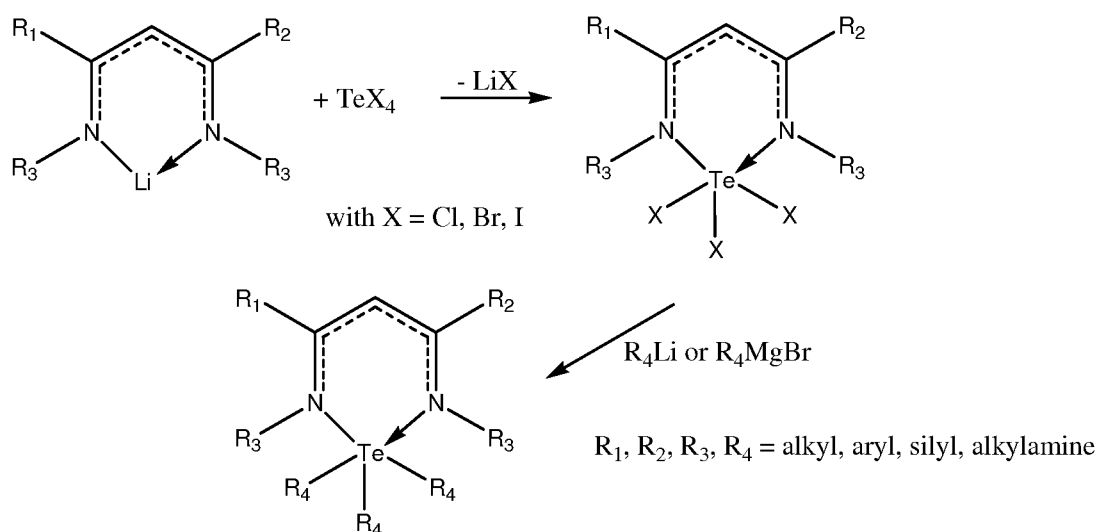


wherein R_1 , R_2 and R_3 they be the same as or different from one another, and each is independently selected from C_1 - C_6 alkyl, C_6 - C_{10} aryl, silyl and C_1 - C_{12} alkylamine (which includes both monoalkylamine as well as dialkylamine).

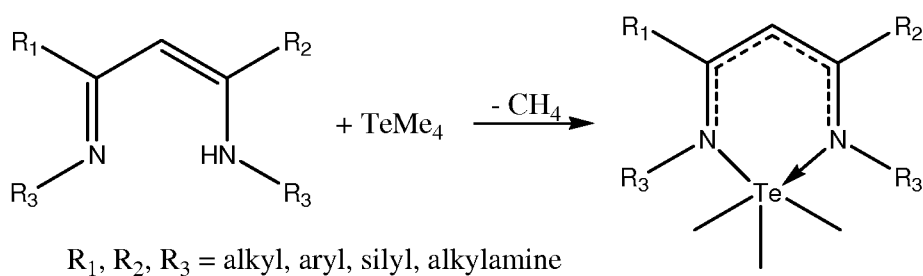
[0094] The beta-diketiminato ligands may for example be synthesized by the following procedure:



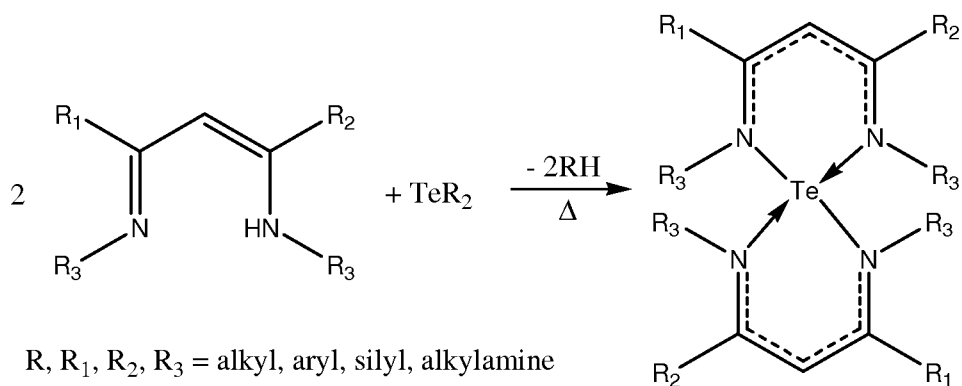
[0095] The tellurium complexes then can be synthesized by the following reaction:



[0096] or alternatively by the following synthesis reaction:

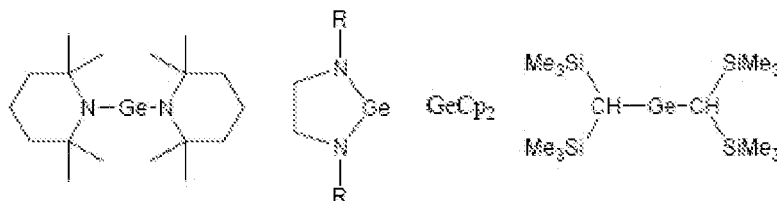


[0097] or by the following synthesis reaction:



[0098] 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.

[0099] 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, C₁-C₆ alkyl, C₆-C₁₀ aryl, C₃-C₈ cycloalkyl, heteroatom groups, and other organo groups.

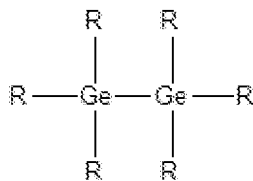
[00100] Another aspect of the invention relates to digermane and strained ring germanium precursors for CVD/ALD of germanium-containing thin films. Previously employed germanium precursors such as germane that have been used for forming GST (germanium-antimony-tellurium) films for phase change memory devices require very high temperature deposition conditions. This in turn makes it difficult to form a pure Ge₂Sb₂Te₅ 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.

[00101] Germanium-germanium bonds are inherently weak (~ 188 kJ/mole) and become less stable with electron withdrawing substituents such as chlorine or NMe₂. Such bonds can readily dissociate to form R₃Ge 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.

[00102] 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-CH₃ (83 kcal/mol), thereby enabling lower temperature film deposition of germanium to be achieved, than has been achievable with the aforementioned conventional germanium precursors.

[00103] The germanium complexes of the invention include those of formulae (I) – (III) below:

(I) alkyl digermanes of the formula



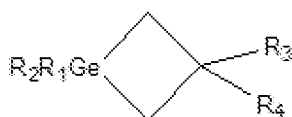
wherein each R may be the same as or different from the others, and each is independently selected from among isopropyl, isobutyl, benzyl, allyl, alkylamino, nitriles, and isonitriles;

(II) alkyl(dialkylamino)germanes of the formula



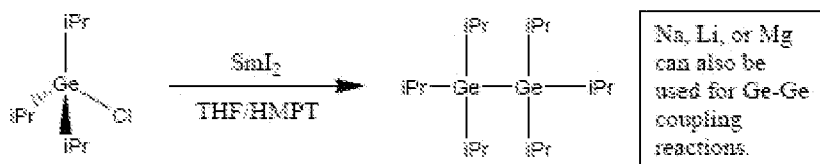
wherein each R may be the same as or different from the others, and each is independently selected from among isopropyl, isobutyl, benzyl, allyl, alkylamino, nitriles, and isonitriles; and

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

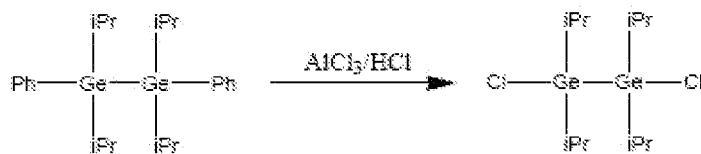


wherein each of R₁, R₂, R₃ and R₄ may be the same as or different from the others, and each is independently selected from among H, C₁-C₆ alkyl, C₆-C₁₀ aryl, C₃-C₈ cycloalkyl, or a heteroatom group.

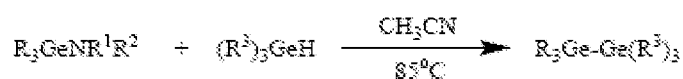
[00104] The complexes (I) can be synthesized, by way of example, according to the following synthesis process:



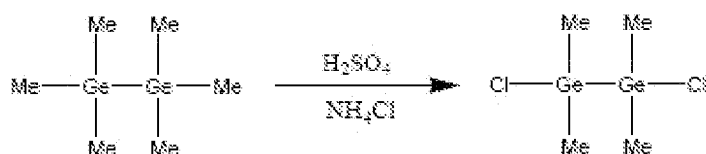
or by the following synthesis:



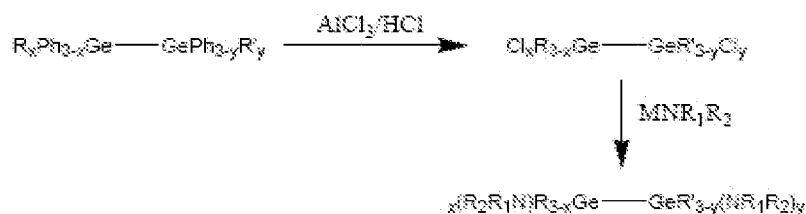
or by a synthesis such as the following:



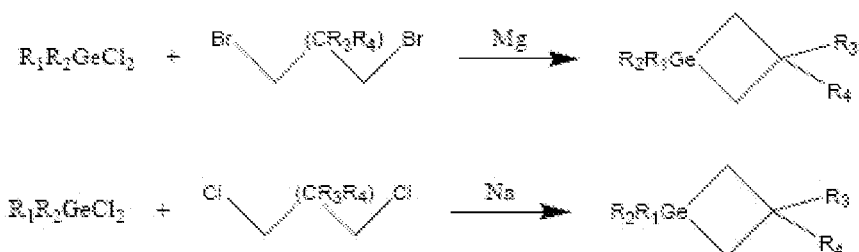
or a synthesis procedure such as:



[00105] The germanium complexes of formula (II) can be formed by the following illustrated procedure:

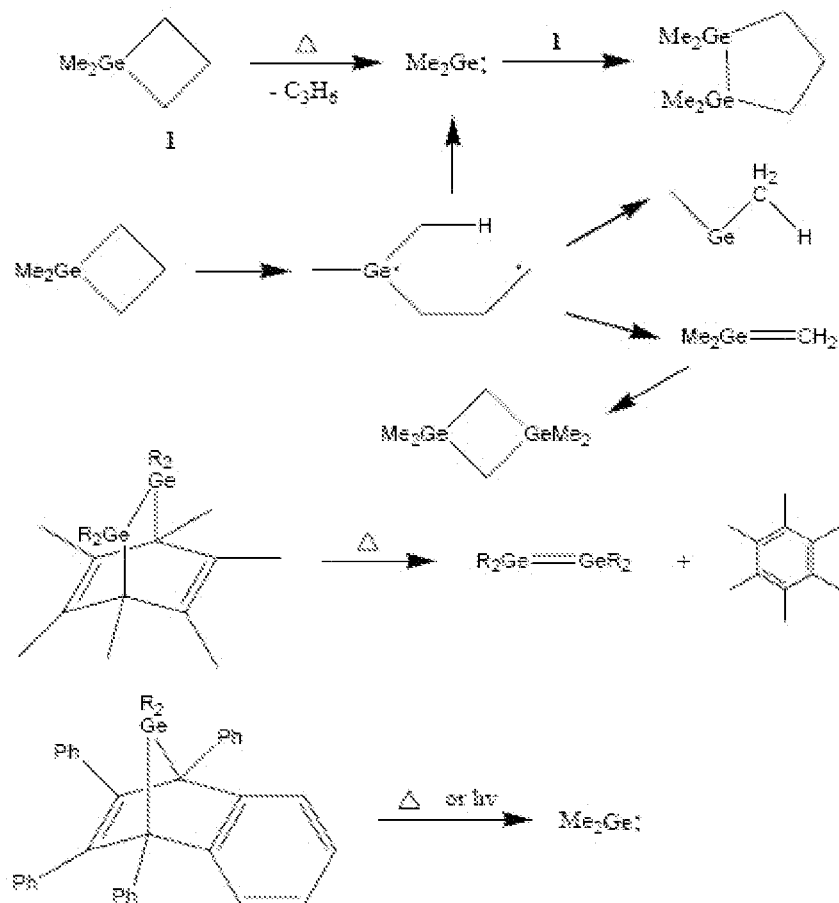


[00106] Illustrative synthesis processes that can be employed for forming germanium complexes of formula (III) includes the following:



[00107] 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.

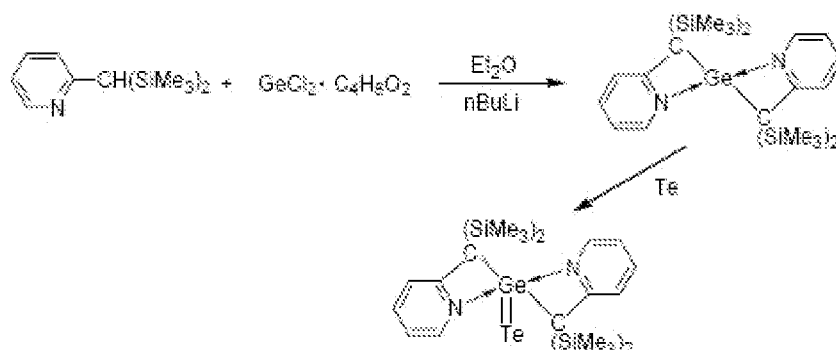
Strained ring alkylgermanes as CVD/ALD precursors for thin metal films



[00108] 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.

[00109] 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

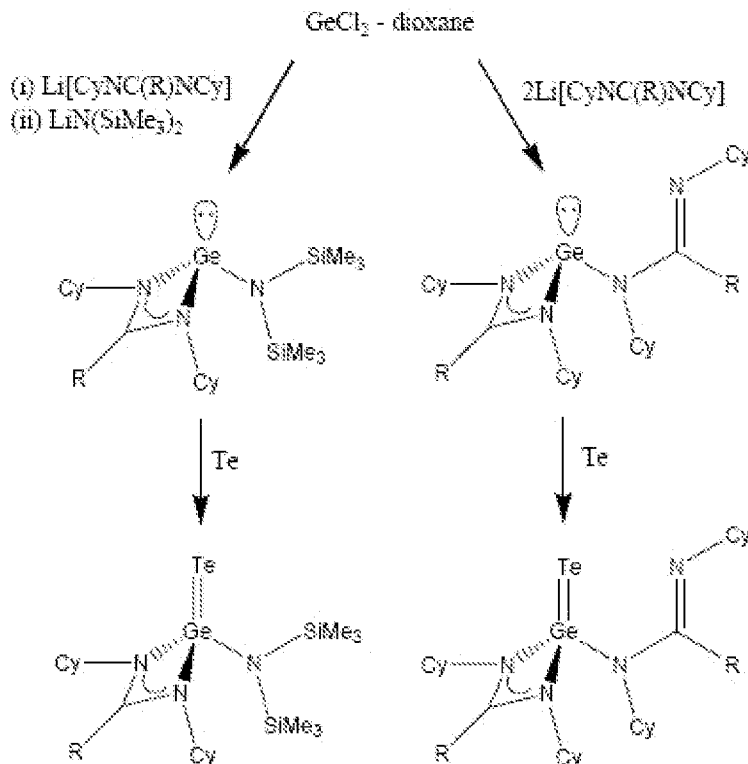
the reaction in the absence of light, depending on the light-sensitivity of the product germanium-tellurium complex. An illustrative synthesis procedure is set out below:



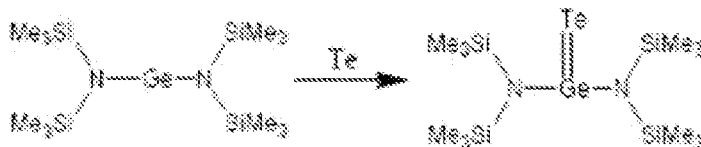
[00110] The single-source Ge-Te precursors of the invention can be advantageously used to facilitate lower temperature deposition processes or to increase GST film growth rates in specific applications.

[00111] Germanium tellurides of the invention, in another embodiment, can be formed by the following synthesis procedure:

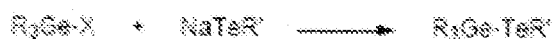
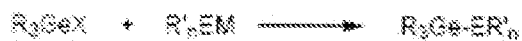
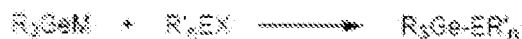
Germanium telluride ALD/CVD precursors



[00112] 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, C₁-C₆ alkyl, C₆-C₁₀ aryl, C₃-C₈ cycloalkyl, heteroatom groups, and other organo groups.

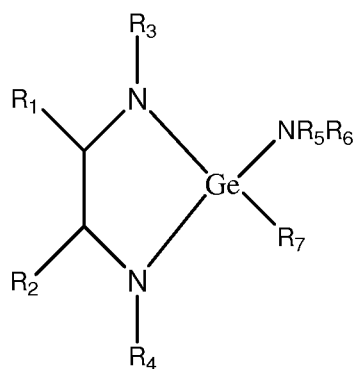
[00113] One Ge-Te complex of the invention is:



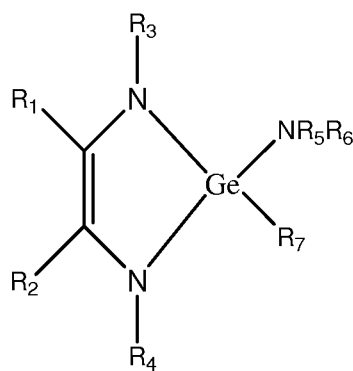
wherein each of the R substituents may be the same as or different from one another, and is independently selected from among H, C₁-C₆ alkyl, C₆-C₁₀ aryl, C₃-C₈ cycloalkyl, heteroatom groups, and other organo groups.

[00114] Another aspect of the present invention relates to highly unsymmetric germanium complexes based on amide ligands, which are useful for low temperature (below 300°C) deposition of a germanium-antimony-tellurium (Ge₂Sb₂Te₅) thin film by a CVD or ALD process. These complexes are selected from among complexes of formulae (I) and (II):

Formula (I):



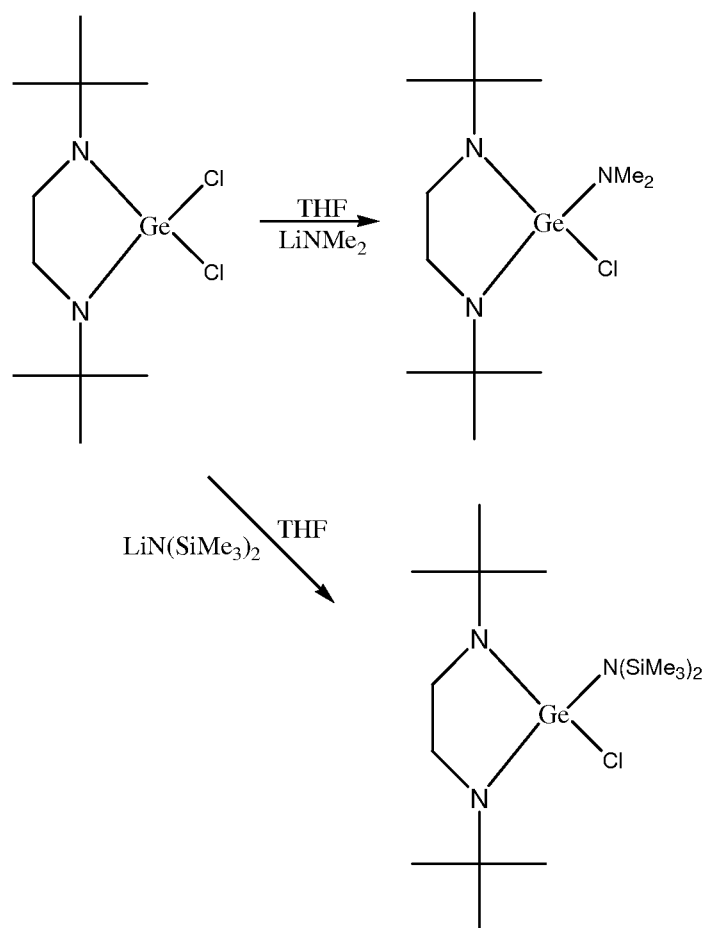
Formula (II):

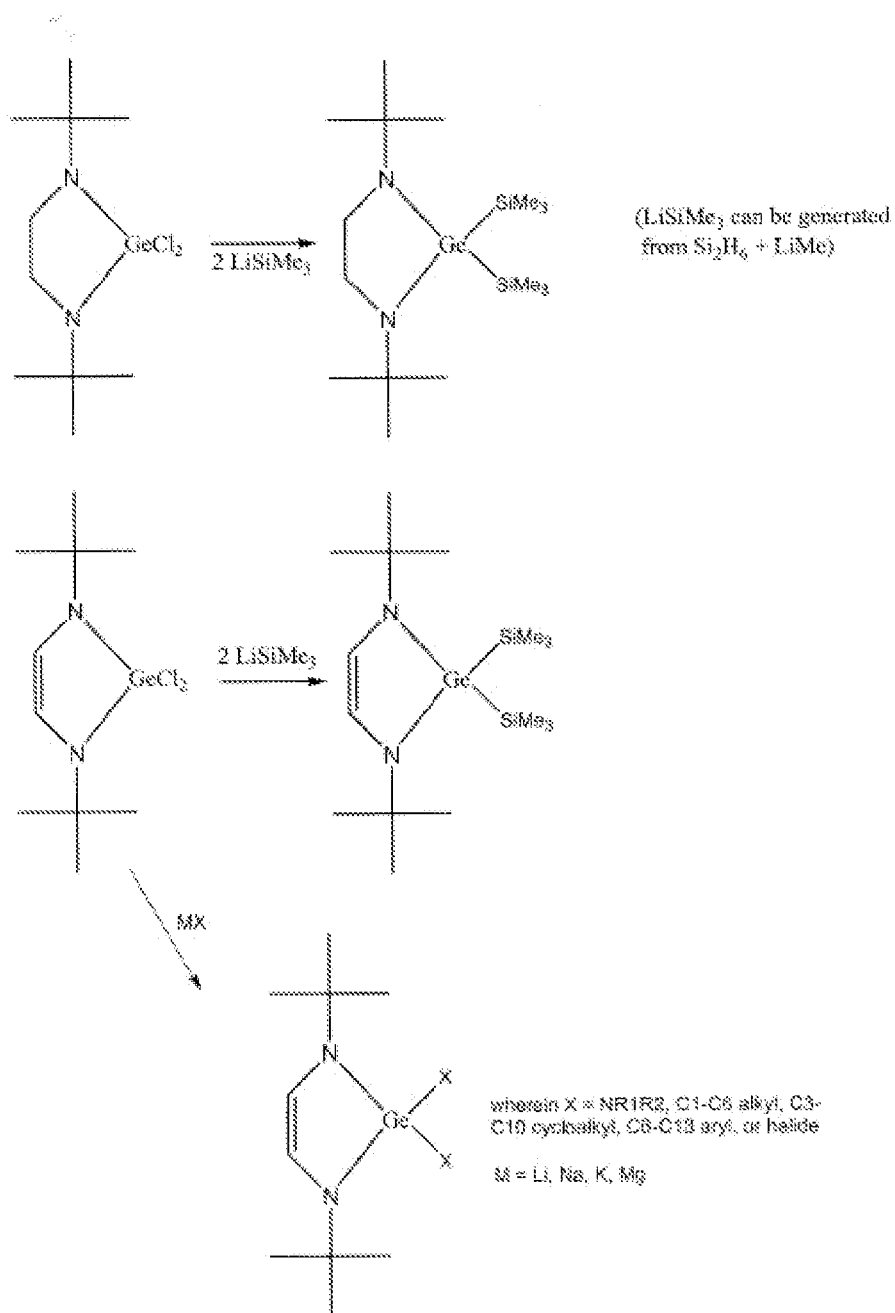


wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 and R_7 may be the same as or different from one another, and each is independently selected from the group consisting of C_1 - C_6 alkyl, C_6 - C_{10} aryl, silyl, alkylsilyl (e.g., trimethylsilyl), hydrogen and halogen, or wherein in lieu of $-NR_5R_6$, the substituent coordinated to the germanium central atom is instead selected from the group consisting of C_1 - C_6 alkyl, C_3 - C_8 cycloalkyl, C_6 - C_{13} aryl, or halide.

[00115] The precursors of formulae (I) and (II) can be delivered to the CVD or ALD chamber by liquid delivery techniques, in which the precursor is dissolved or suspended in a suitable solvent medium. Illustrative of solvent media that may be employed in the broad practice of the present invention are solvents selected from among alkanes (e.g., hexane, heptane, octane and pentane), aromatics (e.g., benzene or toluene), or amines (e.g., triethylamine or tert-butylamine). The precursors can also be delivered as neat liquids, or alternatively by solid delivery techniques, utilizing suitable packaging for volatilization and dispensing. One preferred solid delivery package is the ProE-VapTM solid delivery and vaporizer unit, commercially available from ATMI, Inc. (Danbury, Connecticut, USA).

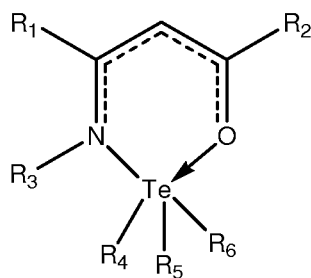
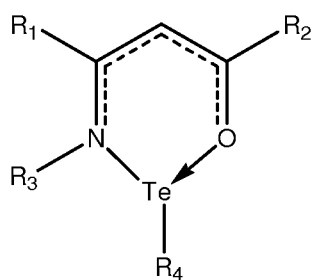
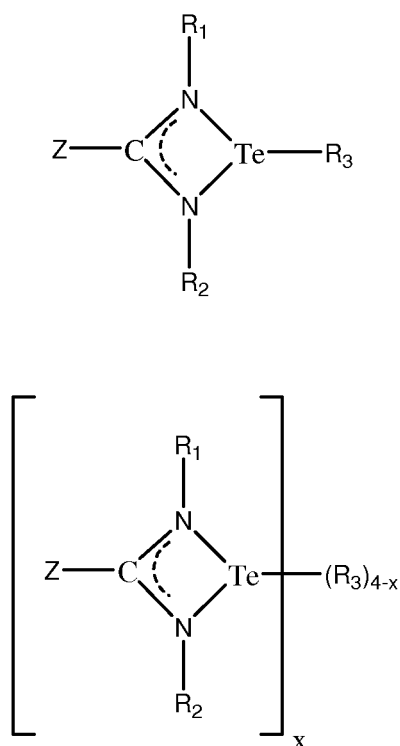
[00116] The germanium complexes of formulae (I) and (II) can be synthesized according to the following synthesis schemes, in illustrative embodiments.





[00117] The invention in another aspect relates to tellurium complexes in which the tellurium central atom is coordinated to a nitrogen atom, to constitute a Te-N ligand complex.

[00118] Illustrative of such Te-N ligand complexes are the following tellurium complexes:



wherein R₁, R₂, R₃, R₄, R₅, R₆ and Z may be the same as or different from one another, and each is independently selected from the group consisting of C₁-C₆ alkyl, C₃-C₈ cycloalkyl, C₆-C₁₀ aryl, silyl, alkylsilyl (e.g., trimethylsilyl), hydrogen and halogen, and wherein x is an integer having a value of from 1 to 3.

[00119] In another aspect, the invention relates to germanium precursors useful in phase change memory device fabrication based on chalcogenide materials that undergo a phase change upon heating and are read out as "0" or "1" based on their electrical resistivity, which changes whether the phase change material in the memory cell is in a crystalline or amorphous state. Chalcogenide materials comprise a large number of binary, ternary, and quaternary alloys of a number of metals and metalloids, e.g., GeSbTe, GeSbInTe, and many others.

[00120] Phase change memory devices require relatively pure alloys, with well controlled composition. Current processes utilize physical vapor deposition to deposit thin films of these materials. CVD and ALD methods are desirable for their inherent scalability to large area wafers and for composition control. A major deficiency in the current art is the high deposition temperature needed with current alkyl (e.g., Me₃Sb, Me₂Te) or halide sources, which typically greatly exceed 300°C and may be as high as 500°C, which exceeds the allowable thermal budget for device integration and can result in the evaporation of the chalcogenide material.

[00121] The invention in another aspect relates to various materials and processes that enable low temperature deposition of chalcogenide alloys.

[00122] In one chemical approach, butyl and propyl (especially t-butyl and iso-propyl) substituted alkyl hydrides are employed as precursor complexes, e.g., complexes of the formula iPr_xMH_{y-x}, wherein: x>1; y = oxidation state of the metal (M) center; and y-x may = 0.

[00123] In another chemical approach, butyl and propyl (especially t-butyl and iso-propyl) substituted alkyl halides are employed as precursor complexes, e.g., complexes of the formula iPr_xMX_{y-x}, wherein: X = F, Cl, Br; x>1; y = oxidation state of the metal (M) center; and y-x may = 0.

[00124] Such precursors can enhance deposition at lower temperatures via beta hydrogen elimination.

[00125] In another embodiment, digermanes are employed to lower the incorporation temperature of germanium. Useful compounds in this respect include Ge₂H₆, Ge₂Me₆, or Ge₂Et₆. Ge₂iPr₆ and Ge₂tBu₆, as well as Ge₂(SiMe₃)₆ and Ge₂Ph₆, in which Me = methyl, Et = ethyl, iPr = isopropyl, tBu = t-butyl, and Ph = phenyl.

[00126] More generally, compounds of the formula Ge₂R₆ may be employed, wherein each of the R's can be the same as or different from the others, and each is independently selected from among H, C₁-C₈ alkyl, C₁-C₈ fluoroalkyl, C₆-C₁₂ aryl, C₆-C₁₂ fluoroaryl, C₃-C₈ cyclo-alkyl, C₃-C₈ cyclo-fluoroalkyl. In addition, Ge₂R₄ compounds including Ge₂Ph₄ can be usefully employed for such purpose, wherein each of the R groups may be as above defined. Additional complexes may be utilized including 5-member ring complexes with Ge in the ring. Ge(II) complexes are also potentially useful in specific applications, such as cyclopentadienyl

compounds of the formula $\text{Ge}(\text{CpR}_5)_2$ wherein Cp is cyclopentadienyl and each of the R's may be the same as or different from one another and each is independently selected as above. Another germanium compound that is usefully employed for phase change memory applications is $\text{Ge}(\text{CH}(\text{SiMe}_3))_2$.

[00127] In another aspect, the antimony component of GST films can be supplied from a precursor such as triphenylantimony, which is inexpensive and light-sensitive in character, and has utility in light/UV-activated deposition processes.

[00128] Delivery approaches for precursor delivery to enable low temperature deposition of chalcogenide alloys include the use of separate bubblers for in each precursor for the phase change memory film, liquid injection of precursor mixtures as an approach to manage disparate volatility characteristics of the several precursors to enable delivery of precise volumetric flows at desired compositions, and the use of mixtures of neat liquid or precursor/solvent compositions, as respective techniques that may be useful in specific applications.

[00129] Film deposition approaches for low temperature deposition of chalcogenide alloys include: the use of continuous CVD in thermal mode, optionally with reducing gases such as hydrogen; employment of pulsed or atomic layer deposition to separate the dose step from the co-reactant such as hydrogen plasma; employment of activation techniques such as UV or other light sources that are "tuned" to the precursor, with a light being continuous with the precursor dosing, or dosed separately to avoid gas-phase reactions; and use of alternative reductive co-reactants such as germane (GeH_4) advantageously dispensed from sub-atmospheric delivery systems, such as the SAGE® dispensing package commercially available from ATMI, Inc. (Danbury, Connecticut, USA), for enhanced safety and reduced cost of ownership for the source gas for the deposition.

[00130] The invention further aspect relates to a low-temperature germanium nitride deposition process using an amidinate-based precursor, as found to be effective in forming germanium nitride at low temperature. FIG. 6 is an Arrhenius plot of deposition log rate, in A/min, as a function of $1/T$, showing the improvement in Ge deposition with ammonia co-reactant for germanium methyl amidinate (GeMAMDN).

[00131] With hydrogen co-reactant the precursor yields an amorphous Ge film with a deposition rate of about 2 A/min at 280°C. When the co-reactant was switched to ammonia, the deposition rate increased dramatically. A factor of 100 in deposition rate was observed at around 240°C, and a deposition rate of 75 A/min was achieved at 200°C. Furthermore, the deposited thin film turned transparent with ammonia co-reactant indicating the formation of germanium nitride. FIG. 7 shows the dominating effect of ammonia co-reactant on the deposition rate.

[00132] The invention in a further aspect relates to N, S, O-heterocyclic germanium CVD/ALD precursors for deposition of germanium metal films at low temperature. Illustrative

of such precursors are $[\{\text{MeC}(\text{iPrN})_2\}_2\text{Ge}]$, $[\{\text{Me}_2\text{N}(\text{iPrN})_2\}_2\text{Ge}]$, $[\{\text{nBuC}(\text{iPrN})_2\}_2\text{Ge}]$, and $[\{\text{MeC}(\text{NCy})_2\}_2\text{Ge}]$. In a specific embodiment, the precursor $[\{\text{MeC}(\text{iPrN})_2\}_2\text{Ge}]$ may be provided in a solution of toluene as a CVD precursor for germanium metal films.

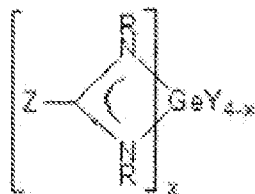
[00133] In the formation of GST films, a high deposition rate, on the order of 400-500 Å/min of GST alloy, and 100 Å/min for Ge, along with low carbon and heteroatom impurity levels in the film, are required. Highly volatile precursors are necessary. Liquid precursors are preferred, however low melting and volatile solids may also be used with a heated bubbler system ($\sim 50^\circ\text{C}$). Heteroatom impurities (Si, O, N) are acceptable below 10%.

[00134] The invention in such respect contemplates the use of Ge(II) and Ge(IV) precursors with the following ligands: amidinates, guanidines, isoureates, diketones, diketoiminates, diketiminates, carbamates, thiocarbamates, silyls, aminotroponimate. Mixed ligand precursors are also included with combinations of the above ligands, or in combination with alkyl, dialkylamino, hydrido, or halogen groups.

[00135] The germanium precursors can be used alone to deposit metallic germanium films thermally or with a co-reactant, or with iPr_2Te or other suitable tellurium precursors to deposit GeTe layers. Similarly, suitable antimony precursors may be employed to form the ternary GST alloy. Co-reactant gases/liquids usefully employed with such precursors include hydrogen, ammonia, plasma, alkylamines, silanes, and germanes.

[00136] The germanium precursors of the invention include:

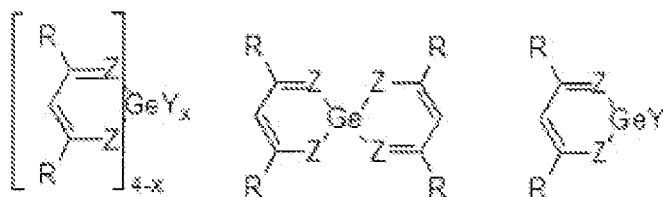
(1) Ge(IV) amidinates, guanidines, and isoureates of the formula:



wherein each R group is independently selected from among H, $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_3\text{-C}_{10}$ cycloalkyl, $\text{C}_6\text{-C}_{13}$ aryl, and $-\text{Si}(\text{R}')_3$ wherein each R' is independently selected from $\text{C}_1\text{-C}_6$ alkyl; and each Z is independently selected from among $\text{C}_1\text{-C}_6$ alkoxy, $-\text{NR}_1\text{R}_2$, H, $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_3\text{-C}_{10}$ cycloalkyl, $\text{C}_6\text{-C}_{13}$ aryl, and $-\text{Si}(\text{R}_4)_3$ wherein each R_4 is independently selected from $\text{C}_1\text{-C}_6$ alkyl;

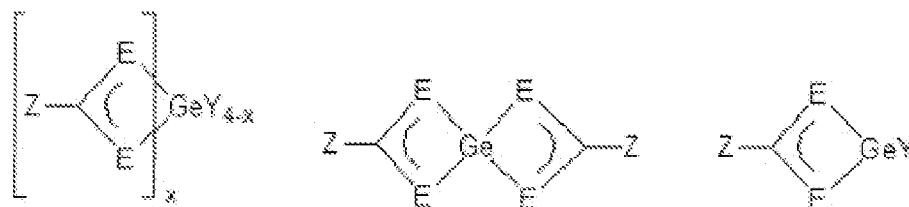
each Y group is independently selected from among $\text{C}_1\text{-C}_6$ alkoxy, $-\text{NR}_1\text{R}_2$, and $\text{C}_1\text{-C}_6$ alkyl, $\text{Si}(\text{R}_4)_3$, and halides (Cl, Br, I), and wherein x is integer from 0 to 4;

(2) Ge beta-diketonates, diketoiminates, diketiminates of the formulae:



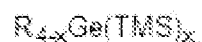
wherein each R group is independently selected from among H, C₁-C₆ alkyl, C₃-C₁₀ cycloalkyl, C₆-C₁₃ aryl, and -Si(R')₃; each Y group is independently selected from among C₁-C₆ alkyl, C₆-C₁₃ aryl, C₁-C₆ alkoxy, NR₁R₂, Si(R₄)₃, and halides (Cl, Br, I), x is integer from 0 to 4, Z atoms are the same or different, selected from O, S, and NR; R is selected from C₁-C₆ alkyl, C₃-C₁₀ cycloalkyl, C₆-C₁₃ aryl, Si(R')₃, R' is C₁-C₆ alkyl, C₆-C₁₃ aryl;

(3) Ge carbamates, thiocarbamates of the formulae:



wherein each Z is independently selected from among H, C₁-C₆ alkyl, C₃-C₁₀ cycloalkyl, C₁-C₆ alkoxy, NR₁R₂, C₆-C₁₃ aryl, and -Si(R₄)₃ wherein each R₄ is independently selected from C₁-C₆ alkyl or aryl; each Y group is independently selected from among C₁-C₆ alkyl, C₁-C₆ alkoxy, NR₁R₂, C₃-C₁₀ cycloalkyl, C₆-C₁₃ aryl, Si(R₄)₃, and halides (Cl, Br, I), x is integer from 0 to 4, and E is either O or S;

(4) Silylgermanes of the formula:



wherein TMS is Si(R'')₃; each R group is independently selected from among H, C₁-C₆ alkyl, C₃-C₁₀ cycloalkyl, C₆-C₁₂ aryl, and x is integer from 0 to 4;

(5) Mixed cyclopentadienyl germanes of the formulae:



CpGe(amidinate) CpGe(guanidinate)

CpGe(beta-diketiminato)

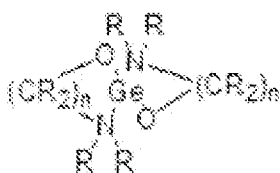
CpGe(beta-diketonate)

CpGe(isoureate)

wherein each R group is independently selected from among H, C₁-C₆ alkyl, C₃-C₁₀ cycloalkyl, C₆-C₁₃ aryl, and -Si(R')₃ wherein each R' is independently selected from C₁-C₆ alkyl; and each Y group is independently selected from among C₁-C₆ alkyl, C₁-C₆ alkoxy, NR₁R₂, C₃-C₁₀ cycloalkyl, C₆-C₁₃ aryl, Si(R₄)₃, and halides (Cl, Br, I), x is an integer having a value of from 0 to 4, and Cp ligands may also include:

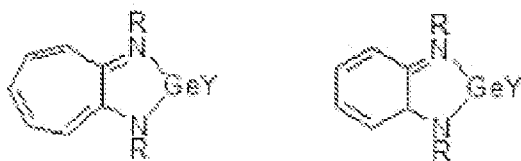


(6) Ge(II) amino-alkoxide of the formula:



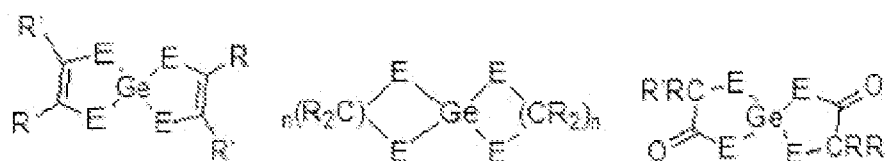
wherein each R group is independently selected from among H, C₁-C₆ alkyl, C₃-C₁₀ cycloalkyl, C₆-C₁₃ aryl, and -Si(R')₃, wherein each R' is independently selected from C₁-C₆ alkyl, and n is an integer having a value of from 2 to 6;

(7) Other N-heterocyclic germylenes of the formulae:



wherein each R group is independently selected from among H, C₁-C₆ alkyl, C₃-C₁₀ cycloalkyl, C₆-C₁₃ aryl, and -Si(R')₃, wherein each R' is independently selected from C₁-C₆ alkyl; and each Y group is independently selected from among C₁-C₆ alkoxy, NR₁R₂, H, C₁-C₆ alkyl, C₃-C₁₀ cycloalkyl, C₆-C₁₃ aryl, Si(R₄)₃, or halides (Cl, Br, I);

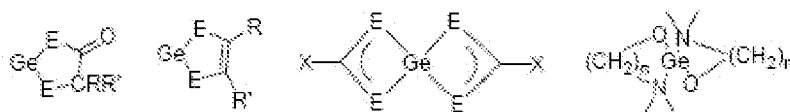
(8) Oxides, dithiolates, thiocarbonates of the formulae:



wherein each R,R' is independently selected from among C₁-C₆ alkyl, C₃-C₁₀ cycloalkyl, C₁-C₆ alkoxy, NR₁R₂, C₆-C₁₃ aryl, and -Si(R₄)₃ wherein each R₄ is independently selected from C₁-C₆ alkyl or aryl, and halides (Cl, Br, I), and E is either O or S.

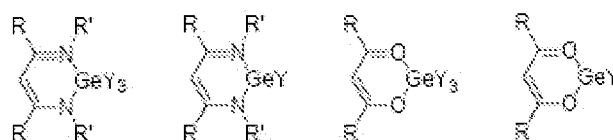
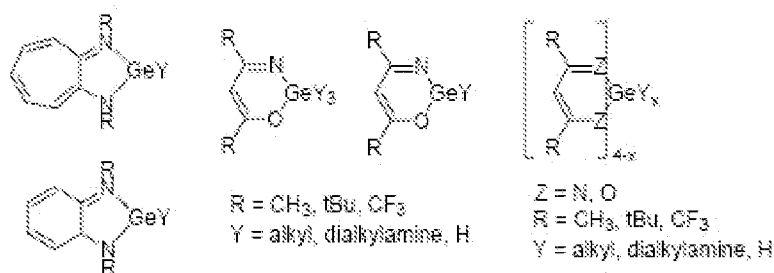
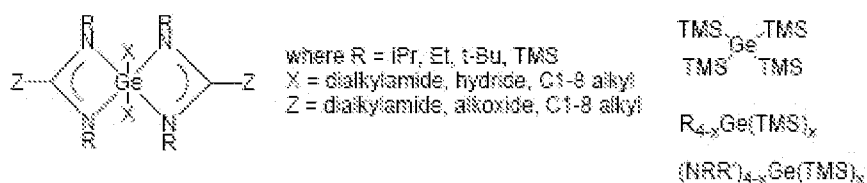
[00137] The ALD/CVD precursors (1)-(8) described above can be prepared in liquid delivery formulations using a suitable solvent such as alkanes (e.g., hexane, heptane, octane, and pentane), aromatics (e.g., benzene or toluene), or amines (e.g., triethylamine, tert-butylamine). Precursors may also be delivered as neat liquids or as solids using a suitable solid delivery and vaporizer unit (such as the ProE-VapTM solid delivery and vaporizer unit commercially available from ATMI, Inc., Danbury, CT, USA).

[00138] Set out below is an identification of various specific germanium precursors of the invention.

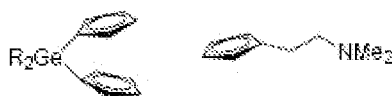


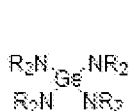
E = O, S

X = C1-C8 alkyl, fluoroalkyl, aryl, dialkylamine, alkoxy

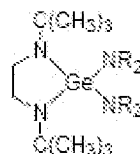
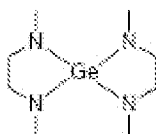
 $R = \text{CH}_3, \text{tBu}, \text{CF}_3$ $Y = \text{alkyl, dialkylamine, H}$  $\text{R}_{4-x}\text{GeCp}_x$ RGeCp $(\text{RR}'\text{N})_{4-x}\text{GeCp}_x$ $\text{RR}'\text{NGeCp}$

where Cp represents Cp, Cp', and other C1-C6 alkyl substituted cyclopentadienyl ligands, and includes ansa-bridged germanes and alkyl(dialkylamines) [examples shown below].

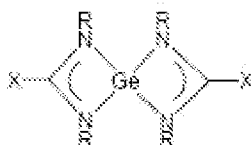
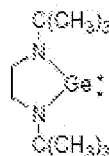
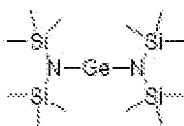
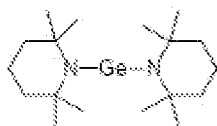


Ge CVD/ALD precursors**Ge(IV) precursors**

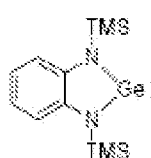
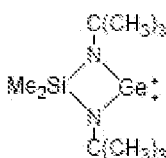
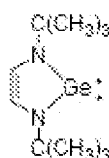
R = Me, Et, iPr, TMS



R = Me, Et, iPr, TMS

Ge(II) precursorswhere X = a nucleophile (e.g. CH₃, MeO, NR₂)

R = Me, Et, iPr, TMS



[00139] The invention in a further aspect contemplates various metal silylamides useful for CVD and ALD deposition of thin films.

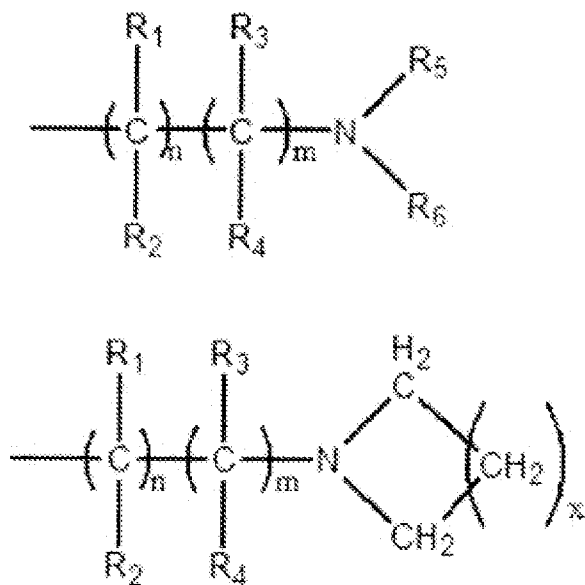
[00140] This aspect of the invention encompasses the synthesis and characterization of a class of metal precursors with disily-azacycloalkyl ligand: $\text{R}_5\text{nM}\{\text{N}[(\text{R}_1\text{R}_2)\text{Si}(\text{CH}_2)_m\text{Si}(\text{R}_3\text{R}_4)]\}\text{ox-n}$; metal silylamides particularly with asymmetric elements in the silylamido ligands, $\text{R}_5\text{nM}\{\text{R}_4\text{N}[\text{Si}(\text{R}_1\text{R}_2\text{R}_3)]\}\text{ox-n}$; carbodiimido insertion reaction with those silylamides to yield the corresponding guanidinate complexes, which can also be used as CVD/ALD precursors.

[00141] The "oligomers" of the above-discussed monomers with the same empirical formula include $[R_5nM\{N[(R_1R_2)Si(CH_2)_mSi(R_3R_4)]\}_{ox-n}]_x$ or $[R_5nM\{R_4N[Si(R_1R_2R_3)]\}_{ox-n}]_x$ where x is an integer having a value of 2, 3, etc.

[00142] The invention also contemplates precursors with open-structured silazane ligands in which at least one of the R_s has a functional group such as amido, alkoxyl, siloxyl and thienyl: $R_5nM\{(R_4R_5R_6)SiN[Si(R_1R_2R_3)]\}_{ox-n}$, and its corresponding guanidates.

[00143] The "oligomers" of the above-discussed monomer with the same empirical formula include $[R_5nM\{(R_4R_5R_6)SiN[Si(R_1R_2R_3)]\}_{ox-n}]_x$ where x is an integer having a value of 2, 3, etc.

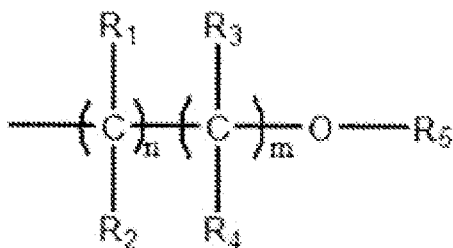
[00144] Each of R_1 , R_2 , R_3 , R_4 , R_6 and R_7 in the about formulae is independently selected from among H, C1-C6 alkyl, C3-C10 cycloalkyl, C6-C10 aryl, $-Si(R_8)_3$ and $-Ge(R_8)_3$ wherein each R_8 is independently selected from C1-C6 alkyl; and $-Si(R_9)_3$ wherein each R_9 is independently selected from C1-C6 alkyl; when suitable, pendant ligands attached to the above-mentioned R_1 , R_2 , R_3 , R_4 , R_6 and R_7 include functional group(s) providing further coordination to the metal center, such as, for example, aminoalkyl, alkoxyalkyl, aryloxyalkyl, imidoalkyl, and acetylalkyl, wherein suitable groups in these classes include those of the following formulae:



aminoalkyls

wherein each of R_1 - R_4 is the same as or different from one another, with each being independently selected from among hydrogen and C1-C6 alkyl; each of R_5 and R_6 is the same as or different from the other, with each being independently selected from among C1-C6 alkyl;

n and m are each selected independently from 0 to 4 with the provision that m and n cannot be 0 at the same time, and x is selected from 1 to 5;



alkoxyalkyls and aryloxyalkyls

wherein each of R1-R4 is the same as or different from one another, with each being independently selected from among hydrogen, C1-C6 alkyl, and C6-C10 aryl; R5 is selected from among C1-C6 alkyl, and C6-C10 aryl; and n and m are selected independently from 0 to 4, with the provision that m and n cannot be 0 at the same time.

[00145] In the metal precursors, each R5 can be independently selected from among H, C1-C6 alkyl, C3-C6 cycloalkyl, C1-C6 alkoxy, -NR1R2, and -C(R3)3, -Si(R8)3 and -Ge(R8)3 wherein each R3 is independently selected from C1-C6 alkyl; and each of R8 and R8 is independently selected from H, C1-C6 alkyl, C5-C10 cycloalkyl, C6-C10 aryl, and -Si(R9)3 wherein each R4 is independently selected from C1-C6 alkyl.

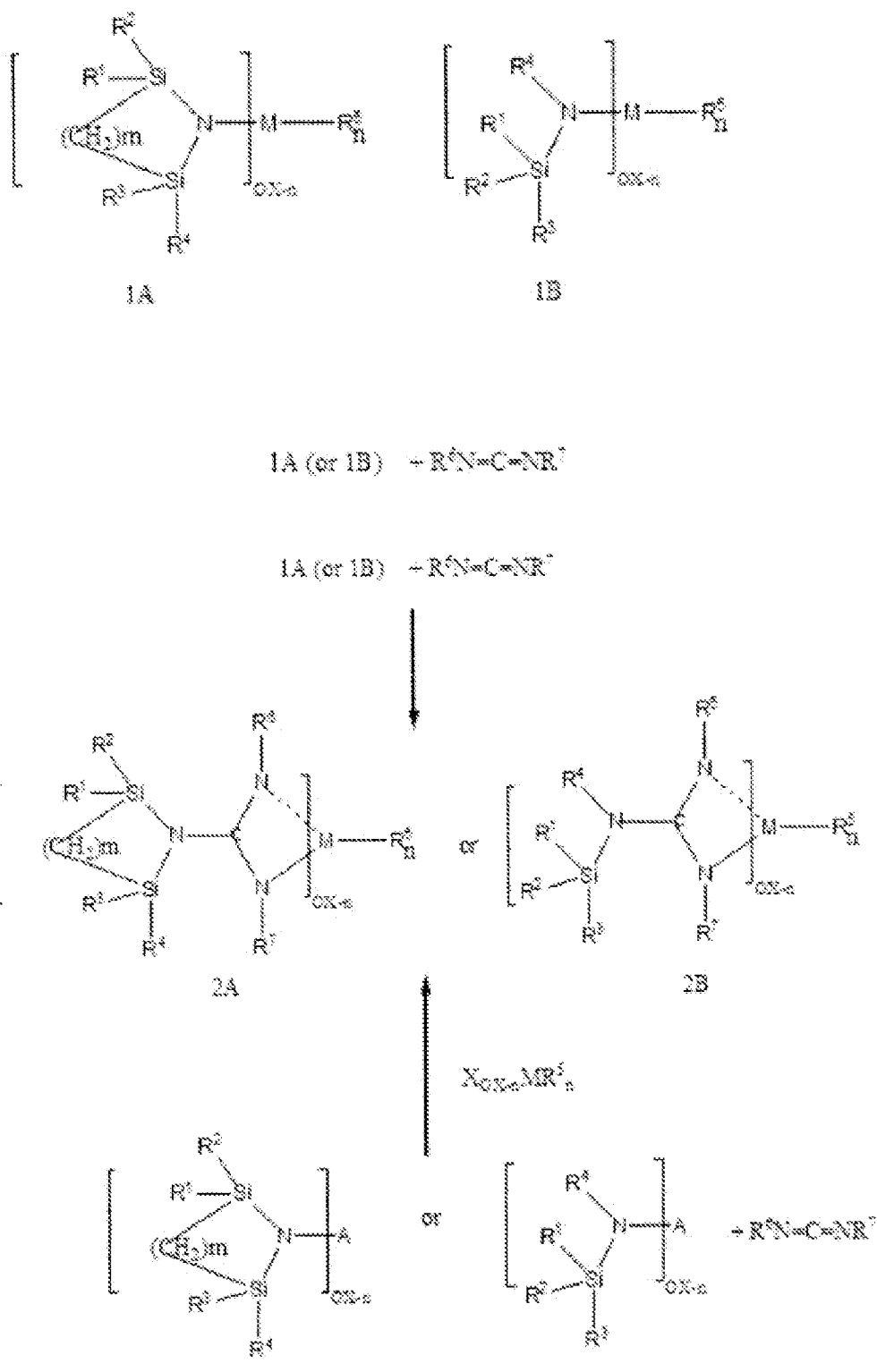
[00146] In such metal precursors, M can be any of the metals mentioned above (Ta, V, Ti, Nb, Pb, Ni, W, Ca, Ba, In, Y, La, Zr, Hf, Ir, Ru, Pt, Cr, Mo, Ge; Al, Si, Ga, Sc, V, Cr, Fe, Sb, lanthanides, Mn, Co, Ni, Zn, Cd, Te, Hg, Au, Cu, Ag, Sr, Ru) but not limited to them only; OX is the allowed oxidation state of the metal M; n is an integer having a value of from 0 to ox; and X is halogen.

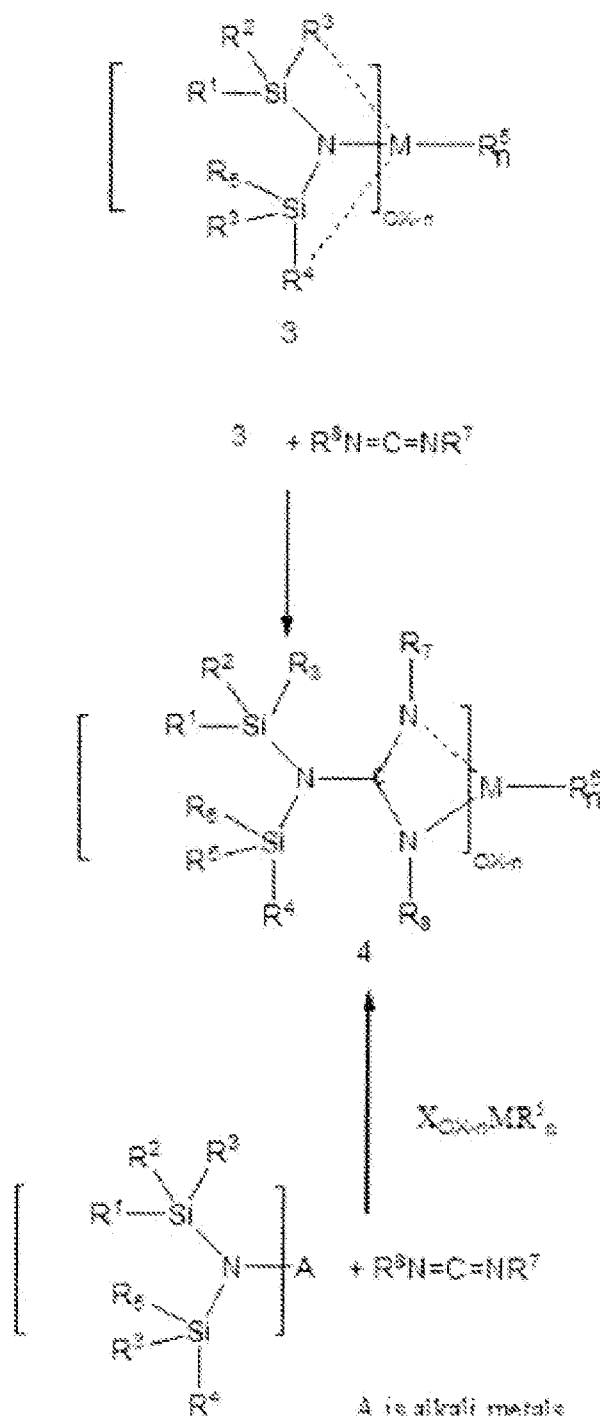
[00147] The above-described precursor materials can be used as low temperature deposition precursors with reducing co-reactants such as hydrogen, H2/plasma, amines, imines, hydrazines, silanes, silyl chalcogenides such as (Me3Si)2Te, germanes such as GeH4, ammonia, alkanes, alkenes, amidines, guanidines, boranes and their derivatives/adducts and alkynes. The precursors may be employed in liquid delivery formulations, and the precursors that are liquids may be used in neat liquid form, with liquid or solid precursors being employed as desired in suitable solvents including alkane solvents (e.g., hexane, heptane, octane, and pentane), aryl solvents (e.g., benzene or toluene), amines (e.g., triethylamine, tert-butylamine), imines, guanidines, amidines and hydrazines.

[00148] The utility of specific solvent compositions for particular precursors may be readily empirically determined, to select an appropriate single component or multiple component

solvent medium for liquid delivery vaporization. Solid delivery systems may be employed, of the type previously described herein.

[00149] The above-described precursors are variously shown below.





[00150] The invention in a further aspect relates to tetraalkylguanidinate and ketiminate complexes useful as CVD and ALD precursors, including a class of metal precursors with tetraalkylguanidine ligand, e.g., in the coordination mode (R⁵)_nM{N=C[(NR¹R²)(NR³R⁴)]}ox-n and the semi-labile coordination mode. Under special circumstances, both coordination modes could theoretically co-exist.

[00151] All of such complexes can be synthesized from the corresponding alkali metal salts with metal halides or alkyls or mixed halides/alkyls/amides or from the direct reactions between tetraalkylguanidine with metal halides with the presence of HX absorbents such as NEt_3 .

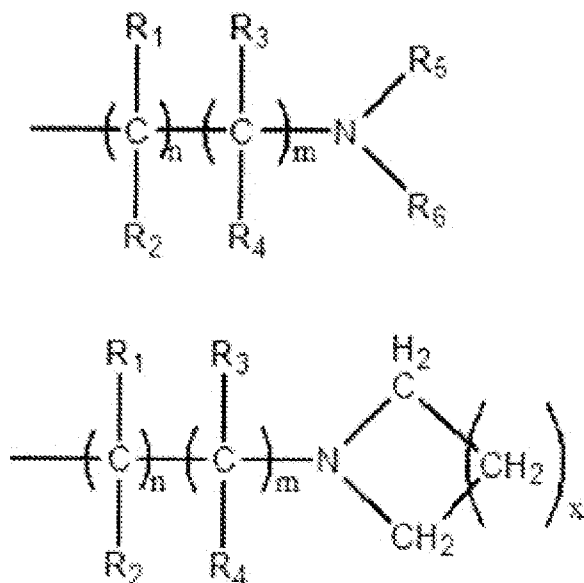
The "oligomers" of such monomer with the same empirical formula include $[(R_5)_nM\{N=C[(NR_1R_2)(NR_3R_4)]\}_{ox-n}]_x$, where x is an integer having the value of 2, 3, etc.

[00152] Four illustrative Ge (IV) precursors have been synthesized and characterized. All of them showed promising thermal behavior and $\text{TMG}_2\text{Ge}(\text{NMe}_2)_2$ is a viscous liquid at room temperature.

[00153] The invention also contemplates the corresponding guanidinate complexes $R_5nM\{R_6NC\{N=C[(NR_1R_2)(NR_3R_4)]\}NR_7\}_{ox-n}$. The "oligomers" of such monomer with the same empirical formula include $[R_5nM\{R_6NC\{N=C[(NR_1R_2)(NR_3R_4)]\}NR_7\}_{ox-n}]_x$, where x is an integer having the value of 2, 3, etc.

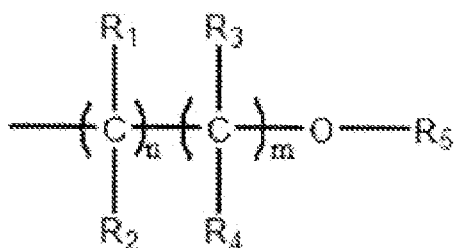
[00154] The invention further encompasses a tetraalkylguanidine insertion reaction with metal amides to yield the corresponding guanidinate complexes, which can also be used as CVD/ALD precursors, as well as ketiminates of the formula $(R_5)_nM\{N=C[(R_1R_2)]\}_{ox-n}$ and its corresponding guanidinate complexes of the formula $R_5nM\{R_6NC[N=C(R_1R_2)]NR_7\}_{ox-n}$. The "oligomers" such monomer with the same empirical formula include $[R_5nM\{R_6NC[N=C(R_1R_2)]NR_7\}_{ox-n}]_x$, where x is an integer having the value of 2, 3, etc.

[00155] In the metal complexes described above, each of R_1 , R_2 , R_3 , R_4 , R_6 and R_7 is independently selected from among H, C1-C6 alkyl, C3-C10 cycloalkyl, C6-C10 aryl, $-\text{Si}(\text{R}_8)_3$ and $-\text{Ge}(\text{R}_8)_3$ wherein each R_8 is independently selected from C1-C6 alkyl; and $-\text{Si}(\text{R}_9)_3$ wherein each R_9 is independently selected from C1-C6 alkyl; when suitable, pendant ligands attached to the above-mentioned R_1 , R_2 , R_3 , R_4 , R_6 and R_7 including functional group(s) providing further coordination to the metal center, such as, for example, aminoalkyl, alkoxyalkyl, aryloxyalkyl, imidoalkyl, and acetylalkyl, wherein suitable groups in these classes include those of the following formula:



aminoalkyls

wherein each of R1-R4 is the same as or different from one another, with each being independently selected from among hydrogen and C1-C6 alkyl; each of R5 and R6 is the same as or different from the other, with each being independently selected from among C1-C6 alkyl; n and m are each selected independently from 0 to 4 with the provision that m and n cannot be 0 at the same time, and x is selected from 1 to 5;



alkoxyalkyls and aryloxyalkyls

wherein each of R1-R4 is the same as or different from one another, with each being independently selected from among hydrogen, C1-C6 alkyl, and C6-C10 aryl; R5 is selected from among C1-C6 alkyl, and C6-C10 aryl; and n and m are selected independently from 0 to 4, with the provision that m and n cannot be 0 at the same time.

[00156] In the metal precursors, each R5 can be independently selected from among H, C1-C6 alkyl, C3-C6 cycloalkyl, C1-C6 alkoxy, -NR1R2, and -C(R3)3, -Si(R8)3 and -Ge(R8)3

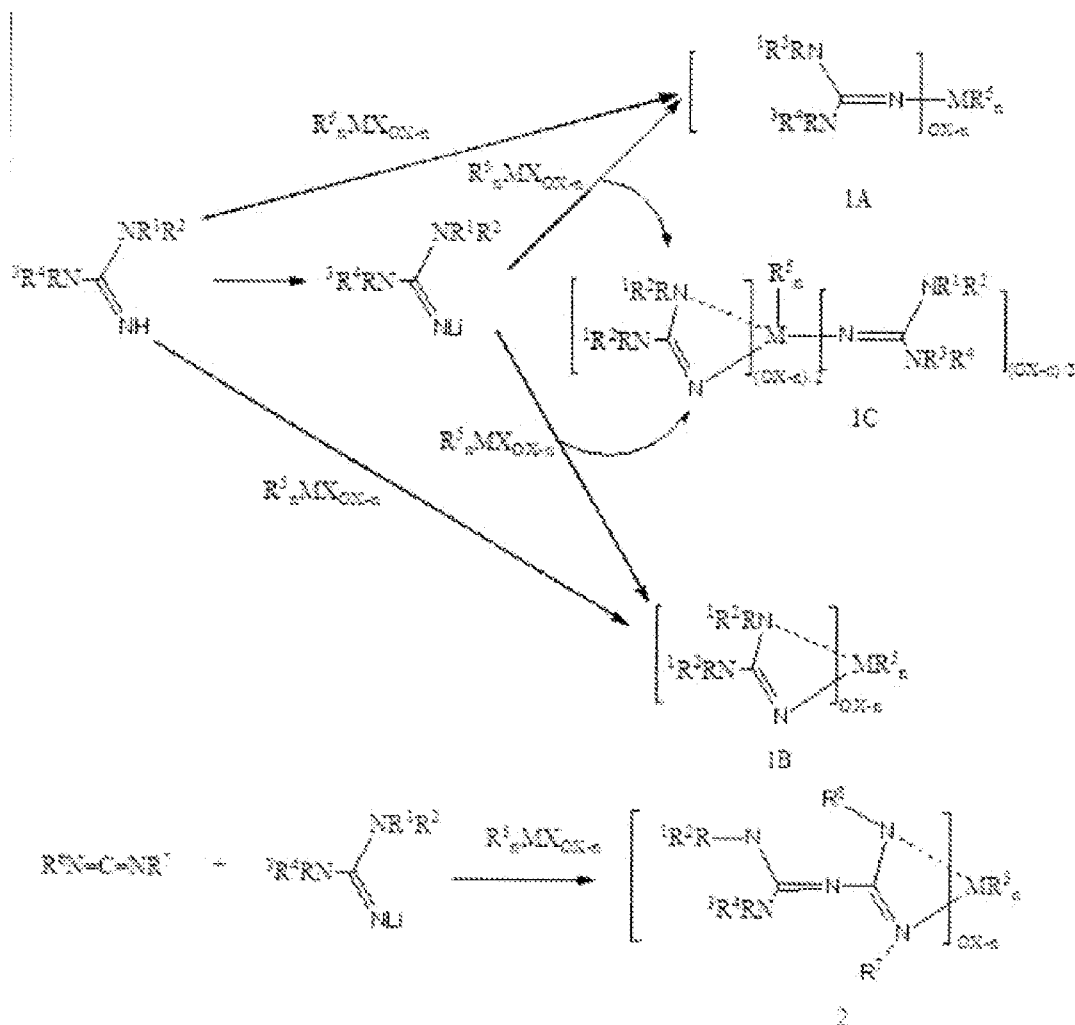
wherein each R3 is independently selected from C1-C6 alkyl; and each of R8 and R8 is independently selected from H, C1-C6 alkyl, C5-C10 cycloalkyl, C6-C10 aryl, and -Si(R9)3 wherein each R4 is independently selected from C1-C6 alkyl.

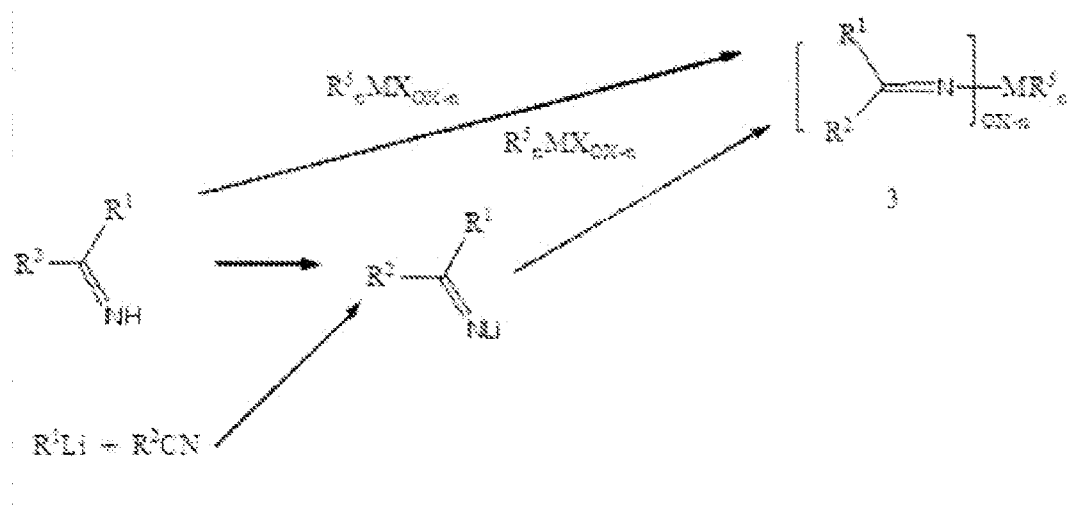
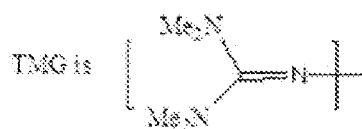
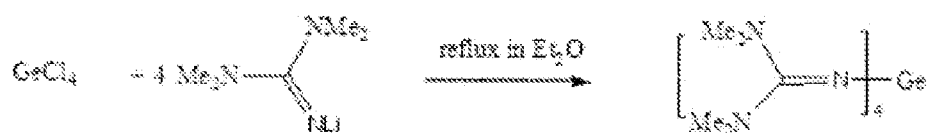
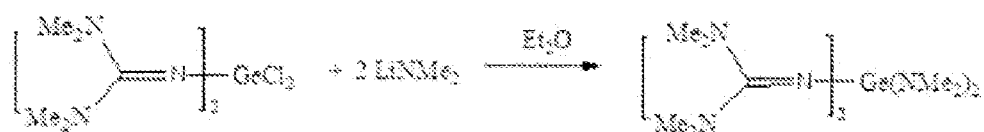
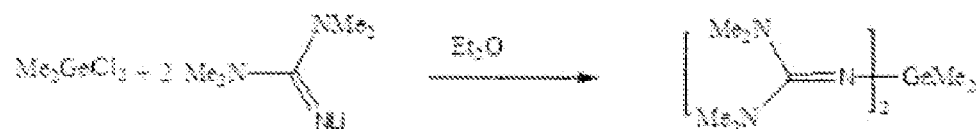
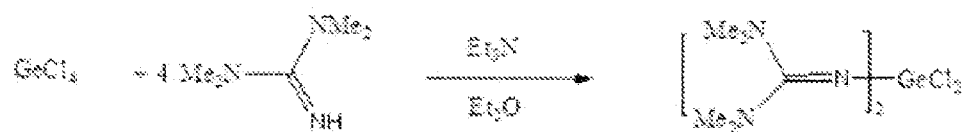
[00157] In such metal precursors, M can be any of the metals mentioned above (Ta, V, Ti, Nb, Pb, Ni, W, Ca, Ba, In, Y, La, Zr, Hf, Ir, Ru, Pt, Cr, Mo, Ge; Al, Si, Ga, Sc, V, Cr, Fe, Sb, lanthanides, Mn, Co, Ni, Zn, Cd, Te, Hg, Au, Cu, Ag, Sr, Ru) but not limited to them only; OX is the allowed oxidation state of the metal M; n is an integer having a value of from 0 to ox; and X is halogen.

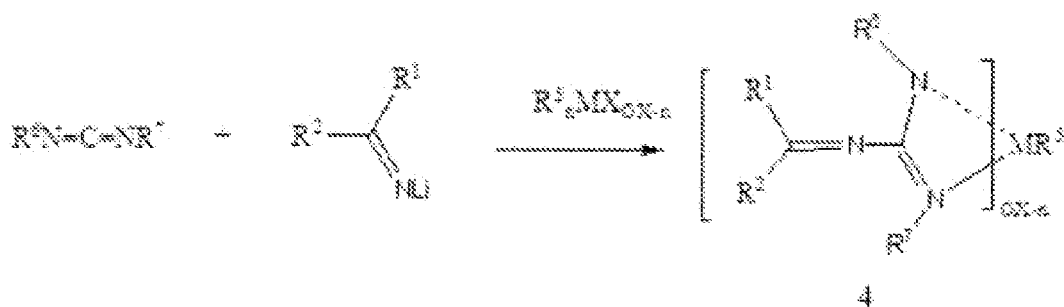
[00158] The above-described precursor materials can be used as low temperature deposition precursors with reducing co-reactants such as hydrogen, H₂/plasma, amines, imines, hydrazines, silanes, silyl chalcogenides such as (Me₃Si)₂Te, germanes such as GeH₄, ammonia, alkanes, alkenes, amidines, guanidines, boranes and their derivatives/adducts and alkynes. The precursors may be employed in liquid delivery formulations, and the precursors that are liquids may be used in neat liquid form, with liquid or solid precursors being employed as desired in suitable solvents including alkane solvents (e.g., hexane, heptane, octane, and pentane), aryl solvents (e.g., benzene or toluene), amines (e.g., triethylamine, tert-butylamine), imines, guanidines, amidines and hydrazines.

[00159] The utility of specific solvent compositions for particular precursors may be readily empirically determined, to select an appropriate single component or multiple component solvent medium for liquid delivery vaporization. Solid delivery systems may be employed, of the type previously described herein.

[00160] The above-described precursors are variously shown below.







[00161] Thermal and elemental analysis is set out in the table below, for the four illustrated precursors previously mentioned as having been characterized.

Precursor	TGA		Elemental analysis				Note
	T ₅₀ (°C)	Residue (%)		C (%)	H (%)	N (%)	
GeTMG-Cl ₂	230	3.3	Calc.	52.29	6.51	22.6	NMR
			Found	51.12	6.29	21.69	
GeTMG-Me ₂	182	1.0	Calc.				NMR
			Found				
GeTMG-NMe ₂	219	2.9	Calc.				NMR
(liquid at R.T.)			Found				
GeTMG ₂	253	1.1	Calc.				NMR
			Found				NMR

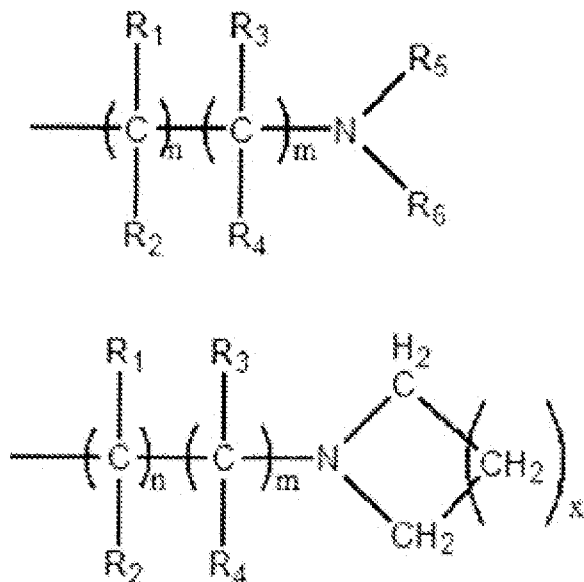
[00162] The above-described precursors are variously shown below.

[00163] The invention in a further aspect relates to dianionic chelate guanidinate ligands useful for CVD and ALD, and includes a class of metal precursors with dianionic chelate guanidine ligands of the formula (R₄)_nM{(R₁)N=C[(NR₂)(NR₃)]}(ox-n)/2.

[00164] All of such precursors can be synthesized from the corresponding alkali metal salts with metal halides or alkyls or mixed halides/alkyls or from direct reactions between guanidines with metal halides with the presence of HX absorbents such as NEt₃. The syntheses of the guanidinate ligands can be done from the corresponding carbodiimides and primary amines.

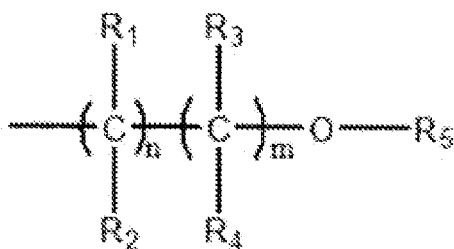
[00165] The "oligomers" of the above-claimed monomer with the same empirical formula include [(R₄)_nM{(R₁)N=C[(NR₂)(NR₃)]}(ox-n)/2]_x, where x is an integer having the value of 2, 3, etc., wherein each R₁, R₂, R₃, R₄, is independently selected from among H, C1-C6 alkyl, C3-C10 cycloalkyl, C6-C10 aryl, -Si(R₅)₃ and -Ge(R₅)₃ wherein each R₅ is independently selected from C1-C6 alkyl; and -Si(R₆)₃ wherein each R₆ is independently selected from C1-C6 alkyl; and when suitable, pendant ligands attached to the above-mentioned R₁, R₂, R₃, R₄ including functional group(s) providing further coordination to the metal

center, such as, for example, aminoalkyl, alkoxyalkyl, aryloxyalkyl, imidoalkyl, and acetylalkyl, wherein suitable groups in these classes include those of the following formula:



aminoalkyls

wherein each of R1-R4 is the same as or different from one another, with each being independently selected from among hydrogen and C1-C6 alkyl; each of R5 and R6 is the same as or different from the other, with each being independently selected from among C1-C6 alkyl; n and m are each selected independently from 0 to 4 with the provision that m and n cannot be 0 at the same time, and x is selected from 1 to 5;



alkoxyalkyls and aryloxyalkyls

wherein each of R1-R4 is the same as or different from one another, with each being independently selected from among hydrogen, C1-C6 alkyl, and C6-C10 aryl; R5 is selected from among C1-C6 alkyl, and C6-C10 aryl; and n and m are selected independently from 0 to 4, with the provision that m and n cannot be 0 at the same time.

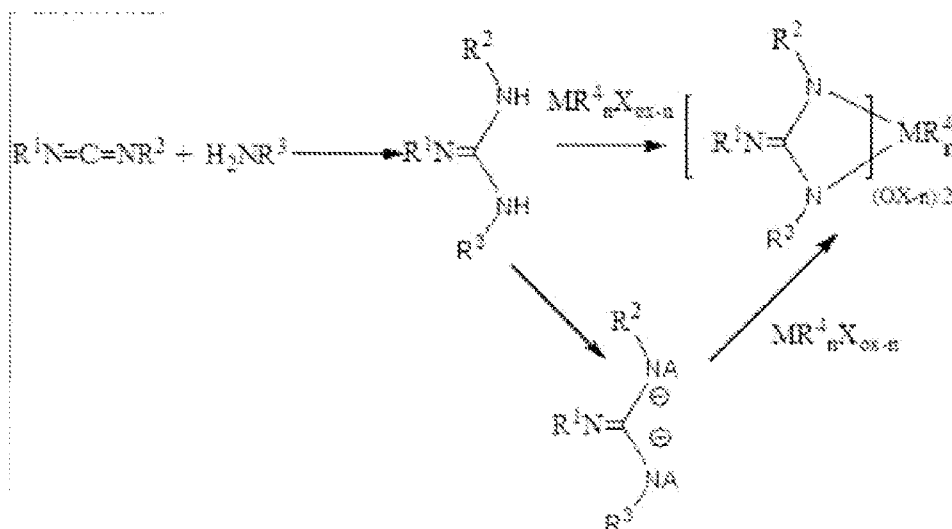
[00166] In the metal precursors, each R5 can be independently selected from among H, C1-C6 alkyl, C3-C6 cycloalkyl, C1-C6 alkoxy, -NR1R2, and -C(R3)3, -Si(R8)3 and -Ge(R8)3 wherein each R3 is independently selected from C1-C6 alkyl; and each of R8 and R8 is independently selected from H, C1-C6 alkyl, C5-C10 cycloalkyl, C6-C10 aryl, and -Si(R9)3 wherein each R4 is independently selected from C1-C6 alkyl.

[00167] In such metal precursors, M can be any of the metals mentioned above (Ta, V, Ti, Nb, Pb, Ni, W, Ca, Ba, In, Y, La, Zr, Hf, Ir, Ru, Pt, Cr, Mo, Ge; Al, Si, Ga, Sc, V, Cr, Fe, Sb, lanthanides, Mn, Co, Ni, Zn, Cd, Te, Hg, Au, Cu, Ag, Sr, Ru) but not limited to them only; OX is the allowed oxidation state of the metal M; n is an integer having a value of from 0 to ox; and X is halogen.

[00168] The above-described precursor materials can be used as low temperature deposition precursors with reducing co-reactants such as hydrogen, H₂/plasma, amines, imines, hydrazines, silanes, silyl chalcogenides such as (Me₃Si)₂Te, germanes such as GeH₄, ammonia, alkanes, alkenes, amidines, guanidines, boranes and their derivatives/adducts and alkynes. The precursors may be employed in liquid delivery formulations, and the precursors that are liquids may be used in neat liquid form, with liquid or solid precursors being employed as desired in suitable solvents including alkane solvents (e.g., hexane, heptane, octane, and pentane), aryl solvents (e.g., benzene or toluene), amines (e.g., triethylamine, tert-butylamine), imines, guanidines, amidines and hydrazines.

[00169] The utility of specific solvent compositions for particular precursors may be readily empirically determined, to select an appropriate single component or multiple component solvent medium for liquid delivery vaporization. Solid delivery systems may be employed, of the type previously described herein.

[00170] The above-described precursors are variously shown below.



A is alkali metals, X is halogens and ox is the allowed oxidation state of M.

[00171] An exemplary ligand $PriN=C(PriNH)_2$ was synthesized and characterized as follows.

[00172] Example

[00173] To a 250 mL flask charged with 12.6 g $PriNCNPri$ (0.1 mol) and 100 ml toluene, 5.9 g $PriNH_2$ (0.1 mol) was added at 0°C gradually. The resulting mixture was then refluxed at 100°C overnight. After work-up, 11.5 g solid $PriN=C(PriNH)_2$ was obtained. (62% yield)
 Anal. Calcd for $C_{10}H_{23}N_3$: C: 64.81%; H: 12.51%; N: 22.68%. Found: C: 64.73%; H: 12.39%; N: 22.48%.

[00174] Selected bond lengths:[Å]

C(1)-N(3)	1.287(3)
C(1)-N(2)	1.358(3)
C(1)-N(1)	1.378(3)

[00175] The invention in a further aspect relates to a highly selective germanium deposition process. Although discussed herein with primary reference to germanium, this process has applicability to other film deposition applications in which the film deposition process is dependent on nucleation processes, e.g., ruthenium deposition.

[00176] Phase Change Memory (PCM) is currently considered the leading contender for non-volatile memory based on its potential to scale down for several generations. Integrated GST based PCM devices have been made in the form of a large, flat layer with "plug" electrodes. Metalorganic Chemical Vapor Deposition (MOCVD) processes are under development for making these films, as it will certainly be necessary to deposit them in 3D geometries as device geometries shrink. In future generations, it will be necessary to scale this operation down to make the entire phase change chalcogenide section a plug within a via of insulating material such as silicon oxide, silicon nitride or low k dielectric.

[00177] An example of this can be seen in FIG. 8, which is a schematic of a GST device structure showing the GST plug, top electrode, bottom electrode, interlayer dielectric and associated layers of the device. Since neither etching nor CMP of this material is well established, making such a plug is not trivial, since a fairly thick layer is needed in order to allow for the bulk phase change that stores information in the form of a resistivity change. It would be desirable to grow the material in a "bottom up" way only in the via, without coating the rest of the structure. In order for this to occur, the deposition process must be highly selective, growing quickly on the desired surfaces and slowly or not at all on others.

[00178] It might also be desirable to have the PCM material have poor contact with sidewalls of the via so as to reduce thermal contact and crosstalk between adjacent cells. Thus it could be desirable to have different sticking coefficients and nucleation likelihood on different surfaces.

[00179] It is also necessary to develop low temperature MOCVD processes for making these films, at temperatures of 300°C or less, since some components are volatile enough that stoichiometry control becomes difficult above this temperature.

[00180] During our investigations of Ge precursors for PCMs, an amide-based precursor was discovered that has very strong selectivity based on surface state of the substrate on which it is being grown. This precursor, $\text{Ge}(\text{NMe}_2)_4$, undergoes a deposition rate change of close to 1000X over an extremely narrow temperature range, just 10-15°C. This is virtually unique behavior and we are aware of no other compound that does this.

[00181] For such a strong effect to be taking place, it seemed likely that it was due to changes in the deposition surface and some kind of autocatalysis. These films were deposited on TiN, which was purchased commercially more than a year previously and cleaved into pieces for these experiments. Ti and TiN rapidly form oxides from exposure to atmosphere, and there is little doubt that the nucleation surface as inserted into the reactor was some form of Ti oxide or oxide nitride mix. Ti changes between various suboxides such as TiO_2 and Ti_2O_3 readily, however, so it is possible that under reducing conditions such as the forming gas which flows through the reactor during heatup on the substrate, or even the hydrogen in which deposition takes place, the surface is altered in a fairly abrupt way at a particular transition temperature. Heatup from room temperature was fixed at 4 minutes in all experiments. This could explain the behavior observed above, with deposition rate increasing from a few Å/min up to 1000 Å/min in a 10-15 degree C window, and with the location of this window shiftable by tens of degrees based on the reactant gas and partial pressure of the gases present.

[00182] In order to test this theory, deposition was carried out on SiO_2 substrates, and on a piece of TiN which was first heated to 400 C in 8T of hydrogen before being cooled to deposition temperature over the course of 10 minutes. The results included a deposition rate at 280 C of about 3 Å/min deposited on TiN that had been exposed to air then placed on a

susceptor. On a SiO₂ substrate, the deposition rate was closer to 0.3 A/min, an order of magnitude lower. Meanwhile, on the substrate which was preheated to 400 C then cooled in a reducing atmosphere in the reactor, deposition rate was close to 600 A/min at 280 C, and the rate was substantially higher at low temperatures. The preheated substrate was the closest simulation of a standard manufacturing process, where a TiN or similar electrode would be deposited in one part of a cluster tool, after which the substrate would be transferred to the CVD deposition module without any air exposure. The 200:1 ratio between deposition rates on preheated TiN and SiO₂ is sufficient to obtain a very high selectivity on any combination of surfaces like this one. It is expected that this ratio would increase still further with clean, "in situ" deposited TiN and SiO₂.

[00183] The most straightforward potential benefit to the unique behavior of this precursor was bottom up fill of the vias to make a plug of chalcogenide phase change memory material. The Ge initial layer can be used as a somewhat more favorable growth site for a complete suite of precursors to help prevent "seams" or voids in the plug.

[00184] If it were desirable, it might also be possible to have a plug of PCM material with poor contact to the side walls, providing better thermal isolation and less cross talk between adjacent PCM cells. Slow deposition and poor nucleation may lead to a poorly adhering layer with pores near the surface.

[00185] A more indirect benefit is creation of a semiconductor compatible nucleation surface for other nucleation sensitive materials. For example, it is well known that Ru metal is difficult to grow in a purely reducing atmosphere; it tends to need some oxygen in its vicinity, for most CVD precursors. In addition, it is very hard to deposit it uniformly on a SiO₂ surface. This Ge precursor can be used to form a nucleation layer on Si at the bottom of a trench or via so that a slightly oxidizing process can be used, since Ge does not bond as strongly to oxygen as Si does, or a reducing process which deposits more easily on clean metal could be used. This approach can be extended to deposition of materials other than Ru, providing they have some surface chemistry sensitivity that can be exploited.

[00186] In a more sophisticated approach, a surface, metal, nitride and/or Ge, can have its surface chemistry changed via reactant gases (for example from oxide to metal) in order to switch it on and off for purposes of deposition from this precursor. This in turn allows a chip surface that may have multiple materials exposed to have different surfaces switched on and off, depending on the layer material and coreactant, relative to Ge deposition. The Ge can then be used as a protective layer for further chemistry modifications, e.g., as a hard mask, a sacrificial layer, etc. This principle can be extended to other elements than Ge upon finding appropriate precursors with this strong sensitivity to surface and deposition temperature.

[00187] Other chemicals and chemical families that may exhibit this behavior include N-coordinated germanium amides, amidinates, guanidates, and N-heterocyclic germynes. The

described process is also applicable to metal-organic CVD or ALD precursors comprising a metal selected from Ge, Sb, Te, Be, Mg, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Hg, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Sn, Pb, As, P, Bi, Al, Ga, In, Tl, and Si, to which is bound at least one weakly coordinating ligand selected from among halogen, B-diketiminato, nitrile, isonitrile, aminotroponimate, carbonyl, phosphido, imido, amine, pyridine, amidinate, guanidinate, nitrosyl, silyl, stibene (R_3Sb), sulfide, and cyclopentadienyl.

[00188] In a broad aspect, the present invention contemplates metal precursors of the formula MA_yB_x wherein M is a metal selected from among Ge, Sb and Te, and A is a ligand selected from the group consisting of all ligands disclosed herein, and $y + x$ equals the oxidation state on metal M.

[00189] While the invention 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 metal complex selected from among complexes of formulae (A), (B), (C), (D) and (E)(I)-(E)(XVI):

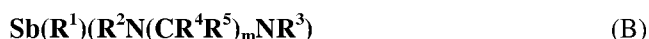


wherein:

R^1 , R^2 , R^3 , and R^4 may be the same as or different from one another, and are independently selected from $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_3\text{-C}_6$ cycloalkyl, $\text{C}_2\text{-C}_6$ alkenyl (e.g., vinyl, allyl, etc.), $\text{C}_3\text{-C}_6$ alkylsilyl, $\text{C}_6\text{-C}_{10}$ aryl,

each of R^5 and R^6 may be the same as or different from one another and are independently selected from hydrogen, $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_3\text{-C}_6$ cycloalkyl, $\text{C}_2\text{-C}_6$ alkenyl (e.g., vinyl, allyl, etc.), $\text{C}_3\text{-C}_6$ alkylsilyl, and $\text{C}_6\text{-C}_{10}$ aryl; and

m is an integer from 1 to 4 inclusive;



wherein:

R^1 , R^2 , and R^3 may be the same as or different from one another, and are independently selected from $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_3\text{-C}_6$ cycloalkyl, $\text{C}_2\text{-C}_6$ alkenyl (e.g., vinyl, allyl, etc.), $\text{C}_3\text{-C}_6$ alkylsilyl, and $\text{C}_6\text{-C}_{10}$ aryl;

each of R^4 and R^5 may be the same as or different from one another and is independently selected from hydrogen, $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_3\text{-C}_6$ cycloalkyl, $\text{C}_2\text{-C}_6$ alkenyl (e.g., vinyl, allyl, etc.), $\text{C}_3\text{-C}_6$ alkylsilyl, and $\text{C}_6\text{-C}_{10}$ aryl; and

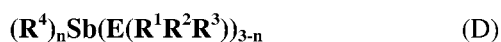
m is an integer from 1 to 4 inclusive;



wherein:

R^1 , R^2 and R^3 may be the same as or different from one another and are independently selected from hydrogen, C_1 - C_6 alkyl, C_3 - C_6 cycloalkyl, C_2 - C_6 alkenyl (e.g., vinyl, allyl, etc.), silyl, C_3 - C_6 alkylsilyl, C_6 - C_{10} aryl and $-NR^4R^5$, wherein each of R^4 and R^5 is selected from among H and C_1 - C_4 ; and

n is an integer from 0 to 3 inclusive;



wherein:

R^1 , R^2 , R^3 , and R^4 may be the same as or different from one another, and are independently selected from C_1 - C_6 alkyl, C_3 - C_6 cycloalkyl, C_3 - C_6 alkylsilyl, C_6 - C_{10} aryl, and alkylamino of the formula $-NR^5R^6$ wherein each of R^5 and R^6 is independently selected from H and C_1 - C_4 alkyl;

E is silicon (Si) or germanium (Ge); and

n is an integer from 0 to 3 inclusive;

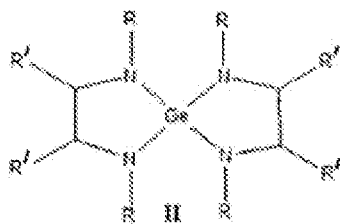
(E) germanium precursors of the following formulae I-XVI:



I

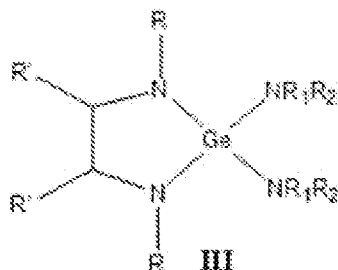
wherein:

R_1 and R_2 may be the same as or different from one another, and are independently selected from H, C_1 - C_6 alkyl, C_2 - C_5 alkenyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-Si(R_3)_3$ wherein each R_3 is independently selected from C_1 - C_6 alkyl;



wherein:

R and R' may be the same as or different from one another, and each R and R' is independently selected from H, C₁-C₆ alkyl, C₂-C₅ alkenyl, C₅-C₁₀ cycloalkyl, C₆-C₁₀ aryl, and -Si(R₃)₃ wherein each R₃ is independently selected from C₁-C₆ alkyl;



wherein:

R, R', R₁ and R₂ may be the same as or different from one another, and each is independently selected from H, C₁-C₆ alkyl, C₂-C₅ alkenyl, C₅-C₁₀ cycloalkyl, C₆-C₁₀ aryl, and -Si(R₃)₃ wherein each R₃ is independently selected from C₁-C₆ alkyl;

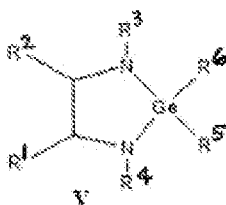


IV

wherein:

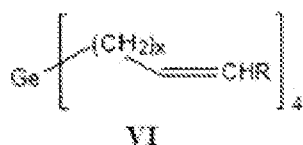
R, R₁ and R₂ may be the same as or different from one another, and each is independently selected from H, C₁-C₆ alkyl, C₂-C₅ alkenyl, C₅-C₁₀ cycloalkyl, C₆-C₁₀ aryl, and -Si(R₃)₃ wherein each R₃ is independently selected from C₁-C₆ alkyl; and

n is an integer from 0 to 4 inclusive;



wherein:

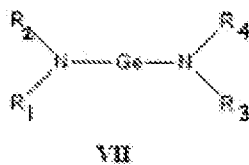
R^1 , R^2 , R^3 , R^4 , R^5 and R^6 may be the same as or different from one another, and each is independently selected from H, C_1 - C_6 alkyl, C_2 - C_5 alkenyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-Si(R_3)_3$ wherein each R_3 is independently selected from C_1 - C_6 alkyl;



wherein:

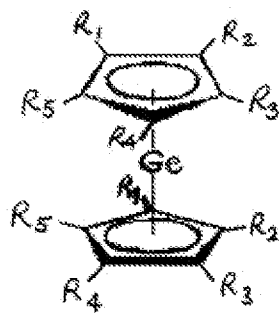
R is selected from H, C_1 - C_6 alkyl, and C_6 - C_{10} aryl; and

x is 0, 1 or 2;



wherein:

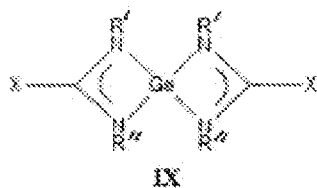
R_1 , R_2 , R_3 and R_4 may be the same as or different from the others, and each is independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-Si(R_3)_3$ wherein each R_3 is independently selected from C_1 - C_6 alkyl;



VIII

wherein:

R_1 , R_2 , R_3 , R_4 , and R_5 may be the same as or different from one another, and each is independently selected from among H, C_1 - C_6 alkyl, silyl, $-\text{Si}(\text{R}')_3$, C_6 - C_{10} cycloalkyl, C_6 - C_{10} aryl, $-(\text{CH}_2)_x\text{NR}'\text{R}''$, and $-(\text{CH}_2)_x\text{OR}'''$, wherein $x = 1, 2$ or 3 , and R' , R'' and R''' may be the same as or different from one another, and each is independently selected from C_1 - C_6 alkyl;

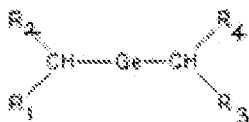


IX

wherein:

R' and R'' may be the same as or different from one another, and are independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl; and

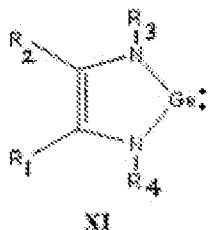
each X is independently selected from among C_1 - C_6 alkyl, C_1 - C_6 alkoxy, $-\text{NR}^1\text{R}^2$, and $-\text{C}(\text{R}^3)_3$, wherein each of R^1 , R^2 and R^3 is independently selected from H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}^4)_3$ wherein each R^4 is independently selected from C_1 - C_6 alkyl;



X

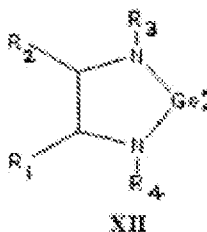
wherein:

R_1 , R_2 , R_3 and R_4 may be same as or different from one another, and are independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl;



wherein:

R_1 , R_2 , R_3 and R_4 may be the same as or different from one another, and are independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl;



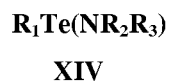
wherein:

R_1 , R_2 , R_3 and R_4 may be the same as or different from one another, and are independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl;



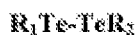
wherein:

R_1 and R_2 may be the same as or different from one another, and are independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl;



wherein:

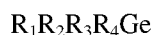
R₁, R₂ and R₃ may be the same as or different from one another, and are independently selected from among H, C₁-C₆ alkyl, C₅-C₁₀ cycloalkyl, C₆-C₁₀ aryl, and -Si(R₃)₃ wherein each R₃ is independently selected from C₁-C₆ alkyl;



XV

wherein:

R₁ and R₂ may be the same as or different from one another, and are independently selected from among H, C₁-C₆ alkyl, C₅-C₁₀ cycloalkyl, C₆-C₁₀ aryl, and -Si(R³)₃ wherein each R³ is independently selected from C₁-C₆ alkyl; and



XVI

wherein:

R₁, R₂, R₃, and R₄ may be the same as or different from one another, and are independently selected from among H, C₁-C₆ alkyl, C₅-C₁₀ cycloalkyl, C₆-C₁₀ aryl, and -Si(R³)₃ wherein each R³ is independently selected from C₁-C₆ alkyl.

2. An antimony complex according to claim 1, selected from complexes of formula (A).
3. An antimony complex according to claim 1, selected from complexes of formula (B).
4. An antimony complex according to claim 1, selected from complexes of formula (C).
5. An antimony complex according to claim 1, wherein when the complex contains dialkylamino moieties, alkyl substituents of all said moieties are not all methyl.
6. An antimony complex according to claim 4, wherein when the complex contains trialkylgermanyli moieties, alkyl substituents of all said moieties are not all methyl.
7. An antimony complex according to claim 4, wherein when the complex contains trialkylsilyl moieties, alkyl substituents of all said moieties are not all methyl.
8. A germanium complex according to claim 1, selected from complexes of formula (E)(I).

9. A germanium complex according to claim 1, selected from complexes of formula (E)(II).
10. A germanium complex according to claim 1, selected from complexes of formula (E)(III).
11. A germanium complex according to claim 1, selected from complexes of formula (E)(IV).
12. A germanium complex according to claim 1, selected from complexes of formula (E)(V).
13. A germanium complex according to claim 1, selected from complexes of formula (E)(VI).
14. A germanium complex according to claim 1, selected from complexes of formula (E)(VII).
15. A germanium complex according to claim 1, selected from complexes of formula (E)(VIII).
16. A germanium complex according to claim 1, selected from complexes of formula (E)(IX).
17. A germanium complex according to claim 1, selected from complexes of formula (E)(X).
18. A germanium complex according to claim 1, selected from complexes of formula (E)(XI).
19. A germanium complex according to claim 1, selected from complexes of formula (E)(XII).
20. A germanium complex according to claim 1, selected from complexes of formula (E)(XIII).
21. A germanium complex according to claim 1, selected from complexes of formula (E)(XIV).
22. A germanium complex according to claim 1, selected from complexes of formula (E)(XV).
23. A germanium complex according to claim 1, selected from complexes of formula (E)(XVI).
24. A packaged precursor supply system comprising a package containing an antimony complex according to claim 1.
25. A packaged precursor supply system comprising a package containing a germanium complex according to claim 1.

26. A germanium complex according to claim 1, with the proviso that said complex is not tetrakisdialkylamidogermane.
27. A germanium complex according to claim 1, wherein when the complex contains dialkylsilyl moieties, alkyl substituents of all said moieties are not all methyl.
28. A vapor of a metal complex of claim 1.
29. A precursor composition comprising a metal complex of claim 1 in a solvent medium.
30. A method of depositing antimony on a substrate, comprising contacting the substrate with precursor vapor comprising vapor of an antimony complex of claim 1.
31. The method of claim 30, comprising chemical vapor deposition.
32. The method of claim 30, comprising atomic layer deposition.
33. The method of claim 30, comprising deposition of germanium on said substrate to form a film containing antimony and germanium.
34. The method of claim 30, comprising deposition of tellurium on said substrate to form a film containing antimony and tellurium.
35. The method of claim 30, comprising deposition of germanium and tellurium on said substrate to form a GST film.
36. A method of depositing metal on a substrate, comprising contacting the substrate with precursor vapor comprising vapor of a metal complex of claim 1.
37. The method of claim 36, wherein said contacting is in the presence of a reducing co-reactant.
38. The method of claim 37, wherein said reducing co-reactant comprises a co-reactant selected from the group consisting of hydrogen, hydrogen plasma, amines, imines, hydrazines, silanes, silyl chalcogenides, $(\text{Me}_3\text{Si})_2\text{Te}$, germanes, GeH_4 , ammonia, alkanes, alkenes and alkynes.

39. The method of claim 36, comprising liquid delivery of the metal complex, and volatilization of the metal complex to form volatilized metal complex as a component of said precursor vapor.

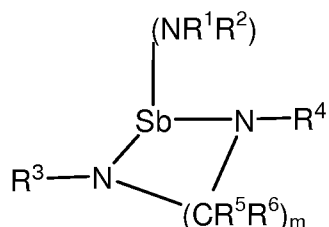
40. The method of claim 36, comprising solid delivery of the metal complex, and volatilization of the metal complex to form volatilized metal complex as a component of said precursor vapor.

41. The method of claim 39, wherein said liquid delivery comprises delivery of the metal complex in a neat liquid form.

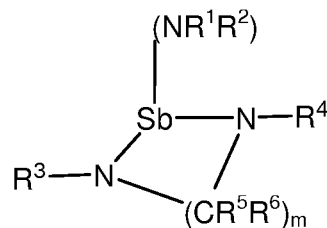
42. The method of claim 39, wherein said liquid delivery comprises delivery of the metal complex dissolved or suspended in a solvent medium.

43. The method of claim 42, wherein said solvent medium comprises at least one solvent species selected from the group consisting of alkanes, hexane, heptane, octane, pentane, aryls, benzene, toluene, amines, triethylamine, tert-butylamine, imines, and hydrazines.

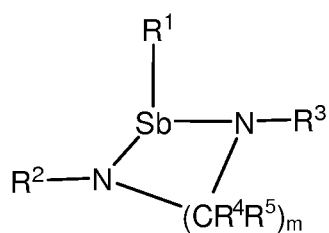
44. A method of making an antimony complex of formula (A) of claim 1, having the formula



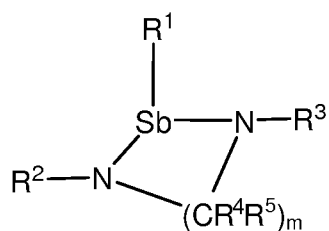
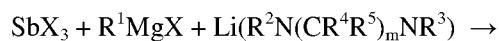
said method comprising conducting a reaction scheme including the reaction:



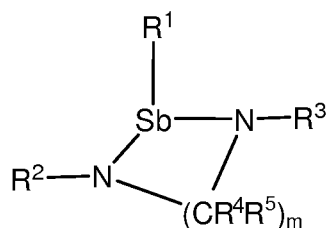
45. A method of making an antimony complex of formula (B) of claim 1, having the formula



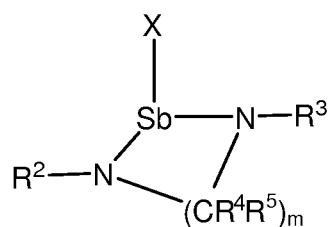
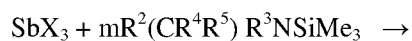
said method comprising conducting a reaction scheme including the reaction:

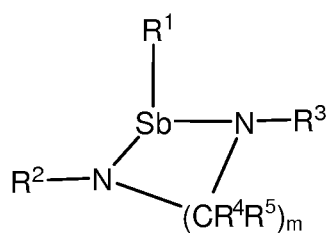


46. A method of making an antimony complex of formula (B) of claim 1, having the formula

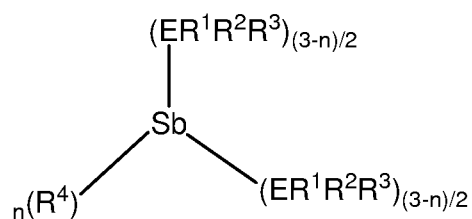


said method comprising conducting a reaction scheme including the reactions:



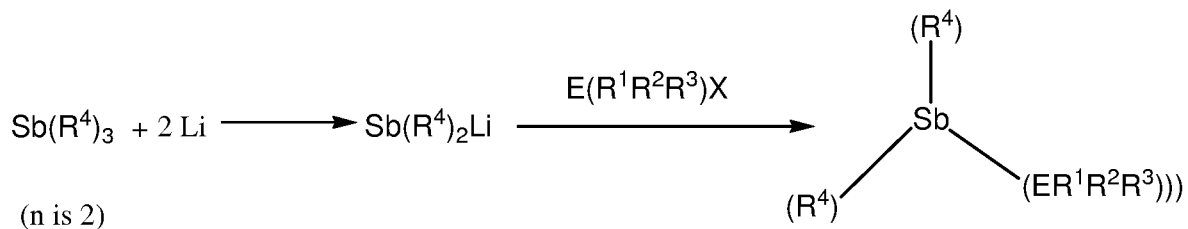
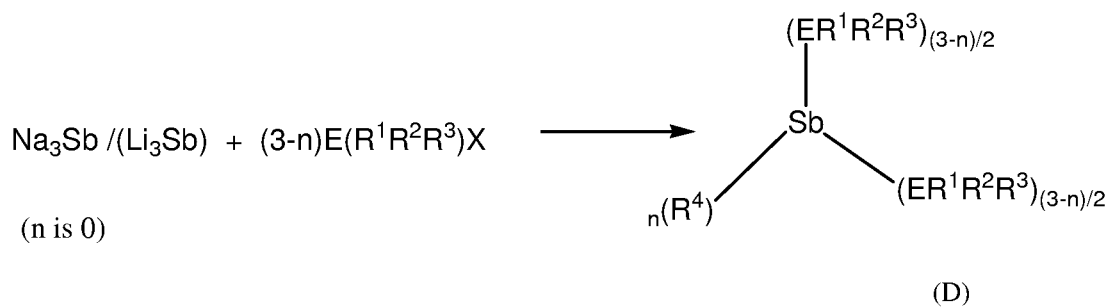


47. A method of making an antimony complex of formula (D) of claim 1, having the formula



E = Ge or Si

said method comprising conducting a reaction scheme including the reaction (D), when n is zero, and the reaction (E), when n is 2:



E = Ge or Si

(E)

wherein X is halo.

48. An antimony precursor selected from the group consisting of $\text{Sb}(\text{NMeEt})_3$, $\text{Sb}(\text{CH}=\text{CMe}_2)_3$ and $\text{Sb}(\text{CH}_2\text{CH}=\text{CH}_2)_3$.

49. A packaged precursor supply system comprising a package containing a metal complex according to claim 1.

50. The packaged precursor supply system according to claim 49, wherein the metal complex is photo-sensitive, and the package comprises a photo-resistant package.

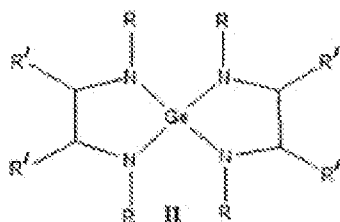
51. A germanium complex selected from among complexes of formulae I-XVI:



I

wherein:

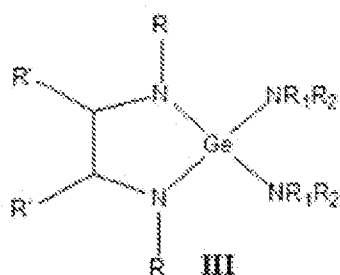
R_1 and R_2 may be the same as or different from one another, and are independently selected from H, $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_2\text{-C}_5$ alkenyl, $\text{C}_5\text{-C}_{10}$ cycloalkyl, $\text{C}_6\text{-C}_{10}$ aryl, and $-\text{Si}(\text{R}_3)_3$ wherein each R_3 is independently selected from $\text{C}_1\text{-C}_6$ alkyl;



II

wherein:

R and R' may be the same as or different from one another, and each R and R' is independently selected from H, $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_2\text{-C}_5$ alkenyl, $\text{C}_5\text{-C}_{10}$ cycloalkyl, $\text{C}_6\text{-C}_{10}$ aryl, and $-\text{Si}(\text{R}_3)_3$ wherein each R_3 is independently selected from $\text{C}_1\text{-C}_6$ alkyl;



wherein:

R, R', R₁ and R₂ may be the same as or different from one another, and each is independently selected from H, C₁-C₆ alkyl, C₂-C₅ alkenyl, C₅-C₁₀ cycloalkyl, C₆-C₁₀ aryl, and -Si(R₃)₃ wherein each R₃ is independently selected from C₁-C₆ alkyl;

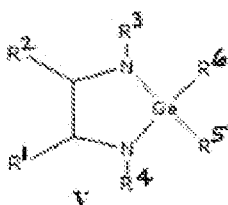


IV

wherein:

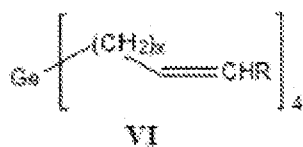
R, R₁ and R₂ may be the same as or different from one another, and each is independently selected from H, C₁-C₆ alkyl, C₂-C₅ alkenyl, C₅-C₁₀ cycloalkyl, C₆-C₁₀ aryl, and -Si(R₃)₃ wherein each R₃ is independently selected from C₁-C₆ alkyl; and

n is an integer from 0 to 4 inclusive;



wherein:

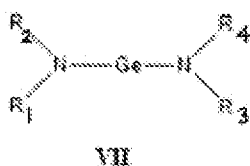
R¹, R², R³, R⁴, R⁵ and R⁶ may be the same as or different from one another, and each is independently selected from H, C₁-C₆ alkyl, C₂-C₅ alkenyl, C₅-C₁₀ cycloalkyl, C₆-C₁₀ aryl, and -Si(R₃)₃ wherein each R₃ is independently selected from C₁-C₆ alkyl;



wherein:

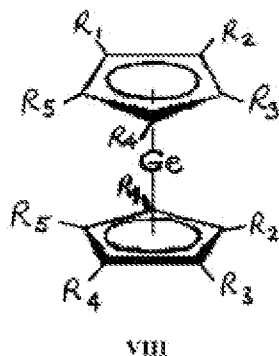
R is selected from H, C₁-C₆ alkyl, and C₆-C₁₀ aryl; and

x is 0, 1 or 2;



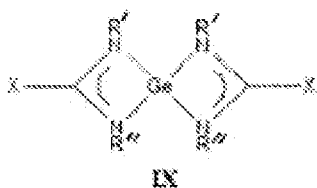
wherein:

R₁, R₂, R₃ and R₄ may be the same as or different from the others, and each is independently selected from among H, C₁-C₆ alkyl, C₅-C₁₀ cycloalkyl, C₆-C₁₀ aryl, and -Si(R₃)₃ wherein each R₃ is independently selected from C₁-C₆ alkyl;



wherein:

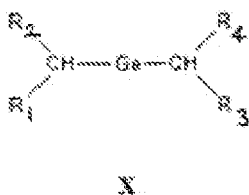
R₁, R₂, R₃, R₄, and R₅ may be the same as or different from one another, and each is independently selected from among H, C₁-C₆ alkyl, silyl, -Si(R')₃, C₆-C₁₀ cycloalkyl, C₆-C₁₀ aryl, -(CH₂)_xNR'R'', and -(CH₂)_xOR''', wherein x = 1, 2 or 3, and R', R'' and R''' may be the same as or different from one another, and each is independently selected from C₁-C₆ alkyl;



wherein:

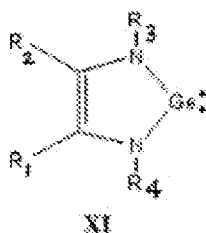
R' and R'' may be the same as or different from one another, and are independently selected from among H, C₁-C₆ alkyl, C₅-C₁₀ cycloalkyl, C₆-C₁₀ aryl, and -Si(R³)₃ wherein each R³ is independently selected from C₁-C₆ alkyl; and

each X is independently selected from among C₁-C₆ alkyl, C₁-C₆ alkoxy, -NR¹R², and -C(R³)₃, wherein each of R¹, R² and R³ is independently selected from H, C₁-C₆ alkyl, C₅-C₁₀ cycloalkyl, C₆-C₁₀ aryl, and -Si(R⁴)₃ wherein each R⁴ is independently selected from C₁-C₆ alkyl;



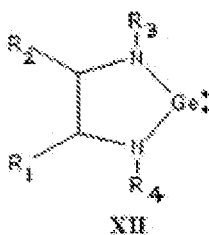
wherein:

R₁, R₂, R₃ and R₄ may be same as or different from one another, and are independently selected from among H, C₁-C₆ alkyl, C₅-C₁₀ cycloalkyl, C₆-C₁₀ aryl, and -Si(R³)₃ wherein each R³ is independently selected from C₁-C₆ alkyl;



wherein:

R₁, R₂, R₃ and R₄ may be the same as or different from one another, and are independently selected from among H, C₁-C₆ alkyl, C₅-C₁₀ cycloalkyl, C₆-C₁₀ aryl, and -Si(R³)₃ wherein each R³ is independently selected from C₁-C₆ alkyl;



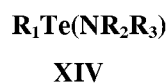
wherein:

R_1 , R_2 , R_3 and R_4 may be the same as or different from one another, and are independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl;



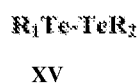
wherein:

R_1 and R_2 may be the same as or different from one another, and are independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl;



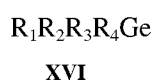
wherein:

R_1 , R_2 and R_3 may be the same as or different from one another, and are independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl;



wherein:

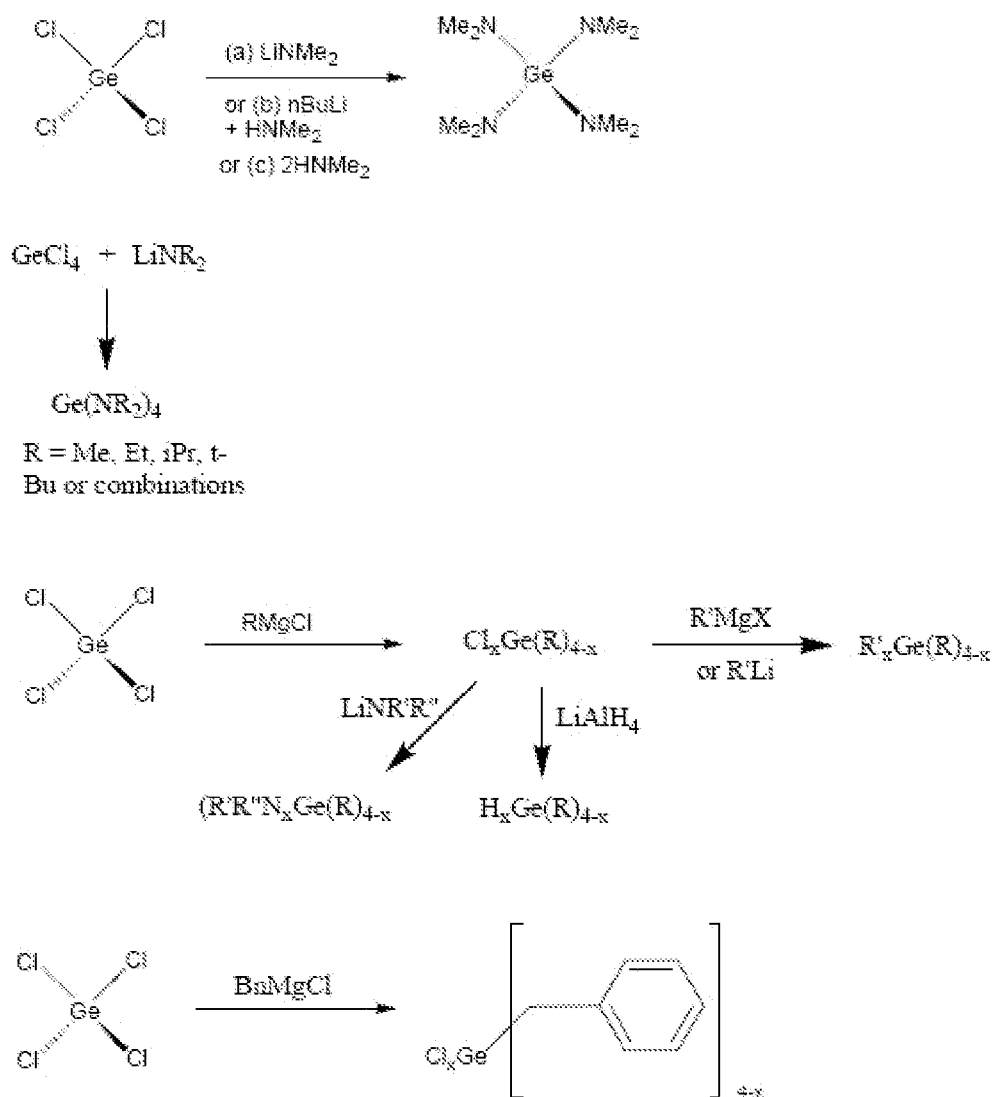
R_1 and R_2 may be the same as or different from one another, and are independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl; and



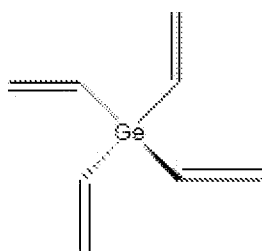
wherein:

R_1 , R_2 , R_3 , and R_4 may be the same as or different from one another, and are independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl.

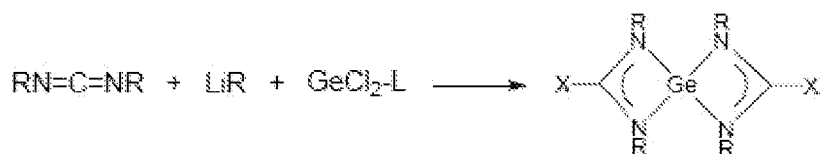
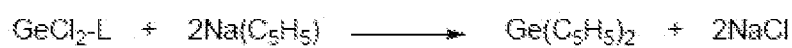
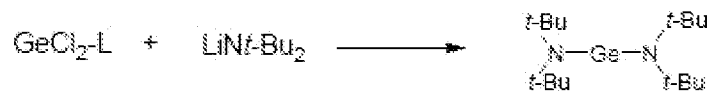
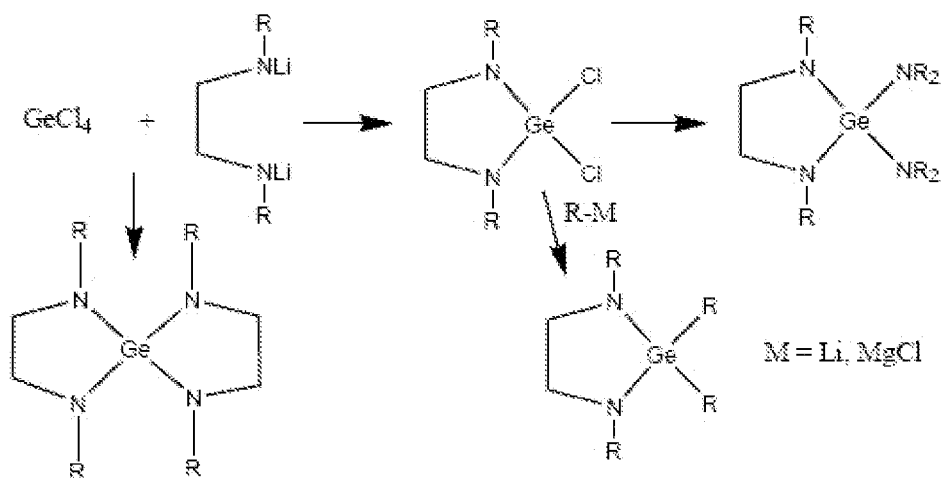
52. A method of making a germanium complex according to claim 51, comprising conducting a reaction scheme including at least one reaction selected from among the following:

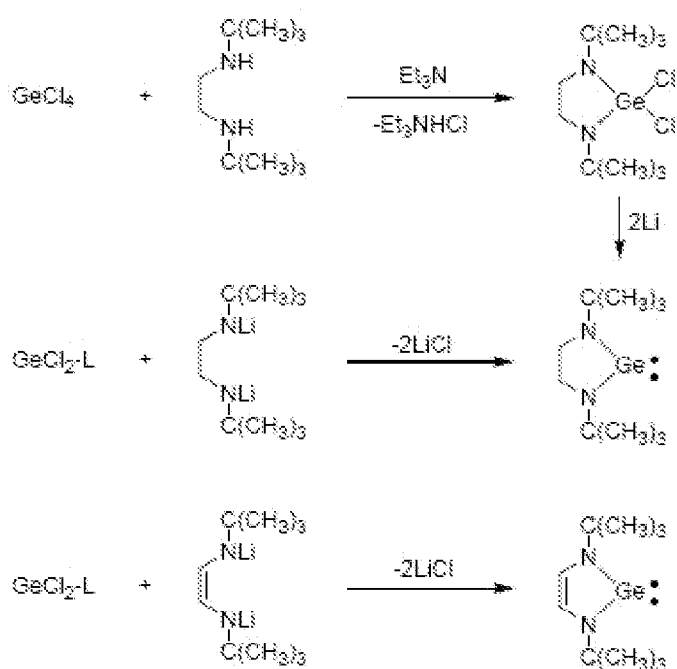


and correspondingly a reaction scheme producing a tetraallylgermanium complex

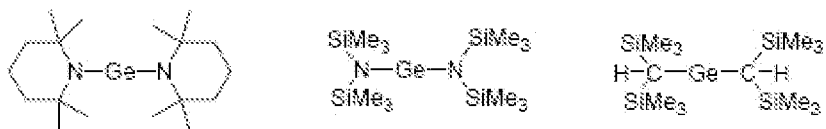


from tetrachlorogermanium starting material using a Grignard reagent R^{*}MgCl, wherein R^{*} is allyl





53. A method of method of depositing germanium on a substrate, comprising contacting the substrate with precursor vapor comprising vapor of a germanium (II) complex selected from among the following:



54. The method of claim 53, comprising chemical vapor deposition.

55. The method of claim 53, comprising atomic layer deposition.

56. A method of method of depositing germanium on a substrate, comprising contacting the substrate with precursor vapor comprising vapor of dialkylaminotriisopropylgermane.

57. A precursor vapor comprising vapor of dialkylaminotriisopropylgermane.

58. The precursor vapor of claim 57, wherein said dialkylaminotriisopropylgermane comprises dimethylaminotriisopropylgermane or ethylmethyaminotriisopropylgermane.

59. A dialkylaminotriisopropylgermane complex.

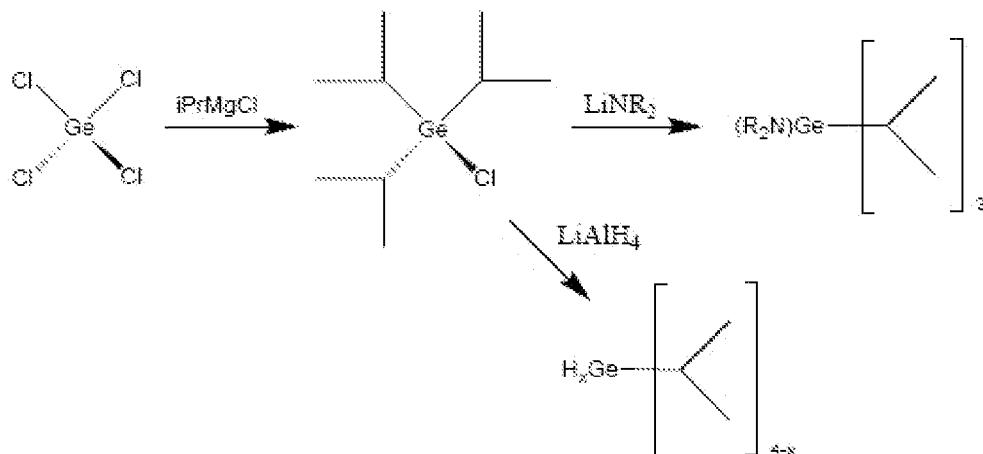
60. The dialkylaminotriisopropylgermane complex of claim 59, wherein each said alkyl is independently selected from C₁-C₆ alkyl.

61. The dialkylaminotriisopropylgermane complex of claim 59, wherein each said alkyl is independently selected from C₁-C₄ alkyl.

62. The method of claim 56, comprising chemical vapor deposition.

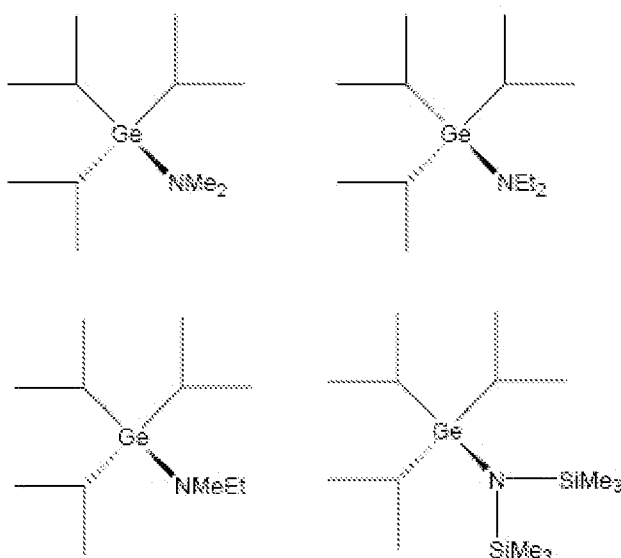
63. The method of claim 56, comprising atomic layer deposition.

64. A method of making a germanium complex, comprising conducting a reaction scheme including the following reactions:



wherein each R is independently selected from alkyl, cycloalkyl, alkylsilyl, aryl and hydrogen.

65. The method of claim 64, comprising forming a germanium complex selected from the following group of germanium complexes:



66. A method of depositing germanium on a substrate, comprising contacting the substrate with bubbler delivery of a precursor vapor comprising vapor of a germanium complex selected from among $\text{Ge}(\text{NMe}_2)_4$, $\text{Ge}(\text{NEtMe})_4$, $\text{Ge}(\text{NEt}_2)_4$, iPr_3GeCl , $\text{iPr}_3\text{GeNMe}_2$, $\text{iPr}_3\text{GeNEtMe}$, $\text{iPr}_3\text{GeNEt}_2$, and digermanes.

67. A method of depositing germanium on a substrate, comprising contacting the substrate with a precursor vapor comprising vapor of a germanium complex having ligands selected from among allyl, benzyl, t-butyl, cyclopentadienyl, hydride, phenyl, alkyl, bidentate amines and N, N-dimethylethylenediamine.

68. A method of forming a GST film on a substrate, comprising contacting the substrate with a precursor vapor comprising vapor of a germanium complex according to claim 1, vapor of an antimony complex, and vapor of a tellurium complex.

69. The method of claim 68, wherein said antimony complex comprises iPr_3Sb or $\text{Sb}(\text{NR}_2)_3$, $\text{Pr}^i\text{Sb}(\text{N}(\text{SiMe}_3)_2)_2$ and said tellurium complex comprises iPr_2Te or $\text{Te}(\text{NR}_2)_2$, wherein each R_2 is independently selected from C_1 - C_6 alkyl.

70. Ethylmethyaminotriisopropylgermane.

71. A method of forming a germanium-containing film on a substrate, comprising contacting the substrate with a precursor vapor comprising vapor of ethylmethyaminotriisopropylgermane.

72. A method of making a microelectronic device, comprising chemical vapor deposition or atomic layer deposition of a metal-containing film on a substrate from a precursor vapor comprising vapor of at least one precursor according to claim 1.

73. A method of making a microelectronic device, comprising chemical vapor deposition or atomic layer deposition of a metal-containing film on a substrate from a precursor vapor comprising vapor of two precursors according to claim 1.

74. The method of claim 73, wherein one of said two precursors comprises an antimony complex and the other of said two precursors comprises a germanium complex.

75. A precursor mixture including germanium precursor, antimony precursor and tellurium precursor, wherein at least one of the germanium precursor and antimony precursor includes a precursor selected from among the metal complexes of formulae (A), (B), (C), (D) and (E)(I)-(XVI) of claim 1.

76. The precursor mixture of claim 75, including an antimony precursor selected from among the metal complexes of formulae (A), (B), (C) and (D) of claim 1.

77. The precursor mixture of claim 75, including a germanium precursor selected from among the metal complexes of formulae (E)(I)-(XVI) of claim 1.

78. A method of forming an antimony-containing film, comprising use of an antimony precursor selected from among the metal complexes of formulae (A), (B), (C) and (D) of claim 1.

79. A method of forming a germanium-containing film, comprising use of a germanium precursor selected from among the metal complexes of formulae (E)(I)-(XVI) of claim 1.

80. A method of forming a film containing antimony and germanium, comprising use of a precursor selected from among the metal complexes of formulae (A), (B), (C), (D) and (E)(I)-(XVI) of claim 1.

81. A method of forming a film containing antimony and tellurium, comprising use of an antimony precursor selected from among the metal complexes of formulae (A), (B), (C), and (D) of claim 1.

82. A method of forming a film containing germanium and tellurium, comprising use of a germanium precursor selected from among the metal complexes of formulae (E)(I)-(XVI) of claim 1.

83. A method of forming a germanium-antimony-tellurium film, comprising use of a precursor selected from among the metal complexes of formulae (A), (B), (C), (D) and (E)(I)-(XVI) of claim 1.

84. A method of manufacturing a phase change memory device, comprising forming a $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film on a substrate, using a precursor selected from among the metal complexes of formulae (A), (B), (C), (D) and (E)(I)-(XVI) of claim 1.

85. A CVD method for forming a Sb- and/or Ge-containing film, comprising use of at least one metal complex of claim 1, in a chemical vapor deposition process.

86. The method of claim 85, wherein a co-reactant is introduced with precursors in said chemical vapor deposition process to incorporate nitrogen and/or oxygen in the film.

87. A CVD method for forming a Sb- and/or Ge-containing film, comprising use of at least one metal complex of claim 1, in an atomic layer deposition process.

88. The method of claim 87, wherein said Sb- and/or Ge-containing film comprises a GST film, and said atomic layer deposition process is carried out in a pulse cycle for introduction of Ge, Sb and Te precursors in a sequence of Te-Ge-Te-Sb-Te-Ge-Te-Sb-Te.

89. The method of claim 88, wherein said pulse cycle is conducted until a predetermined film thickness is achieved.

90. A method of depositing a film containing antimony and/or germanium on a substrate, said method comprising use of a precursor of claim 1 in a deposition process comprising rapid vapor deposition (RVD).

91. The method of claim 90, further comprising atomic layer deposition (ALD).

92. The method of claim 90, wherein a first precursor vapor is contacted with the substrate to form a saturated surface layer of the precursor, followed by exposure to a second precursor vapor, and thereafter by exposure to a third precursor vapor, with inert gas purges being carried out between the respective precursor vapor contacting steps, in which at least one of the first, second and third precursors comprises said precursor of claim 1, and in which the precursor vapor contacting and intervening purges are repetitively conducted until a predetermined thickness of deposited film material has been achieved.

93. An antimony complex according to claim 1, selected from complexes of formula (D).

94. An antimony precursor, selected from the group consisting of:

(F) aminidates, guanidates and isoureates of the formula:



wherein:

where each R^1 and R^2 is independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-Si(R^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl;

each X is independently selected from among C_1 - C_6 alkoxy, $-NR^4R^5$, and $-C(R^6)_3$, wherein each of R^4 , R^5 and R^6 is independently selected from H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-Si(R^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl;

each R^7 is independently selected from among C_1 - C_6 alkoxy, $-NR^8R^9$, and $-C(R^{10})_3$, wherein each of R^8 , R^9 and R^{10} is independently selected from H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, $-Si(R^3)_3$, and $-Ge(R^3)_3$ wherein each R^3 is independently selected from C_1 - C_6 alkyl; and

n is an integer from 0 to 3;

(G) tetra-alkyl guanidates of the formula:



wherein:

each of R^1 and R^2 is independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-Si(R^9)_3$ wherein each R^9 is independently selected from C_1 - C_6 alkyl;

each of R^3 and R^4 is independently selected from H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(R^9)_3$ wherein each R^9 is independently selected from C_1 - C_6 alkyl;

each R^5 is independently selected from among C_1 - C_6 alkoxy, $-\text{NR}^6\text{R}^7$, and $-\text{C}(\text{R}^8)_3$, wherein each of R^6 , R^7 and R^8 is independently selected from H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, $-\text{Si}(R^9)_3$, and $-\text{Ge}(R^9)_3$ wherein each R^9 is independently selected from C_1 - C_6 alkyl; and

n is an integer from 0 to 3.

(H) carbamates and thiocarbamates of the formula:



wherein:

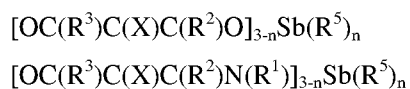
each X is independently selected from among C_1 - C_6 alkoxy, $-\text{NR}^1\text{R}^2$, and $-\text{C}(\text{R}^3)_3$, wherein each of R^1 , R^2 and R^3 is independently selected from H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}^5)_3$ wherein each R^5 is independently selected from C_1 - C_6 alkyl;

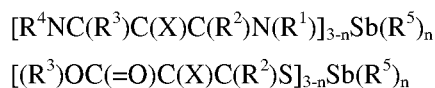
each R^4 is independently selected from among C_1 - C_6 alkoxy, $-\text{NR}^1\text{R}^2$, and $-\text{C}(\text{R}^3)_3$, wherein each of R^1 , R^2 and R^3 is independently selected from H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-\text{Si}(\text{R}^5)_3$, $-\text{Ge}(\text{R}^5)_3$ wherein each R^5 is independently selected from C_1 - C_6 alkyl;

E is either O or S; and

n is an integer from 0 to 3;

(I) beta-diketonates, diketoiminates, and diketiiminates, of the formulae:





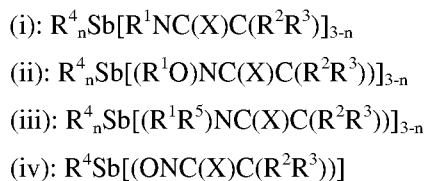
where each of R^1, R^2, R^3 and R^4 is independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-Si(R^6)_3$ wherein each R^6 is independently selected from C_1 - C_6 alkyl;

each X is independently selected from among C_1 - C_6 alkoxy, $-NR^6R^7$, and $-C(R^8)_3$, wherein each of R^6, R^7 and R^8 is independently selected from H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-Si(R^6)_3$ wherein each R^6 is independently selected from C_1 - C_6 alkyl;

each R^5 is independently selected from among guanidinate, aminidate, isoureate, allyl, C_1 - C_6 alkoxy, $-NR^9R^{10}$, and $-C(R^{11})_3$, wherein each of R^9, R^{10} and R^{11} is independently selected from H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, $-Si(R^6)_3$, and $-Ge(R^6)_3$ wherein each R^6 is independently selected from C_1 - C_6 alkyl; and

n is an integer from 0 to 3.

(J) allyls of the formulae:



where each R^1, R^2, R^3 and R^5 is independently selected from among H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-Si(R^6)_3$ wherein each R^6 is independently selected from C_1 - C_6 alkyl;

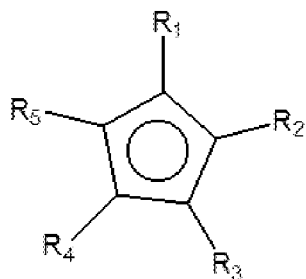
each X is independently selected from among C_1 - C_6 alkoxy, $-NR^1R^2$, and $-C(R^3)_3$, wherein each of R^1, R^2 and R^3 is independently selected from H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, and $-Si(R^6)_3$ wherein each R^6 is independently selected from C_1 - C_6 alkyl;

each R^4 is independently selected from among guanidines, aminidates, isoureates, beta-diketonates, diketiminates, diketiminates, C_1 - C_6 alkoxy, $-NR^7R^8$, and $-C(R^9)_3$, wherein each

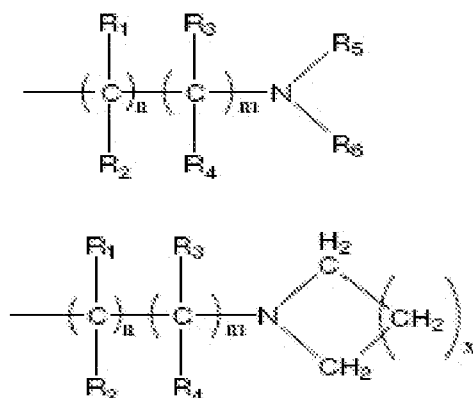
of R^7 , R^8 and R^9 is independently selected from H, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, C_6 - C_{10} aryl, - $Si(R^6)_3$, and $-Ge(R^6)_3$ wherein each R^6 is independently selected from C_1 - C_6 alkyl; and

n is an integer from 0 to 3.

(L) cyclopentadienyl (Cp) antimony compounds wherein the Cp moiety is of the formulae:



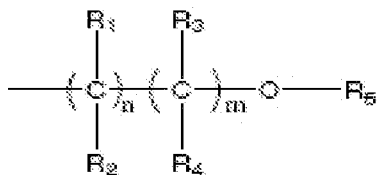
wherein each of R_1 , R_2 , R_3 , R_4 and R_5 can be the same as or different from the others, and each is independently selected from among hydrogen, C_1 - C_{12} alkyl, C_1 - C_{12} alkylamino, C_6 - C_{10} aryl, C_1 - C_{12} alkoxy, C_3 - C_6 alkylsilyl, C_2 - C_{12} alkenyl, $R^1R^2NMR^3$, wherein R^1 , R^2 and R^3 may be the same as or different from one another and each is independently selected from C_1 - C_6 alkyl, and pendant ligands including functional group(s) providing further coordination to the antimony central atom, and selected from among aminoalkyl, alkoxyalkyl, aryloxyalkyl, imidoalkyl, and acetylalkyl, having the following formulae:



aminoalkyls

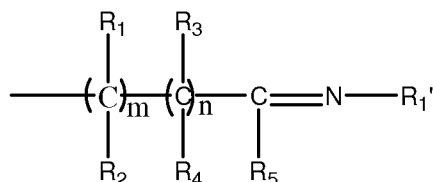
wherein: the methylene ($-CH_2-$) moiety could alternatively be another divalent hydrocarbyl moiety; each of R_1 - R_4 is the same as or different from one another, with each being independently selected from among hydrogen, C_1 - C_6 alkyl and C_6 - C_{10} aryl; each of R_5 and R_6 is

the same as or different from the other, with each being independently selected from among C₁-C₆ alkyl; n and m are each selected independently as having a value of from 0 to 4, with the proviso that m and n cannot be 0 at the same time, and x is selected from 1 to 5;

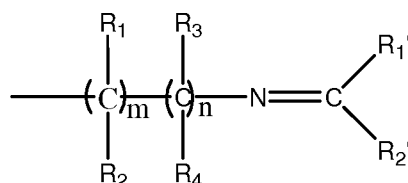


alkoxyalkyls and aryloxyalkyls

wherein each of R₁-R₄ is the same as or different from one another, with each being independently selected from among hydrogen, C₁-C₆ alkyl, and C₆-C₁₀ aryl; R₅ is selected from among C₁-C₆ alkyl, and C₆-C₁₀ aryl; and n and m are selected independently as having a value of from 0 to 4, with the proviso that m and n cannot be 0 at the same time;

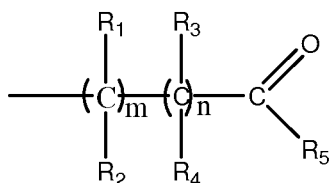


and



imidoalkyl

wherein each of R₁, R₂, R₃, R₄, R₅ is the same as or different from one another, with each being independently selected from among hydrogen, C₁-C₆ alkyl, and C₆-C₁₀ aryl; each of R₁', R₂' is the same as or different from one another, with each being independently selected from C₁-C₆ alkyl, and C₆-C₁₀ aryl; and n and m are selected independently from 0 to 4, with the proviso that m and n cannot be 0 at the same time;



acetylalkyls

wherein each of $\text{R}_1\text{-R}_4$ is the same as or different from one another, with each being independently selected from among hydrogen, $\text{C}_1\text{-C}_6$ alkyl, and $\text{C}_6\text{-C}_{10}$ aryl; R_5 is selected from among $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_6\text{-C}_{10}$ aryl, and $\text{C}_1\text{-C}_5$ alkoxy; and n and m are selected independently from 0 to 4, with the proviso that m and n cannot be 0 at the same time;

wherein non-Cp ligand(s) of the antimony Cp compound can optionally include ligands selected from the group consisting of guanidates, aminidates, isoureates, allyls, beta-diketonates, diketoiminates, and diketiminates; and

(M) alkyls, alkoxides and silyls with pendent ligands, of the formulae:

- (i): $\text{R}^5_n\text{Sb}[(\text{R}^1\text{R}^2)\text{N}(\text{CH}_2)_m\text{C}(\text{R}^1\text{R}^2)]_{3-n}$
- (ii): $\text{R}^5_n\text{Sb}[(\text{R}^1\text{R}^2)\text{N}(\text{CH}_2)_m\text{Si}(\text{R}^1\text{R}^2)]_{3-n}$
- (iii): $\text{R}^5_n\text{Sb}[(\text{R}^1\text{R}^2)\text{N}(\text{CH}_2)_m\text{O}]_{3-n}$

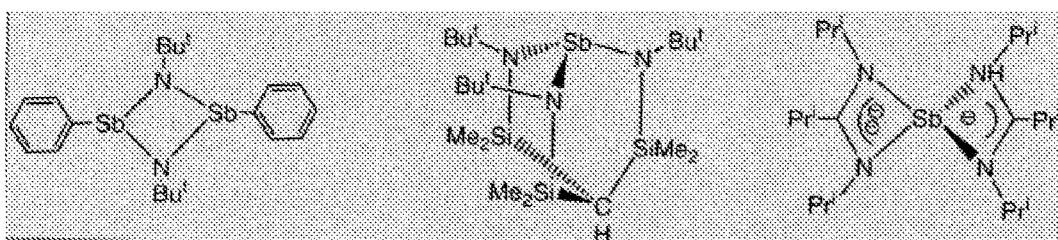
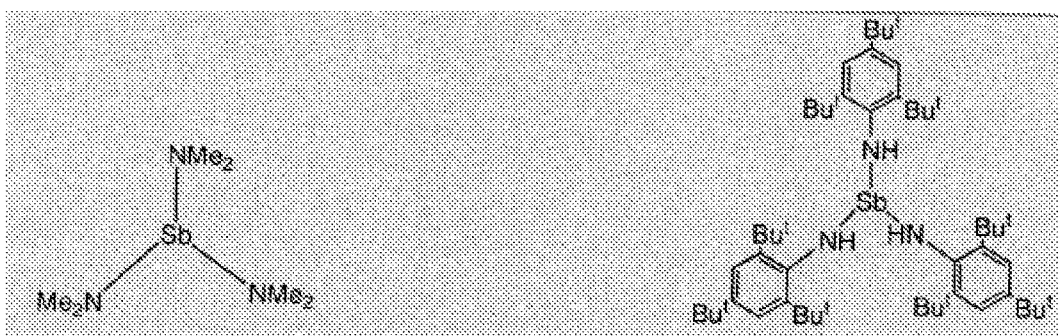
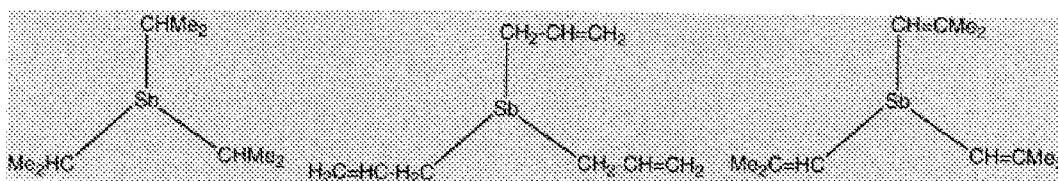
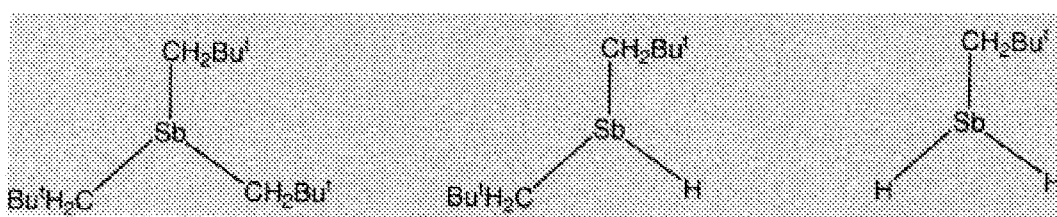
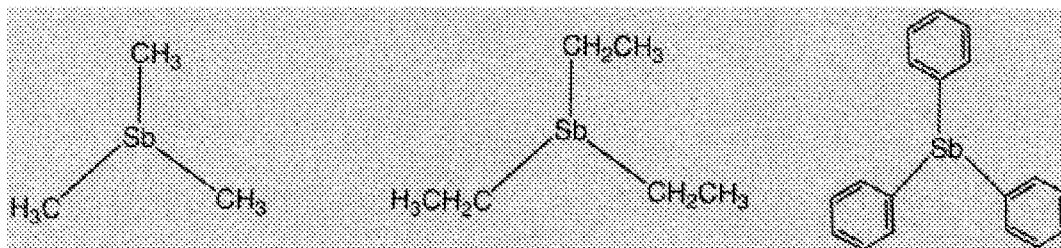
where each of R^1 and R^2 is independently selected from among H, $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_5\text{-C}_{10}$ cycloalkyl, $\text{C}_6\text{-C}_{10}$ aryl, and $-\text{Si}(\text{R}^3)_3$ wherein each R^3 is independently selected from $\text{C}_1\text{-C}_6$ alkyl;

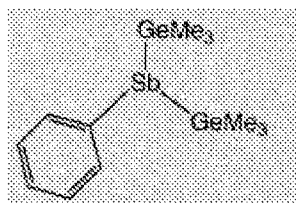
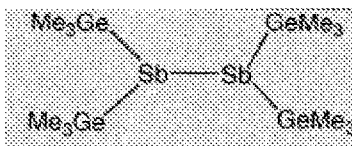
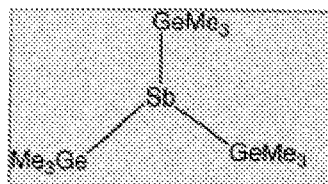
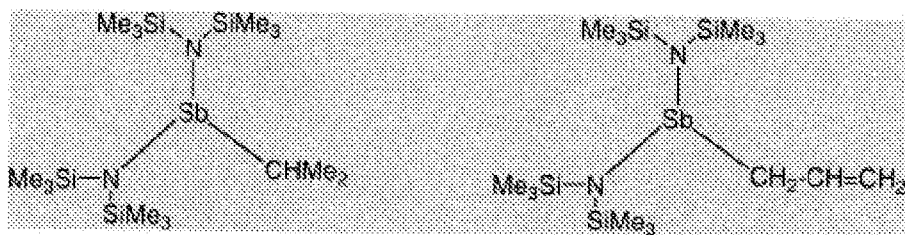
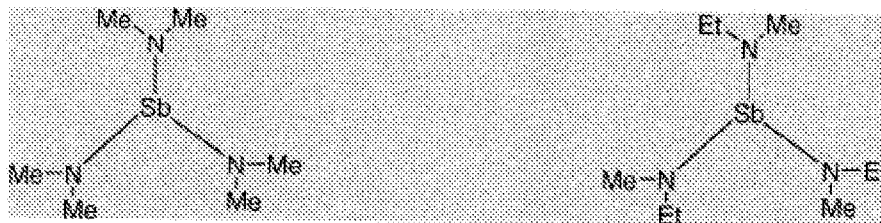
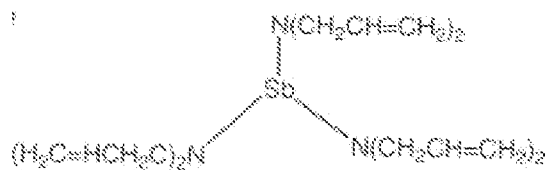
each R^5 is independently selected from among guanidates, aminidates, isoureates, beta-diketonates, diketoiminates, diketiminates, $\text{C}_1\text{-C}_6$ alkoxy, $-\text{NR}^6\text{R}^7$, and $-\text{C}(\text{R}^8)_3$, wherein each of R^6 , R^7 and R^8 is independently selected from H, $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_5\text{-C}_{10}$ cycloalkyl, $\text{C}_6\text{-C}_{10}$ aryl, $-\text{Si}(\text{R}^3)_3$, and $-\text{Ge}(\text{R}^3)_3$ wherein each R^3 is independently selected from $\text{C}_1\text{-C}_6$ alkyl;

n is an integer from 0 to 3;

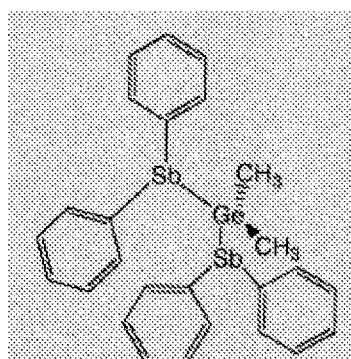
m is integer from 0 to 4.

95. An antimony precursor selected from the group consisting of:





and



96. A method of depositing antimony, comprising contacting a substrate with a precursor vapor comprising vapor of an antimony precursor of claim 94 and vapor of a co-reactant selected from the group consisting of hydrogen, H₂ /plasma, amines, imines, hydrazines, silanes, silyl chalcogenides, germanes, ammonia, alkanes, alkenes, and alkynes.

97. The method of claim 96, wherein said co-reactant vapor comprises vapor of a germane precursor and vapor of a tellurium precursor.

98. A precursor composition comprising a solvent solution or suspension of an antimony precursor of claim 94.

99. The precursor composition of claim 98, wherein the solvent solution comprises a solvent selected from the group consisting of alkanes, hexane, heptane, octane, and pentane, aryl solvents, benzene, toluene, amines, triethylamine, tert-butylamine, imines and hydrazines.

100. The method of claim 96, comprising solid delivery of the antimony precursor.

101. A method of depositing antimony, comprising contacting a substrate with a precursor vapor comprising vapor of an antimony precursor of claim 95 and vapor of a co-reactant selected from the group consisting of hydrogen, H₂ /plasma, amines, imines, hydrazines, silanes, silyl chalcogenides, germanes, ammonia, alkanes, alkenes, and alkynes.

102. The method of claim 101, wherein said co-reactant vapor comprises vapor of a germane precursor and vapor of a tellurium precursor.

103. A precursor composition comprising a solvent solution or suspension of an antimony precursor of claim 95.

104. The precursor composition of claim 103, wherein the solvent solution comprises a solvent selected from the group consisting of alkanes, hexane, heptane, octane, and pentane, aryl solvents, benzene, toluene, amines, triethylamine, tert-butylamine, imines and hydrazines.

105. The method of claim 101, comprising solid delivery of the antimony precursor.

106. A tellurium complex comprising tellurium having beta-diketiminato ligands coordinated therewith.

107. A method of forming a tellurium-containing film, comprising use of a tellurium complex as claimed in claim 106.

108. The method of claim 107, comprising CVD or ALD with said tellurium complex as a precursor therefor.

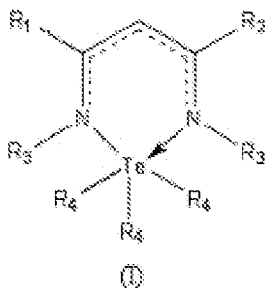
109. The method of claim 108, wherein said tellurium-containing film comprises at least one of germanium and antimony.

110. 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 $\text{X} = \text{Cl}, \text{Br}, \text{or I}$, to generate LTeX_3 by salt elimination, followed by a reaction with either a lithium or a Grignard reagent to produce LTeR_3 wherein $\text{R} = \text{alkyl, aryl, amide, or silyl}$.

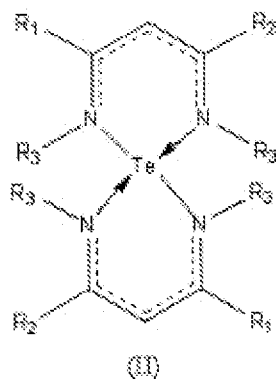
111. The method of claim 110, wherein the ligand is selected from the group consisting of isopropyl, n-butyl, tert-butyl and amine-substituted alkyl groups.

112. The method of claim 110, wherein the ligand is ethylene-dimethylamine.

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

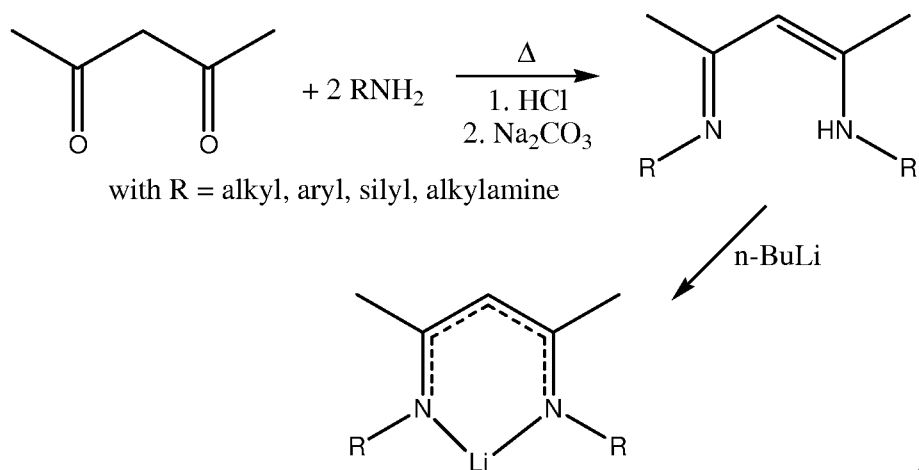


wherein R_1 , R_2 and R_3 they be the same as or different from one another, and each is independently selected from $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_6\text{-C}_{10}$ aryl, silyl and $\text{C}_1\text{-C}_{12}$ alkylamine; and

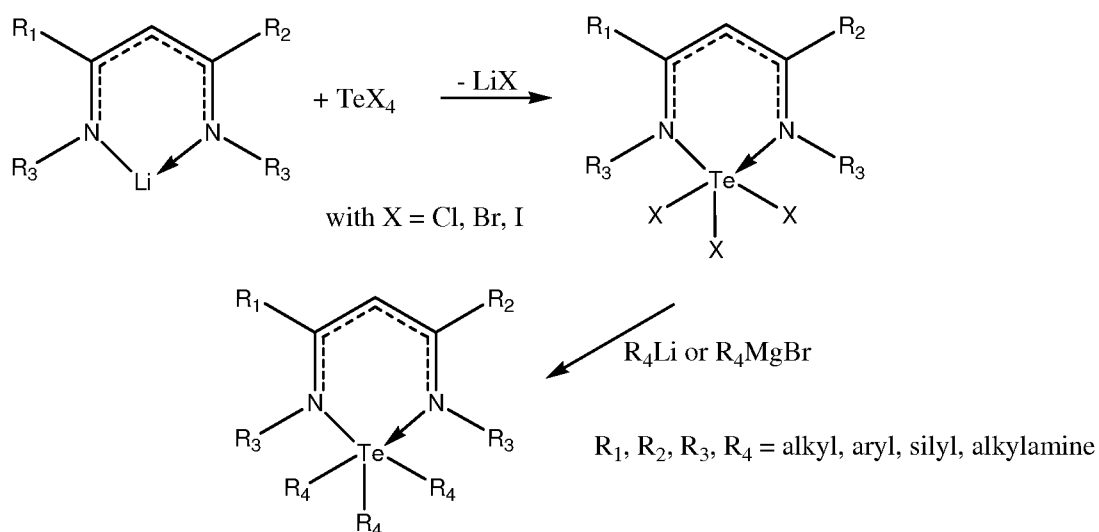


wherein R_1 , R_2 and R_3 they be the same as or different from one another, and each is independently selected from C_1 - C_6 alkyl, C_6 - C_{10} aryl, silyl and C_1 - C_{12} alkylamine.

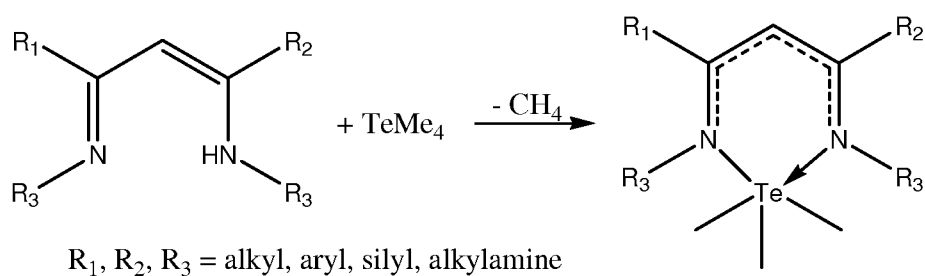
114. A method of making a tellurium complex, comprising synthesizing a beta-diketiminato ligand by the following procedure:



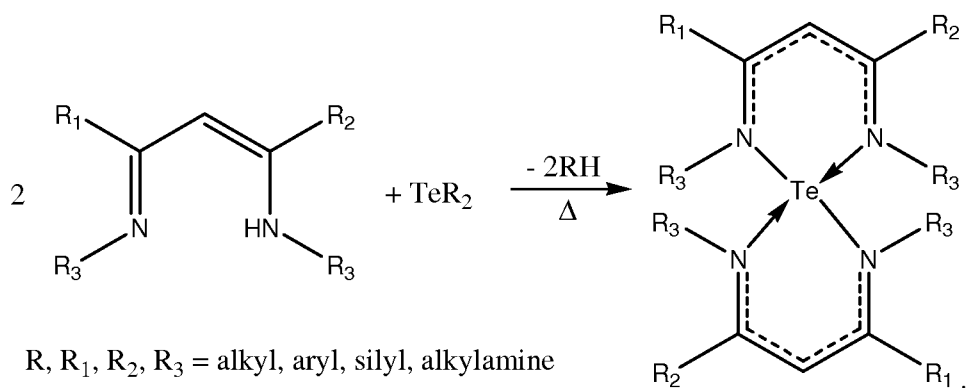
and synthesizing said tellurium complex by the following reaction:



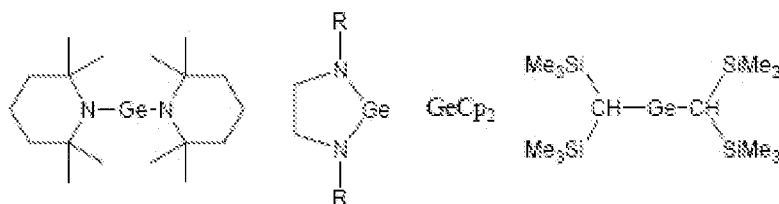
or alternatively by the following synthesis reaction:



or by the following synthesis reaction:



115. A germanium complex selected from among:



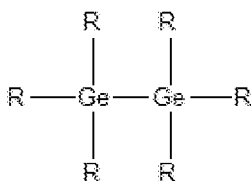
wherein the R groups in the second formula may be the same as or different from one another, and each is independently selected from among H, C₁-C₆ alkyl, C₆-C₁₀ aryl, C₃-C₈ cycloalkyl, heteroatom groups, and other organo groups.

116. 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.

117. 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.

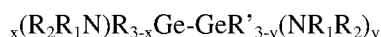
118. A germanium complex selected from among complexes of formulae (I) – (III):

(I) alkyl digermanes of the formula



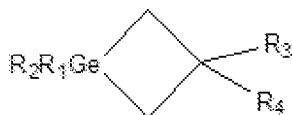
wherein each R may be the same as or different from the others, and each is independently selected from among isopropyl, isobutyl, benzyl, allyl, alkylamino, nitriles, and isonitriles;

(II) alkyl(dialkylamino)germanes of the formula



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.

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

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

121. The method of claim 120, wherein said oxidative addition reaction is conducted in a solvent medium comprising tetrahydrofuran.

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

123. The method of claim 122, 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.

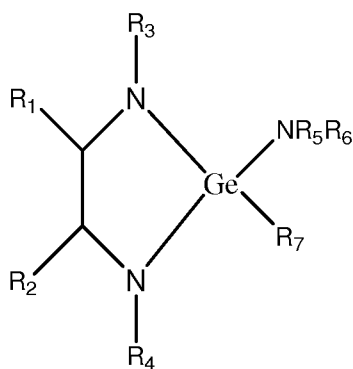
124. The method of claim 122, wherein said chemical vapor deposition or atomic layer deposition process is conducted at temperature below 300°C .

125. A germanium telluride complex having the formula:

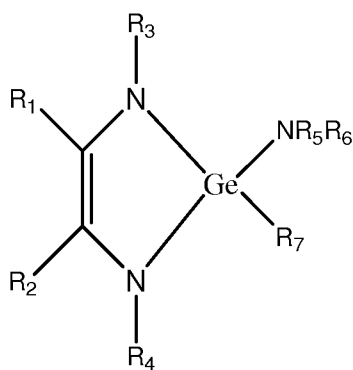


wherein each of the R substituents may be the same as or different from one another, and is independently selected from among H, C₁-C₆ alkyl, C₆-C₁₀ aryl, C₃-C₈ cycloalkyl, heteroatom groups, and other organo groups.

126. A germanium complex, selected from among complexes of formulae (I) and (II):



Formula (I); and



Formula (II),

wherein R₁, R₂, R₃, R₄, R₅, R₆ and R₇ may be the same as or different from one another, and each is independently selected from the group consisting of C₁-C₆ alkyl, C₆-C₁₀ aryl, silyl, alkylsilyl, hydrogen and halogen, or wherein in lieu of -NR₅R₆, the substituent coordinated to

the germanium central atom is instead selected from the group consisting of C₁-C₆ alkyl, C₃-C₈ cycloalkyl, C₆-C₁₃ aryl, and halide.

127. A germanium complex according to claim 126, of Formula (I).

128. A germanium complex according to claim 126, of Formula (II).

129. A method of depositing germanium on a substrate, comprising contacting the substrate with a germanium precursor as claimed in claim 126.

130. The method of claim 129, wherein said germanium precursor comprises a germanium complex of Formula (I).

131. The method of claim 129, wherein said germanium precursor comprises a germanium complex of Formula (II).

132. The method of claim 129, wherein said contacting is conducted in a chemical vapor deposition process.

133. The method of claim 129, wherein said contacting is conducted in an atomic layer deposition process.

134. The method of claim 129, further comprising delivering the germanium precursor to said contacting, by a liquid delivery process.

135. The method of claim 134, wherein the germanium precursor in said delivering is in a solvent medium comprising a solvent selected from the group consisting of alkanes, hexane, heptane, octane and pentane, aromatics, benzene, toluene, amines, triethylamine and tert-butylamine.

136. The method of claim 134, wherein the germanium precursor in said delivering is in a neat liquid form.

137. The method of claim 129, further comprising delivering the germanium precursor to said contacting, by a solid delivery process.

138. The method of claim 137, wherein said solid delivery process comprises vaporization of the germanium precursor in a solid form, in a supply package, and dispensing of vapor of the germanium precursor from said supply package for said delivering.

140. The method of claim 129, wherein said contacting is carried out at temperature below 300°C.

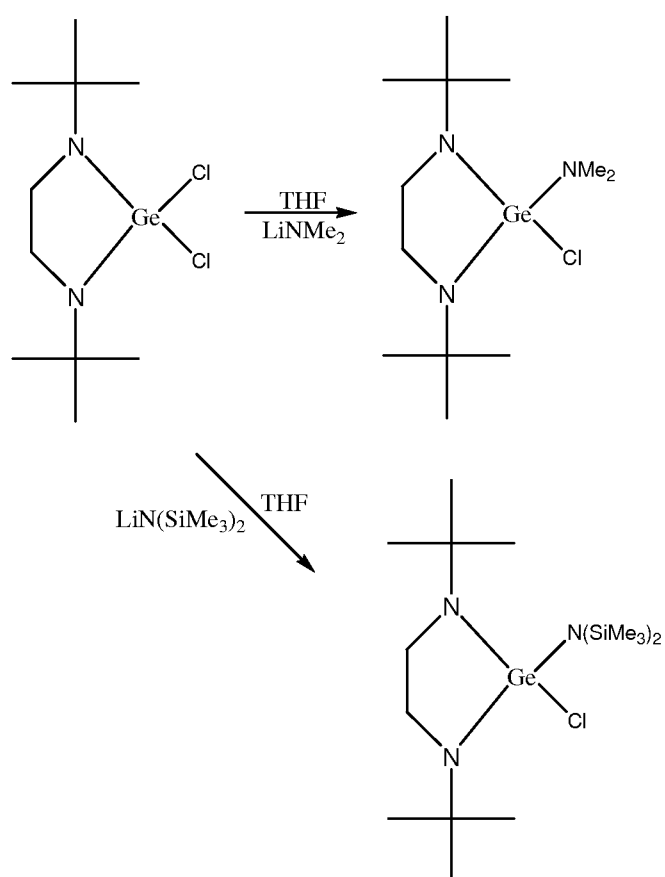
141. The method of claim 140, wherein said contacting is conducted in a process including deposition of antimony and tellurium to form a germanium-antimony-tellurium film.

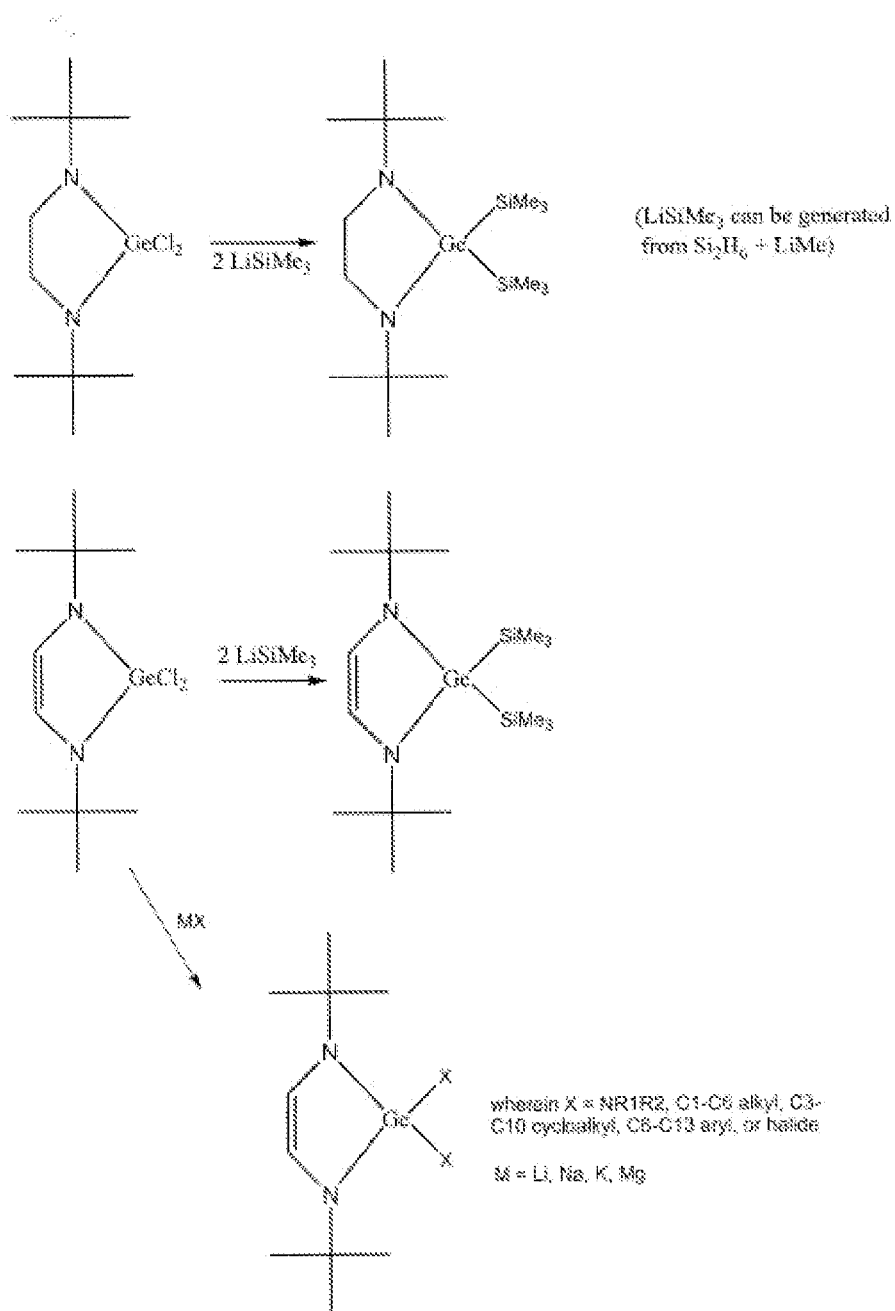
142. The method of claim 141, wherein said process comprises chemical vapor deposition.

143. The method of claim 141, wherein said process comprises atomic layer deposition.

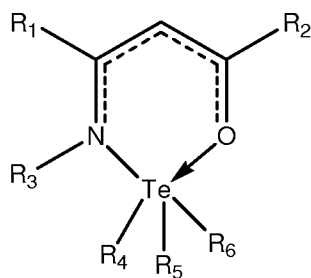
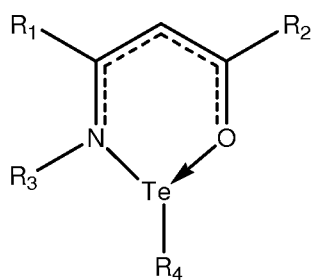
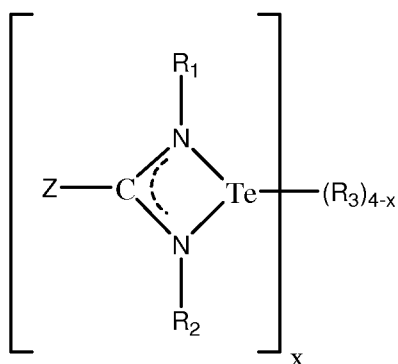
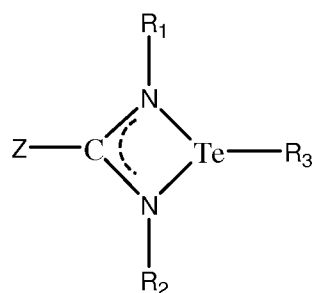
144. The method of claim 141, wherein said process is carried out in the fabrication of a phase change memory device.

145. A method of making a germanium complex, comprising a reaction selected from among reactions of the following reaction scheme:





146. A tellurium-nitrogen ligand complex, selected from among complexes of the formulae:



wherein R₁, R₂, R₃, R₄, R₅, R₆ and Z may be the same as or different from one another, and each is independently selected from the group consisting of C₁-C₆ alkyl, C₃-C₈ cycloalkyl, C₆-C₁₀ aryl, silyl, alkylsilyl, hydrogen and halogen, and wherein *x* is an integer having a value of from 1 to 3.

147. A method of depositing tellurium on a substrate, comprising contacting the substrate with a tellurium complex as claimed in claim 146.

148. The method of claim 147, wherein said contacting is conducted in a chemical vapor deposition process.

149. The method of claim 147, wherein said contacting is conducted in an atomic layer deposition process.

150. The method of claim 147, further comprising delivering the tellurium complex to said contacting, by a liquid delivery process.

151. The method of claim 150, wherein the tellurium complex in said delivering is in a solvent medium comprising a solvent selected from the group consisting of alkanes, hexane, heptane, octane and pentane, aromatics, benzene, toluene, amines, triethylamine and tert-butylamine.

152. The method of claim 150, wherein the tellurium complex in said delivering is in a neat liquid form.

153. The method of claim 147, further comprising delivering the tellurium complex to said contacting, by a solid delivery process.

154. The method of claim 153, wherein said solid delivery process comprises vaporization of the tellurium complex in a solid form, in a supply package, and dispensing of vapor of the tellurium complex from said supply package for said delivering.

155. The method of claim 147, wherein said contacting is carried out at temperature below 300°C.

156. The method of claim 147, wherein said contacting is conducted in a process including deposition of germanium and antimony to form a germanium-antimony-tellurium film.

157. The method of claim 156, wherein said process comprises chemical vapor deposition.

158. The method of claim 156, wherein said process comprises atomic layer deposition.

159. The method of claim 156, wherein said process is carried out in the fabrication of a phase change memory device.

160. The method of claim 147, wherein said contacting is conducted in a process for deposition of GeSbTe or GeSbInTe.

161. A method of forming a chalcogenide metal alloy film on a substrate, comprising contacting the substrate with an alkyl metal hydride precursor or an alkyl metal halide precursor for a metal of said chalcogenide metal alloy film.

162. The method of claim 161, wherein said precursor comprises an alkyl metal hydride precursor including butyl and/or propyl alkyl substituents.

163. The method of claim 162, wherein said alkyl metal hydride precursor has the formula iPr_xMH_{y-x} , wherein: $x > 1$; y = oxidation state of the metal (M) center; and $y-x$ may = 0.

164. The method of claim 161, wherein said precursor comprises an alkyl metal halide precursor including butyl and/or propyl alkyl substituents.

165. The method of claim 164, wherein said alkyl metal halide precursor has the formula iPr_xMX_{y-x} , wherein: $X = F, Cl, Br$; $x > 1$; y = oxidation state of the metal (M) center; and $y-x$ may = 0.

166. A method of forming a germanium-containing film on a substrate, comprising contacting the substrate with a digermane precursor.

167. The method of claim 166, wherein said digermane precursor comprises a digermane selected from the group consisting of Ge_2H_6 , Ge_2Me_6 , or Ge_2Et_6 , Ge_2iPr_6 , Ge_2tBu_6 , $Ge_2(SiMe_3)_6$ and Ge_2Ph_6 , in which Me = methyl, Et = ethyl, iPr = isopropyl, tBu = t-butyl, and Ph = phenyl.

168. A method of forming a germanium-containing film on a substrate, comprising contacting the substrate with a germanium precursor selected from among:
compounds of the formula Ge_2R_6 , wherein each of the R's can be the same as or different from the others, and each is independently selected from among H, C_1 - C_8 alkyl, C_1 - C_8 fluoroalkyl, C_6 - C_{12} aryl, C_6 - C_{12} fluoroaryl, C_3 - C_8 cyclo-alkyl, and C_3 - C_8 cyclo-fluoroalkyl;

compounds of the formula Ge_2R_4 wherein each of the R's can be the same as or different from the others, and each is independently selected from among H, $\text{C}_1\text{-C}_8$ alkyl, $\text{C}_1\text{-C}_8$ fluoroalkyl, $\text{C}_6\text{-C}_{12}$ aryl, $\text{C}_6\text{-C}_{12}$ fluoroaryl, $\text{C}_3\text{-C}_8$ cyclo-alkyl, and $\text{C}_3\text{-C}_8$ cyclo-fluoroalkyl;

Ge_2Ph_4 ;

5-member ring complexes with Ge in the ring;

cyclopentadienyl compounds of the formula $\text{Ge}(\text{CpR}_5)_2$ wherein Cp is cyclopentadienyl and each of the R's may be the same as or different from one another and each is independently selected from among H, $\text{C}_1\text{-C}_8$ alkyl, $\text{C}_1\text{-C}_8$ fluoroalkyl, $\text{C}_6\text{-C}_{12}$ aryl, $\text{C}_6\text{-C}_{12}$ fluoroaryl, $\text{C}_3\text{-C}_8$ cyclo-alkyl, and $\text{C}_3\text{-C}_8$ cyclo-fluoroalkyl;

above; and

$\text{Ge}(\text{CH}(\text{SiMe}_3))_2$.

169. The method of claim 168, wherein said contacting is conducted in a chemical vapor deposition process.

170. The method of claim 168, wherein said contacting is conducted in an atomic layer deposition process.

171. A process for depositing an antimony component of and antimony-containing film on a substrate, comprising contacting the substrate with triphenylantimony.

172. The process of claim 171, wherein said contacting is conducted under activating light or UV radiation effective to enhance deposition of antimony from said triphenylantimony, in relation to deposition in the absence of said activating light or UV radiation.

173. A method of forming a chalcogenide alloy film on a substrate, comprising contacting the substrate with precursor compositions for said chalcogenide alloy, wherein said method comprises one of:

bubbler delivery of respective ones of said precursor compositions for said chalcogenide alloy;

liquid injection of said precursor compositions in mixture with one another;

use of mixtures of neat liquids comprising said precursor compositions; and

use of solvent compositions of said precursors, or selected ones thereof.

174. A method of forming a chalcogenide alloy film on a substrate, comprising contacting the substrate with precursor compositions for said chalcogenide alloy, wherein said method comprises one of:

use of continuous CVD and thermal mode, optionally with reducing gas as an ambient;

employment of pulsed or atomic layer deposition to separate a precursor dose step from a co-reactant;

employment of an activation technique comprising UV or other light source that is tuned to a precursor; and

use of a reductive co-reactant dispensed from a sub-atmospheric pressure delivery system.

175. The method of claim 174, wherein said reductive co-reactant comprises germane.

176. The method of claim 173, comprising deposition of said chalcogenide alloy film on the substrate at temperature below 300°C.

177. The method of claim 174, comprising deposition of said chalcogenide alloy film on the substrate at temperature below 300°C.

178. A method of forming a germanium-containing film on a substrate, comprising contacting the substrate with germanium methyl amidinate in an ambient atmosphere comprising ammonia co-reactant.

179. The method of claim 178, wherein said germanium-containing film comprises germanium nitride.

180. A germanium precursor, selected from the group consisting of $[\{\text{MeC}(\text{iPrN})_2\}_2\text{Ge}]$, $[\{\text{Me}_2\text{N}(\text{iPrN})_2\}_2\text{Ge}]$, $[\{\text{nBuC}(\text{iPrN})_2\}_2\text{Ge}]$, and $[\{\text{MeC}(\text{NCy})_2\}_2\text{Ge}]$.

181. A germanium precursor, comprising $[\{\text{MeC}(\text{iPrN})_2\}_2\text{Ge}]$ in toluene solution.

182. A method of forming a germanium-containing film on a substrate, comprising contacting the substrate with a precursor selected from the group consisting of Ge(II) and Ge(IV) precursors each having at least one of the following ligands: amidinates, guanidines, isoureates, diketones, diketoiminates, diketiminates, carbamates, thiocarbamates, silyls, and aminotroponimate.

183. The method of claim 182, wherein the precursor also includes at least one additional ligand, selected from the group consisting of alkyl, dialkylamino, hydrido, and halogen groups.

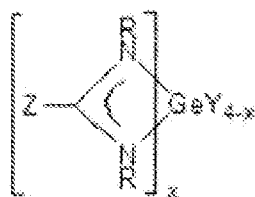
184. A method of forming a germanium- and tellurium-containing film on a substrate, comprising contacting the substrate with a germanium precursor and a tellurium precursor, in

the presence of a co-reactant selected from the group consisting of hydrogen, ammonia, plasma, alkylamines, silanes, and germanes.

185. The method of claim 184, conducted at temperature below 300°C.

186. A germanium precursor, selected from the group consisting of:

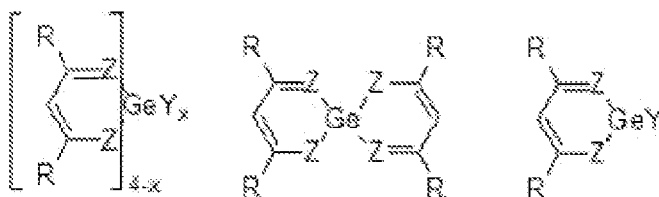
(1) Ge(IV) amidinates, guanidinates, and isoureates of the formula:



wherein each R group is independently selected from among H, C₁-C₆ alkyl, C₃-C₁₀ cycloalkyl, C₆-C₁₃ aryl, and -Si(R')₃ wherein each R' is independently selected from C₁-C₆ alkyl; and each Z is independently selected from among C₁-C₆ alkoxy, -NR₁R₂, H, C₁-C₆ alkyl, C₃-C₁₀ cycloalkyl, C₆-C₁₃ aryl, and -Si(R₄)₃ wherein each R₄ is independently selected from C₁-C₆ alkyl;

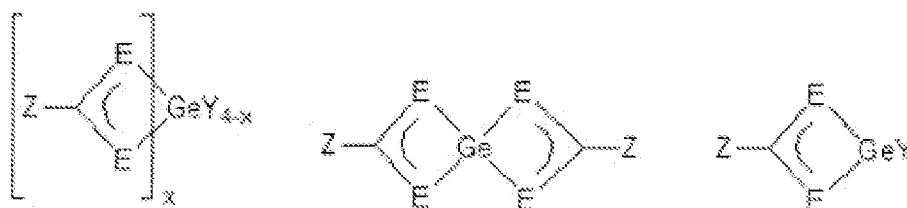
each Y group is independently selected from among C₁-C₆ alkoxy, -NR₁R₂, and C₁-C₆ alkyl, Si(R₄)₃, and halides (Cl, Br, I), and wherein x is integer from 0 to 4;

(2) Ge beta-diketonates, diketoiminates, diketiminates of the formulae:



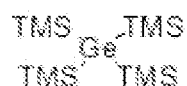
wherein each R group is independently selected from among H, C₁-C₆ alkyl, C₃-C₁₀ cycloalkyl, C₆-C₁₃ aryl, and -Si(R')₃; each Y group is independently selected from among C₁-C₆ alkyl, C₆-C₁₃ aryl, C₁-C₆ alkoxy, NR₁R₂, Si(R₄)₃, and halides (Cl, Br, I), x is integer from 0 to 4, Z atoms are the same or different, selected from O, S, and NR; R is selected from C₁-C₆ alkyl, C₃-C₁₀ cycloalkyl, C₆-C₁₃ aryl, Si(R')₃, R' is C₁-C₆ alkyl, C₆-C₁₃ aryl;

(3) Ge carbamates, thiocarbamates of the formulae:



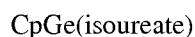
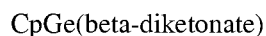
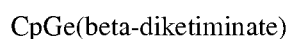
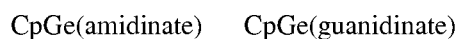
wherein each Z is independently selected from among H, C₁-C₆ alkyl, C₃-C₁₀ cycloalkyl, C₁-C₆ alkoxy, NR₁R₂, C₆-C₁₃ aryl, and -Si(R₄)₃ wherein each R₄ is independently selected from C₁-C₆ alkyl or aryl; each Y group is independently selected from among C₁-C₆ alkyl, C₁-C₆ alkoxy, NR₁R₂, C₃-C₁₀ cycloalkyl, C₆-C₁₃ aryl, Si(R₄)₃, and halides (Cl, Br, I), x is integer from 0 to 4, and E is either O or S;

(4) silylgermanes of the formula:



wherein TMS is Si(R'')₃; each R group is independently selected from among H, C₁-C₆ alkyl, C₃-C₁₀ cycloalkyl, C₆-C₁₂ aryl, and x is integer from 0 to 4;

(5) mixed cyclopentadienyl germanes of the formulae:

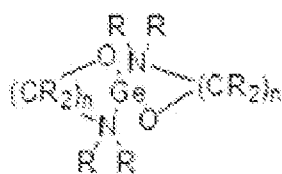


wherein each R group is independently selected from among H, C₁-C₆ alkyl, C₃-C₁₀ cycloalkyl, C₆-C₁₃ aryl, and -Si(R')₃ wherein each R' is independently selected from C₁-C₆ alkyl; and each Y group is independently selected from among C₁-C₆ alkyl, C₁-C₆ alkoxy, NR₁R₂, C₃-C₁₀

cycloalkyl, C₆-C₁₃ aryl, Si(R₄)₃, and halides (Cl, Br, I), x is an integer having a value of from 0 to 4, and Cp ligands may also include:

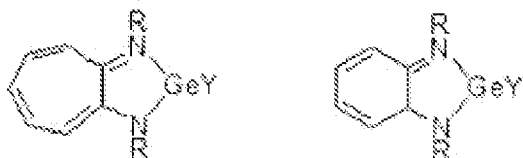


(6) Ge(II) amino-alkoxide of the formula:



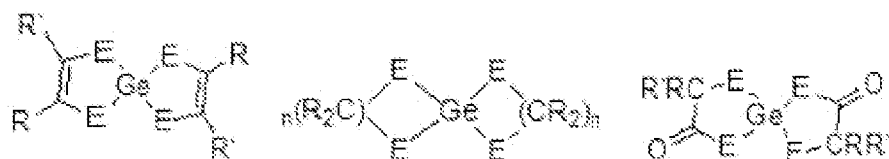
wherein each R group is independently selected from among H, C₁-C₆ alkyl, C₃-C₁₀ cycloalkyl, C₆-C₁₃ aryl, and -Si(R')₃, wherein each R' is independently selected from C₁-C₆ alkyl, and n is an integer having a value of from 2 to 6;

(7) other N-heterocyclic germylenes of the formulae:



wherein each R group is independently selected from among H, C₁-C₆ alkyl, C₃-C₁₀ cycloalkyl, C₆-C₁₃ aryl, and -Si(R')₃, wherein each R' is independently selected from C₁-C₆ alkyl; and each Y group is independently selected from among C₁-C₆ alkoxy, NR₁R₂, H, C₁-C₆ alkyl, C₃-C₁₀ cycloalkyl, C₆-C₁₃ aryl, Si(R₄)₃, or halides (Cl, Br, I); and

(8) oxides, dithiolates, thiocarbonates of the formulae:



wherein each R,R' is independently selected from among C₁-C₆ alkyl, C₃-C₁₀ cycloalkyl, C₁-C₆ alkoxy, NR₁R₂, C₆-C₁₃ aryl, and -Si(R₄)₃ wherein each R₄ is independently selected from C₁-C₆ alkyl or aryl, and halides (Cl, Br, I), and E is either O or S.

187. The germanium precursor of claim 186, selected from among precursors (1).

188. The germanium precursor of claim 186, selected from among precursors (2).

189. The germanium precursor of claim 186, selected from among precursors (3).

190. The germanium precursor of claim 186, selected from among precursors (4).

191. The germanium precursor of claim 186, selected from among precursors (5).

192. The germanium precursor of claim 186, selected from among precursors (6).

193. The germanium precursor of claim 186, selected from among precursors (7).

194. The germanium precursor of claim 186, selected from among precursors (8).

195. The germanium precursor of claim 186, in a solvent solution.

196. The germanium precursor of claim 195, wherein the solvent solution comprises a solvent selected from the group consisting of alkanes, hexane, heptane, octane, and pentane, aromatics, benzene, toluene, amines, triethylamine, and tert-butylamine.

197. A method of forming a germanium-containing film on a substrate, comprising contacting the substrate with a germanium precursor of claim 186.

198. The method of claim 197, comprising chemical vapor deposition.

199. The method of claim 197, comprising atomic layer deposition.

200. The method of claim 197, comprising liquid delivery chemical vapor deposition.

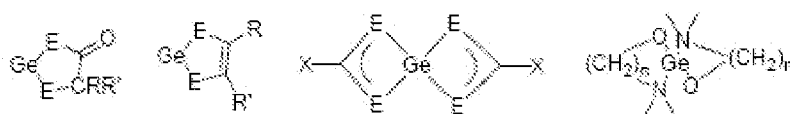
201. The method of claim 197, comprising solid delivery chemical vapor deposition.

202. The method of claim 197, comprising liquid delivery atomic layer deposition.

203. The method of claim 197, comprising solid delivery atomic layer deposition.

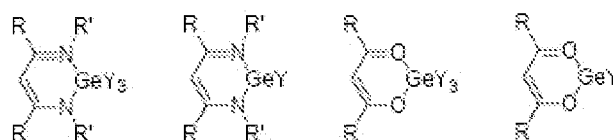
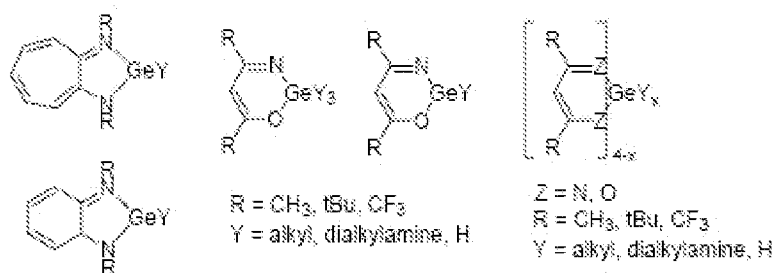
204. The method of claim 197, conducted at temperature below 300°C.

205. A germanium precursor, selected from the group consisting of:

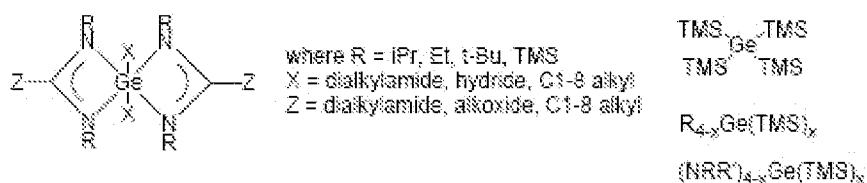


E = O, S

X = C1-C8 alkyl, fluoroalkyl, aryl, dialkylamine, alkoxy

R = CH₃, tBu, CF₃

Y = alkyl, dialkylamine, H

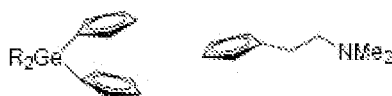
R_{4-x}GeCp_x

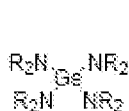
RGeCp

(RR'N)_{4-x}GeCp_x

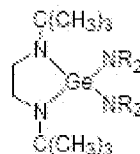
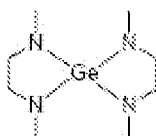
RR'NGeCp

where Cp represents Cp, Cp', and other C1-C6 alkyl substituted cyclopentadienyl ligands, and includes ansa-bridged germanes and alkyl(dialkylamines) [examples shown below].

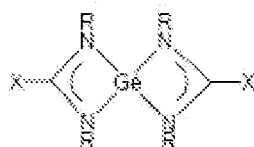
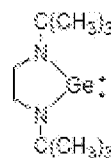
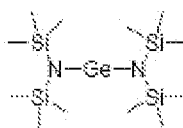
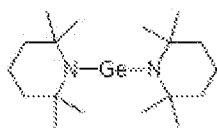


Ge CVD/ALD precursors**Ge(IV) precursors**

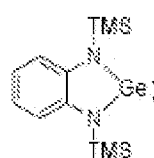
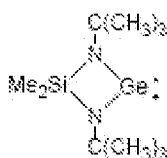
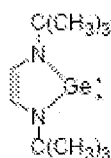
R = Me, Et, iPr, TMS



R = Me, Et, iPr, TMS

Ge(II) precursorswhere X = a nucleophile (e.g. CH₃, MeO, NR₂)

R = Me, Et, iPr, TMS



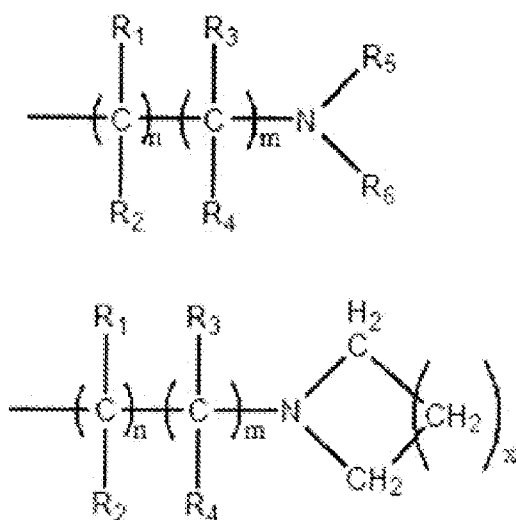
206. A method of forming a germanium-containing film on a substrate, comprising contacting the substrate with a germanium precursor as claimed in claim 205.

207. The method of claim 206, conducted at temperature below 300°C.

208. A metal precursor, selected from among metal silylamides having a disily-azacycloalkyl ligand, of the formula $\text{R}_5\text{nM}\{\text{N}[(\text{R}_1\text{R}_2)\text{Si}(\text{CH}_2)_m\text{Si}(\text{R}_3\text{R}_4)]\}_{\text{ox-n}}$; metal silylamides having asymmetric elements in the silylamido ligands, of the formula $\text{R}_5\text{nM}\{\text{R}_4\text{N}[\text{Si}(\text{R}_1\text{R}_2\text{R}_3)]\}_{\text{ox-n}}$

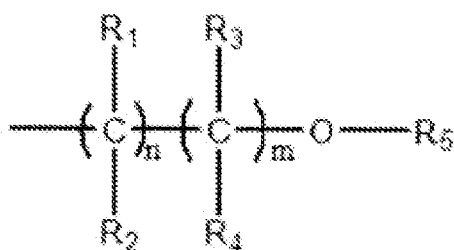
n; guanidinate complexes formed by carbodiimido insertion reaction with said silylamides; oligomers of the above-discussed metal silylamides, of the formula $[R_5nM\{N[(R_1R_2)Si(CH_2)_mSi(R_3R_4)]\}_{ox-n}]_x$ or $[R_5nM\{R_4N[Si(R_1R_2R_3)]\}_{ox-n}]_x$ where x is an integer having a value of at least 2; precursors with open-structured silazane ligands in which at least one of the Rs has a functional group selected from among amido, alkoxy, siloxyl and thienyl, of the formula $R_5nM\{(R_4R_5R_6)SiN[Si(R_1R_2R_3)]\}_{ox-n}$, and corresponding guanidates thereof; oligomers of said precursors with open-structured silazane ligands, of the formula $[R_5nM\{(R_4R_5R_6)SiN[Si(R_1R_2R_3)]\}_{ox-n}]_x$ wherein x is an integer having a value of at least 2;

wherein each of each of R1, R2, R3, R4, R6 and R7 may be the same as or different from the others, and each is independently selected from among H, C1-C6 alkyl, C3-C10 cycloalkyl, C6-C10 aryl, -Si(R8)3 and -Ge(R8)3 wherein each R8 is independently selected from C1-C6 alkyl; and -Si(R9)3 wherein each R9 is independently selected from C1-C6 alkyl; optionally with pendant ligands attached to the above-mentioned R1, R2, R3, R4, R6 and R7 including functional group(s) providing further coordination to the metal center, selected from among aminoalkyl, alkoxyalkyl, aryloxyalkyl, imidoalkyl, and acetylalkyl, of the following formulae:



aminoalkyls

wherein each of R1-R4 is the same as or different from one another, with each being independently selected from among hydrogen and C1-C6 alkyl; each of R5 and R6 is the same as or different from the other, with each being independently selected from among C1-C6 alkyl; n and m are each selected independently from 0 to 4 with the provision that m and n cannot be 0 at the same time, and x is selected from 1 to 5;



alkoxyalkyls and aryloxyalkyls

wherein each of R1-R4 is the same as or different from one another, with each being independently selected from among hydrogen, C1-C6 alkyl, and C6-C10 aryl; R5 is selected from among C1-C6 alkyl, and C6-C10 aryl; and n and m are selected independently from 0 to 4, with the provision that m and n cannot be 0 at the same time; and

wherein in the metal precursors, each R5 can be independently selected from among H, C1-C6 alkyl, C3-C6 cycloalkyl, C1-C6 alkoxy, -NR1R2, and -C(R3)3, -Si(R8)3 and -Ge(R8)3 wherein each R3 is independently selected from C1-C6 alkyl; and each of R8 and R8 is independently selected from H, C1-C6 alkyl, C5-C10 cycloalkyl, C6-C10 aryl, and -Si(R9)3 wherein each R4 is independently selected from C1-C6 alkyl; and

wherein in such metal precursors, the metal M is selected from the group consisting of Ta, V, Ti, Nb, Pb, Ni, W, Ca, Ba, In, Y, La, Zr, Hf, Ir, Ru, Pt, Cr, Mo, Ge; Al, Si, Ga, Sc, V, Cr, Fe, Sb, lanthanides, Mn, Co, Ni, Zn, Cd, Te, Hg, Au, Cu, Ag, Sr, and Ru; OX is the oxidation state of the metal M; n is an integer having a value of from 0 to ox; and X is halogen.

209. A method of forming a metal-containing film on a substrate, comprising contact in a substrate with a metal precursor as claimed in claim 208.

210. The method of claim 209, conducted a temperature below 300°C.

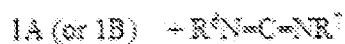
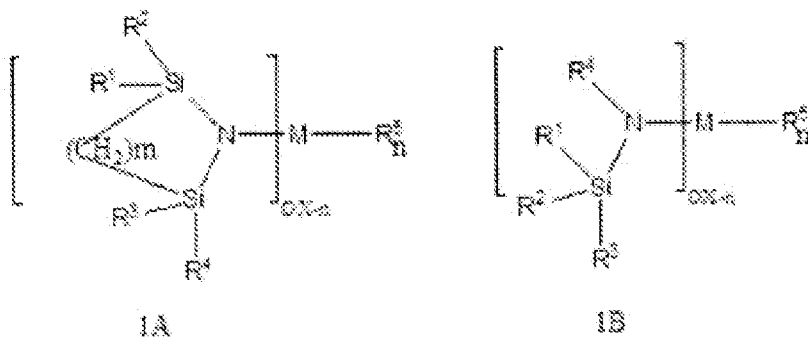
211. The method of claim 209, wherein said contacting is conducted in the presence of a co-reactant selected from the group consisting of hydrogen, H2/plasma, amines, imines, hydrazines, silanes, silyl chalcogenides, (Me3Si)2Te, germanes, GeH4, ammonia, alkanes, alkenes, amidines, guanidines, boranes and their corresponding derivatives/adducts and alkynes.

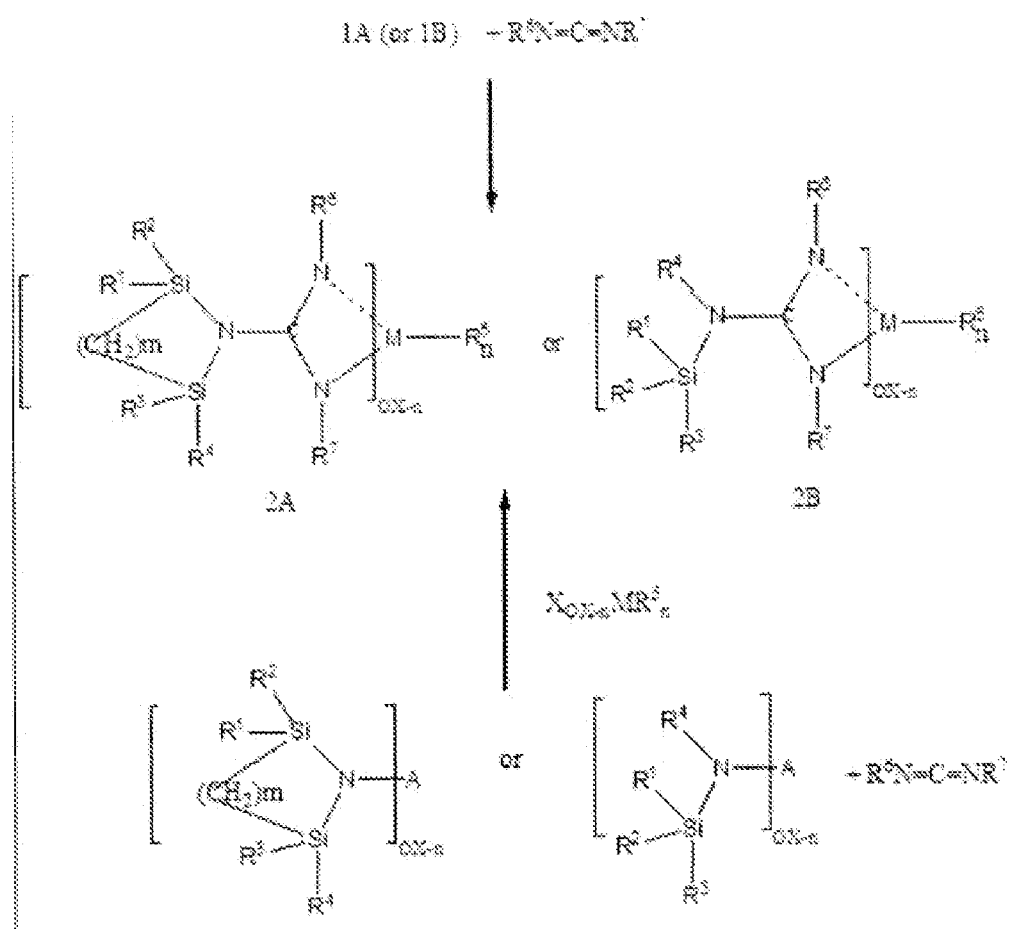
212. The method of claim 209, comprising liquid delivery of said metal precursor to the contacting.

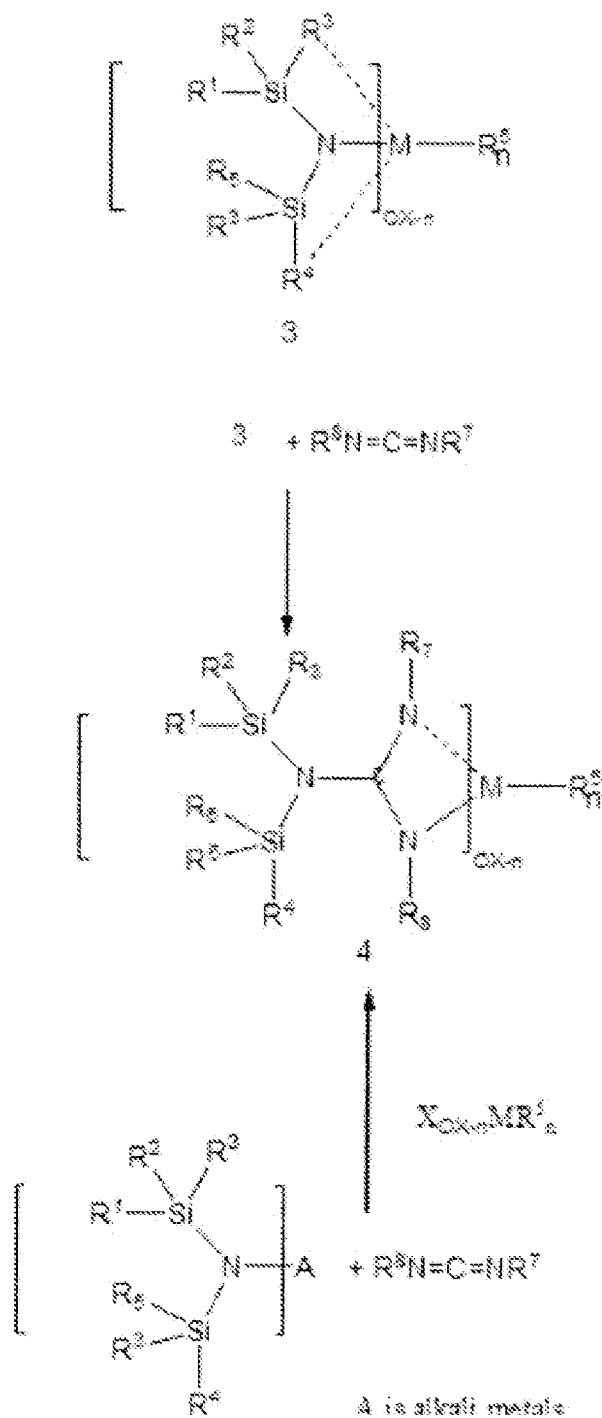
213. The method of claim 209, comprising solid delivery of said metal precursor to the contacting.

214. The method of claim 212, wherein said metal precursor is transported in said delivery in a solution comprising a solvent selected from the group consisting of alkane solvents, hexane, heptane, octane, pentane, aryl solvents, benzene, toluene, amines, triethylamine, tert-butylamine, imines, guanidines, amidines and hydrazines.

215. A metal precursors selected from the group consisting of



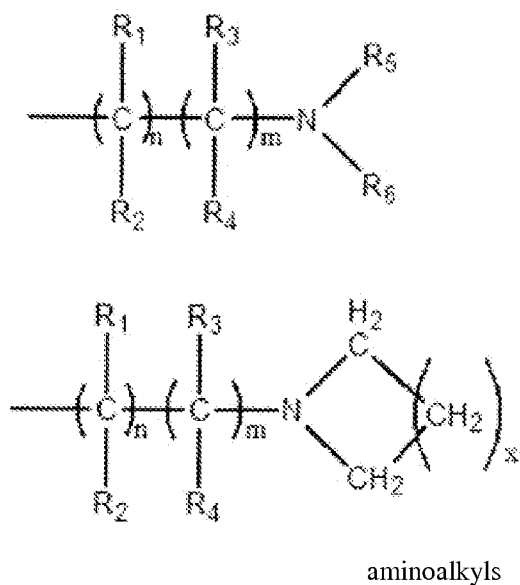




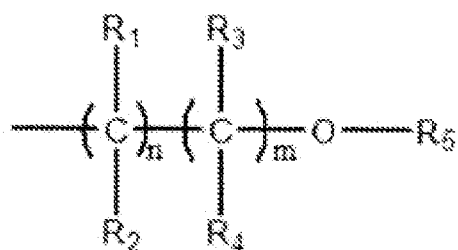
216. A metal precursor, selected from among: tetraalkylguanidinate and ketiminate complexes having a tetraalkylguanidine ligand, of the formula $(R^5)_nM\{N=C[(NR^1R^2)(NR^3R^4)]\}_{ox-n}$; oligomers of said tetraalkylguanidinate and ketiminate complexes, having the formula $[(R^5)_nM\{N=C[(NR^1R^2)(NR^3R^4)]\}_{ox-n}]_x$, where x is an integer having a value of at least 2;

guanidinate complexes of the formula $R_5nM\{R_6NC\{N=C[(NR_1R_2)(NR_3R_4)]\}NR_7\}ox-n$; oligomers of the guanidinate complexes, having the formula $[R_5nM\{R_6NC\{N=C[(NR_1R_2)(NR_3R_4)]\}NR_7\}ox-n]_x$, where x is an integer having a value of at least 2; guanidinate complexes formed by tetraalkylguanidine insertion reaction with metal amides; ketiminates of the formula $(R_5)_nM\{N=C[(R_1R_2)]\}ox-n$ and corresponding guanidinate complexes of the formula $R_5nM\{R_6NC[N=C(R_1R_2)]NR_7\}ox-n$; and oligomers of the formula $[R_5nM\{R_6NC[N=C(R_1R_2)]NR_7\}ox-n]_x$, where x is an integer having a value of at least 2;

wherein in said metal precursors, each of R_1 , R_2 , R_3 , R_4 , R_6 and R_7 is independently selected from among H, C1-C6 alkyl, C3-C10 cycloalkyl, C6-C10 aryl, $-Si(R_8)_3$ and $-Ge(R_8)_3$ wherein each R_8 is independently selected from C1-C6 alkyl; and $-Si(R_9)_3$ wherein each R_9 is independently selected from C1-C6 alkyl; optionally with pendant ligands attached to R_1 , R_2 , R_3 , R_4 , R_6 and R_7 including functional group(s) providing further coordination to the metal center, selected from among aminoalkyl, alkoxyalkyl, aryloxyalkyl, imidoalkyl, and acetylalkyl, of the formulae:



wherein each of R_1 - R_4 is the same as or different from one another, with each being independently selected from among hydrogen and C1-C6 alkyl; each of R_5 and R_6 is the same as or different from the other, with each being independently selected from among C1-C6 alkyl; n and m are each selected independently from 0 to 4 with the provision that m and n cannot be 0 at the same time, and x is selected from 1 to 5;



alkoxyalkyls and aryloxyalkyls

wherein each of R1-R4 is the same as or different from one another, with each being independently selected from among hydrogen, C1-C6 alkyl, and C6-C10 aryl; R5 is selected from among C1-C6 alkyl, and C6-C10 aryl; and n and m are selected independently from 0 to 4, with the provision that m and n cannot be 0 at the same time;

wherein in said metal precursors, each R5 can be independently selected from among H, C1-C6 alkyl, C3-C6 cycloalkyl, C1-C6 alkoxy, -NR1R2, and -C(R3)3, -Si(R8)3 and -Ge(R8)3 wherein each R3 is independently selected from C1-C6 alkyl; and each of R8 and R8 is independently selected from H, C1-C6 alkyl, C5-C10 cycloalkyl, C6-C10 aryl, and -Si(R9)3 wherein each R4 is independently selected from C1-C6 alkyl; and

wherein in such metal precursors, the metal M is selected from the group consisting of Ta, V, Ti, Nb, Pb, Ni, W, Ca, Ba, In, Y, La, Zr, Hf, Ir, Ru, Pt, Cr, Mo, Ge; Al, Si, Ga, Sc, V, Cr, Fe, Sb, lanthanides, Mn, Co, Ni, Zn, Cd, Te, Hg, Au, Cu, Ag, Sr and Ru; OX is the oxidation state of the metal M; n is an integer having a value of from 0 to ox; and X is halogen.

217. A method of forming a metal-containing film on a substrate, comprising contact in a substrate with a metal precursor as claimed in claim 216.

218. The method of claim 217, conducted a temperature below 300°C.

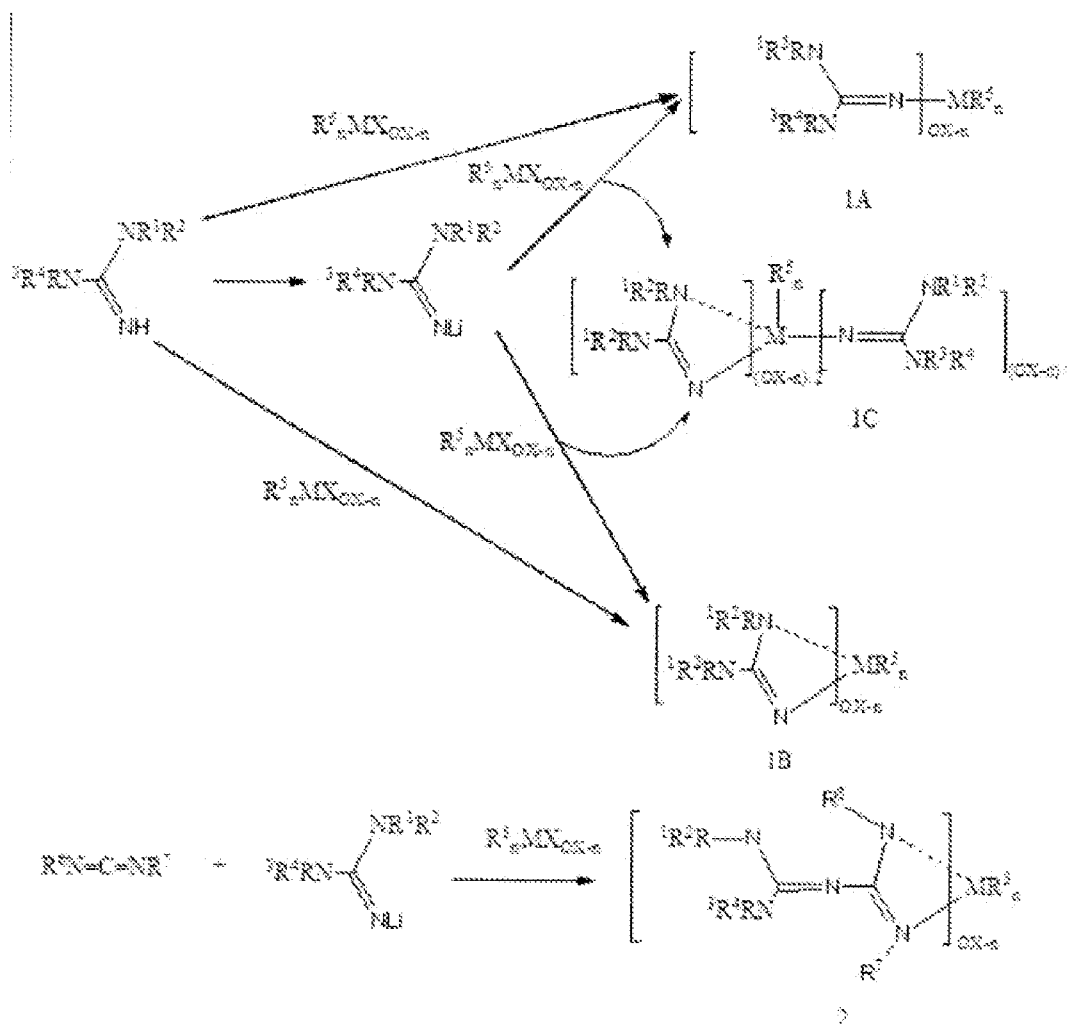
219. The method of claim 217, wherein said contacting is conducted in the presence of a co-reactant selected from the group consisting of hydrogen, H2/plasma, amines, imines, hydrazines, silanes, silyl chalcogenides, (Me3Si)2Te, germanes, GeH4, ammonia, alkanes, alkenes, amidines, guanidines, boranes and their corresponding derivatives/adducts and alkynes.

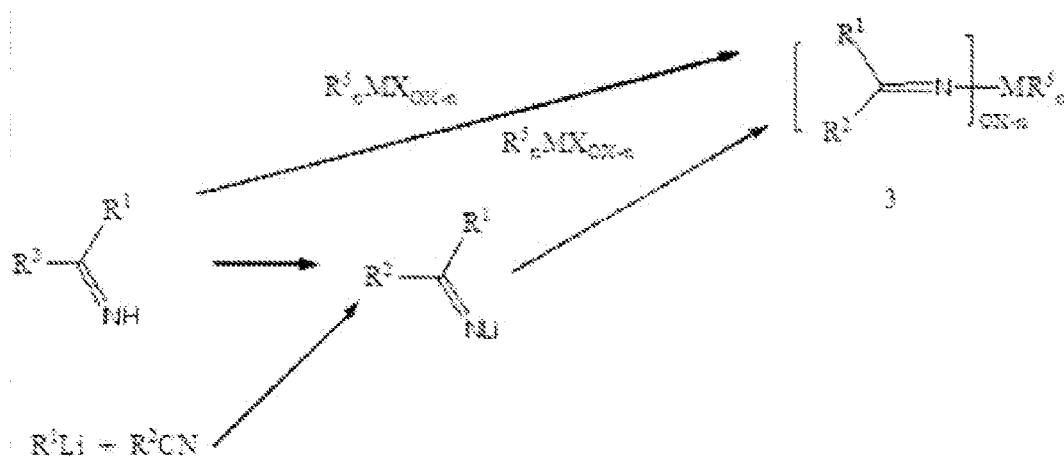
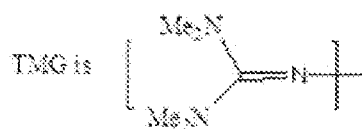
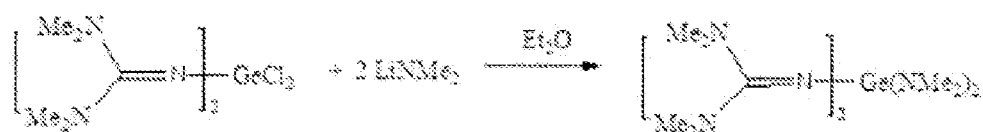
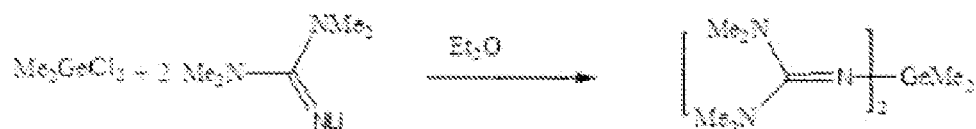
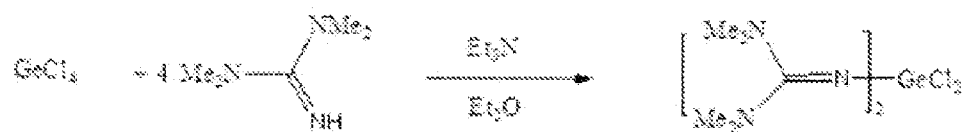
220. The method of claim 217, comprising liquid delivery of said metal precursor to the contacting.

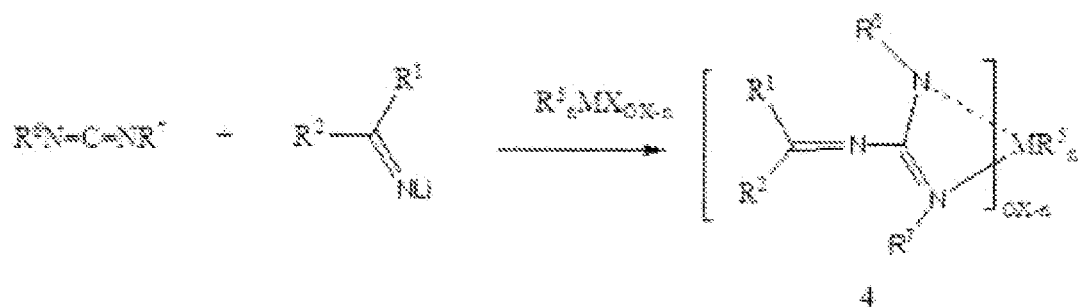
221. The method of claim 217, comprising solid delivery of said metal precursor to the contacting.

222. The method of claim 220, wherein said metal precursor is transported in said delivery in a solution comprising a solvent selected from the group consisting of alkane solvents, hexane, heptane, octane, pentane, aryl solvents, benzene, toluene, amines, triethylamine, tert-butylamine, imines, guanidines, amidines and hydrazines.

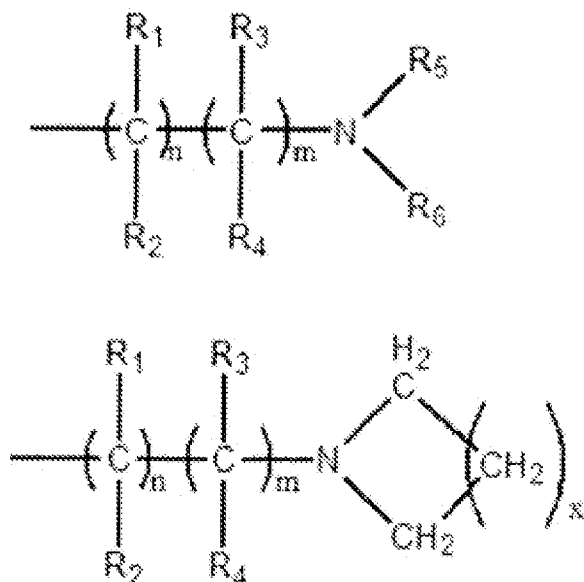
223. A metal precursor, selected from among complexes in the following reaction scheme:







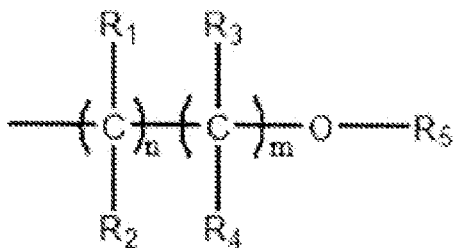
224. A metal precursor, selected from among: metal precursors with dianionic chelate guanidine ligands of the formula $(R_4)_nM\{(R_1)N=C[(R_2)(R_3)]\}(ox-n)/2$; oligomers of said metal precursors with dianionic chelate guanidine ligands, of the formula $[(R_4)_nM\{(R_1)N=C[(R_2)(R_3)]\}(ox-n)/2]_x$, where x is an integer having a value of at least 2, wherein each R_1 , R_2 , R_3 and R_4 is independently selected from among H, C1-C6 alkyl, C3-C10 cycloalkyl, C6-C10 aryl, $-Si(R_5)_3$ and $-Ge(R_5)_3$ wherein each R_5 is independently selected from C1-C6 alkyl; and $-Si(R_6)_3$ wherein each R_6 is independently selected from C1-C6 alkyl; optionally with pendant ligands attached to the above-mentioned R_1 , R_2 , R_3 and R_4 including functional group(s) providing further coordination to the metal center, selected from among aminoalkyl, alkoxyalkyl, aryloxyalkyl, imidoalkyl, and acetylalkyl, of the formula:



aminoalkyls

wherein each of R_1 - R_4 is the same as or different from one another, with each being

independently selected from among hydrogen and C1-C6 alkyl; each of R5 and R6 is the same as or different from the other, with each being independently selected from among C1-C6 alkyl; n and m are each selected independently from 0 to 4 with the provision that m and n cannot be 0 at the same time, and x is selected from 1 to 5;



alkoxyalkyls and aryloxyalkyls

wherein each of R1-R4 is the same as or different from one another, with each being independently selected from among hydrogen, C1-C6 alkyl, and C6-C10 aryl; R5 is selected from among C1-C6 alkyl, and C6-C10 aryl; and n and m are selected independently from 0 to 4, with the provision that m and n cannot be 0 at the same time;

wherein in the metal precursors, each R5 can be independently selected from among H, C1-C6 alkyl, C3-C6 cycloalkyl, C1-C6 alkoxy, -NR1R2, and -C(R3)3, -Si(R8)3 and -Ge(R8)3 wherein each R3 is independently selected from C1-C6 alkyl; and each of R8 and R8 is independently selected from H, C1-C6 alkyl, C5-C10 cycloalkyl, C6-C10 aryl, and -Si(R9)3 wherein each R4 is independently selected from C1-C6 alkyl; and

wherein in the metal precursors, the metal M is selected from the group consisting of Ta, V, Ti, Nb, Pb, Ni, W, Ca, Ba, In, Y, La, Zr, Hf, Ir, Ru, Pt, Cr, Mo, Ge; Al, Si, Ga, Sc, V, Cr, Fe, Sb, lanthanides, Mn, Co, Ni, Zn, Cd, Te, Hg, Au, Cu, Ag, Sr and Ru; OX is the allowed oxidation state of the metal M; n is an integer having a value of from 0 to ox; and X is halogen.

225. A method of forming a metal-containing film on a substrate, comprising contact in a substrate with a metal precursor as claimed in claim 224.

226. The method of claim 225, conducted a temperature below 300°C.

227. The method of claim 225, wherein said contacting is conducted in the presence of a co-reactant selected from the group consisting of hydrogen, H2/plasma, amines, imines, hydrazines, silanes, silyl chalcogenides, (Me3Si)2Te, germanes, GeH4, ammonia, alkanes,

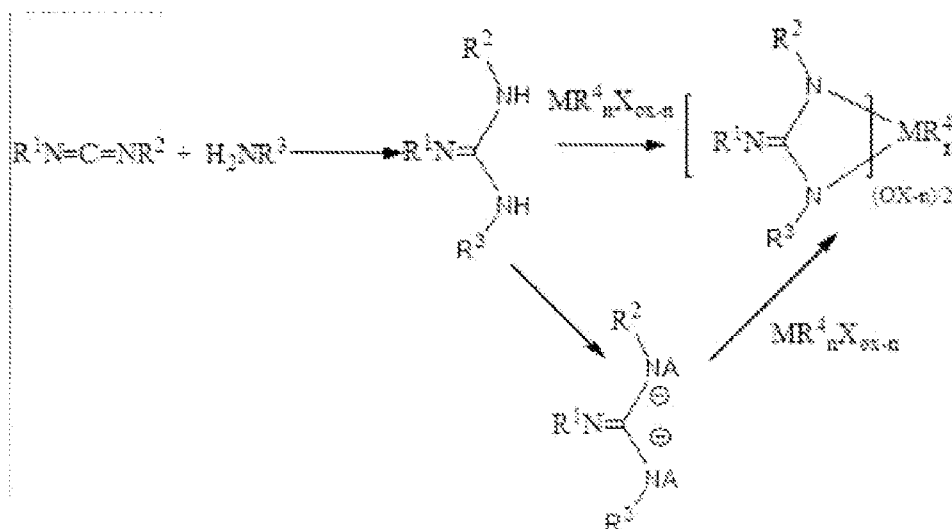
alkenes, amidines, guanidines, boranes and their corresponding derivatives/adducts and alkynes.

228. The method of claim 225, comprising liquid delivery of said metal precursor to the contacting.

229. The method of claim 225, comprising solid delivery of said metal precursor to the contacting.

230. The method of claim 228, wherein said metal precursor is transported in said delivery in a solution comprising a solvent selected from the group consisting of alkane solvents, hexane, heptane, octane, pentane, aryl solvents, benzene, toluene, amines, triethylamine, tert-butylamine, imines, guanidines, amidines and hydrazines.

231. A metal precursor synthesized by the following reaction scheme:



A is alkali metals, X is halogens and ox is the allowed oxidation state of M.

232. $\text{PriN}=\text{C}(\text{PriNH})_2$.

233. A phase change memory device comprising a phase change memory material in a via of insulating material and in contact with respective electrode elements.

234. The phase change memory device of claim 233, wherein said phase change memory material comprises a germanium-antimony-tellurium material.

235. The phase change memory device of claim 233, wherein said phase change memory material is in a plug form in said via.

236. The phase change memory device of claim of 233, wherein said insulating material comprises silicon oxide, silicon nitride or low k dielectric material.

237. $\text{Ge}(\text{NMe}_2)_4$.

238. A microelectronic device structure, comprising germanium deposited thereon from a germanium precursor comprising $\text{Ge}(\text{NMe}_2)_4$.

239. A method of making a microelectronic device structure, comprising depositing germanium from a germanium precursor on a substrate, wherein said germanium precursor comprises $\text{Ge}(\text{NMe}_2)_4$.

240. The method of claim 239, wherein said substrate comprises a metal nitride surface and a silicon oxide surface.

241. A via-sized and via-shaped body of GST material, adapted to fit in a via in a microelectronic device structure.

242. A method of selective deposition of a metal on a surface including conductive material and non-conductive material, comprising contacting the surface with a metal precursor comprising said metal, wherein said metal precursor comprises a metal-coordinated ligand selected from the group consisting of N-coordinating amides, amidinates, guanidates, N-heterocycles, halogens, beta-diketiminates, nitriles, isonitriles, aminotroponiminates, carbonyls, phosphidos, imidos, amines, pyridines, nitrosyls, silyls, stibenes (R_3Sb), sulfides, and cyclopentadienyls.

243. The method of claim 242, wherein said metal of said metal precursor is selected from the group consisting of Ge, Sb, Te, Be, Mg, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Hg, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Sn, Pb, As, P, Bi, Al, Ga, In, Tl, and Si.

244. A metal precursor of the formula MA_yB_x wherein M is a metal selected from among Ge, Sb and Te, and A is a ligand selected from the group consisting of all ligands disclosed in the specification hereof, and $y + x$ equals the oxidation state on metal M.

245. A method of forming a metal-containing film on a substrate, comprising contacting the substrate with a metal precursor as claimed in claim 244.

246. The method of claim 245, comprising conducting said contacting in a chemical vapor deposition process.

247. The method of claim 245, comprising conducting said contacting in an atomic layer deposition process.

248. The method of claim 246, wherein said chemical vapor deposition process comprises liquid delivery or solid delivery of the metal precursor to the contacting.

249. The method of claim 247, wherein said atomic layer deposition process comprises liquid delivery or solid delivery of the metal precursor to the contacting.

250. The method of claim 245, wherein said metal-containing film comprises a GST film, and said contacting is conducted at temperature below 300°C.