CLAIMS

What is claimed is:

1. A method of forming a smooth, amorphous germanium-containing film on a substrate by a vapor deposition process, comprising volatilizing a germanium precursor to form a germanium precursor vapor, optionally combining the precursor vapor with a component selected from the group consisting of ammonia, hydrogen, helium, argon, and nitrogen, and contacting the precursor vapor with a substrate for vapor deposition of the germanium-containing film thereon, wherein the germanium precursor comprises a germanium amidinate compound or complex.

2. The method of claim 1, wherein the germanium-containing film further comprises tellurium, said method comprising volatilizing a tellurium precursor to form a tellurium precursor vapor, and contacting the tellurium precursor vapor with the substrate for vapor deposition of the film thereon.

3. The method of claim 2, wherein the tellurium precursor is selected from the group consisting of tellurium compositions of the formulae:

R_1TeR_2

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 -$Si(R^3)_3$ wherein each R^3 is independently selected from C_1-C_6 alkyl;

$R_1Te(NR_2R_3)$

wherein:

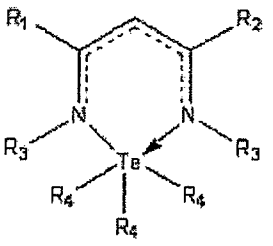
R_1, R_2 and R_3 may be the same as or different from one another, and are independently selected from among H, C_1-C_6 alkyl, C_5-C_{10} cycloalkyl, C_6-C_{10} aryl, and -$Si(R_3)_3$ wherein each R_3 is independently selected from C_1-C_6 alkyl;

R_1Te-TeR_2

wherein:

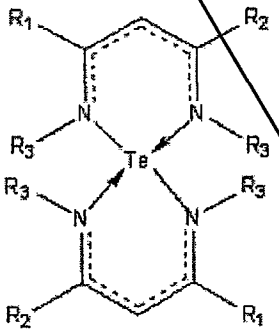
R_1 and R_2 may be the same as or different from one another, and are independently selected from among H, C_1-C_6 alkyl, C_5-C_{10} cycloalkyl, C_6-C_{10} aryl, and -$Si(R^3)_3$ wherein each R^3 is independently selected from C_1-C_6 alkyl;

tellurium complexes with beta-diketiminate ligands,



(I)

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



(II)

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

4. The method of claim 2, wherein the germanium- and tellurium-containing film further comprises antimony, said method comprising volatilizing an antimony precursor to form an antimony precursor vapor, and contacting the antimony precursor vapor with the substrate for vapor deposition of the film thereon.

5. The method of claim 4, wherein the antimony precursor is selected from the group consisting of antimony compositions of the formulae:

$$\mathbf{Sb(NR^1R^2)(R^3N(CR^5R^6)_mNR^4)}$$

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, 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;

$$\mathbf{Sb(R^1)(R^2N(CR^4R^5)_mNR^3)}$$

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;

$$\mathbf{Sb(R^1)_{3-n}(NR^2R^3)_n}$$

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.

$$(R^4)_nSb(E(R^1R^2R^3))_{3-n}$$

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 alylsilyl, 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;

aminidates, guanidates and isoureates of the formula:

$$R^7{}_nSb[R^1NC(X)NR^2]_{3-n}$$

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;

tetra-alkyl guanidates of the formula:

$R^5_nSb[(R^1R^2)NC(NR^3R^4)N)]_{3-n}$

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 -$Si(R^9)_3$ 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, –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, -$Si(R^9)_3$, and -$Ge(R^9)_3$ wherein each R^9 is independently selected from C_1-C_6 alkyl; and

n is an integer from 0 to 3;

carbamates and thiocarbamates of the formula:

$R^4_nSb[(EC(X)E]_{3-n}$

wherein:

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 -$Si(R^5)_3$ 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, –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 -$Si(R^5)_3$, -$Ge(R^5)_3$ 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;

beta-diketonates, diketoiminates, and diketiiminates, of the formulae:

$[OC(R^3)C(X)C(R^2)O]_{3-n}Sb(R^5)_n$
$[OC(R^3)C(X)C(R^2)N(R^1)]_{3-n}Sb(R^5)_n$
$[R^4NC(R^3)C(X)C(R^2)N(R^1)]_{3-n}Sb(R^5)_n$
$[(R^3)OC(=O)C(X)C(R^2)S]_{3-n}Sb(R^5)_n$

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.

allyls of the formulae:

(i): $R^4{}_nSb[R^1NC(X)C(R^2R^3)]_{3-n}$

(ii): $R^4{}_nSb[(R^1O)NC(X)C(R^2R^3))]_{3-n}$

(iii): $R^4{}_nSb[(R^1R^5)NC(X)C(R^2R^3))]_{3-n}$

(iv): $R^4Sb[(ONC(X)C(R^2R^3))]$

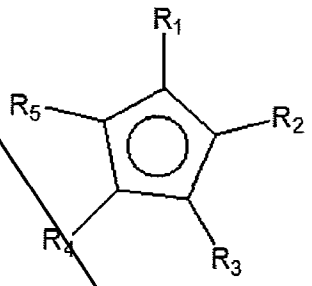
where each R^1,R^2, R^3 and R^5 is independently selected from among H, C_1-C_6 alkyl, C_5-C_{10} cycloalkyl, C_6-C_{10} aryl, and -$Si(R^6)_3$ wherein each R^6 is independently selected from C_1-C_6 alkyl;

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;

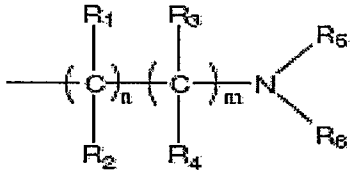
each R^4 is independently selected from among guanidinates, aminidates, isoureates, beta-diketonates, diketoiminates, diketiiminates, C_1-C_6 alkoxy, –NR^7R^8, and -$C(R^9)_3$, wherein each of R^7, R^8 and R^9 is independently selected from H, C_1-C_6 alkyl, C_5-C_{10} cycloalkyl, C_6-C_{10} aryl, -$Si(R^6)_3$,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

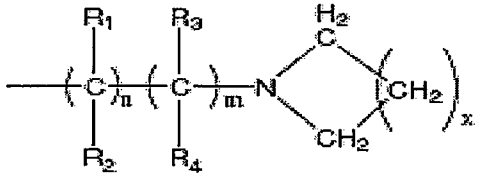
n is an integer from 0 to 3;

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:

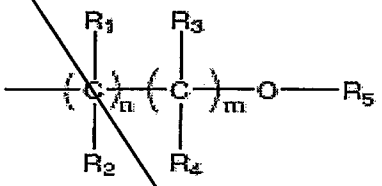




aminoalkyls

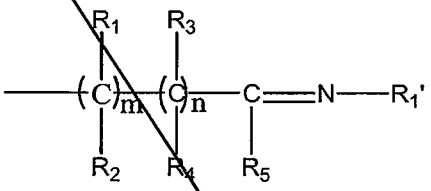
wherein: the methylene ($-CH_2-$) moiety could alternatively be another divalent hydrocarbyl moiety; each of R_1-R_4 is the same as or different from one another, with each being independently selected from among hydrogen, C_1-C_6 alkyl and C_6-C_{10} aryl; each of R_5 and R_6 is the same as or

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;

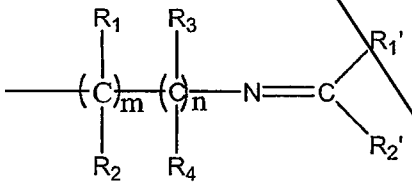


alkoxyalkyls and aryloxyalkyls

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;



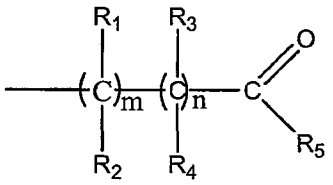
and



imidoalkyls

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 guanidinates, aminidates, isoureates, allyls, beta-diketonates, diketoiminates, and diketiiminates; and

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

(i): $R^5{}_nSb[(R^1R^2)N(CH_2)_mC(R^1R^2)]_{3-n}$

(ii): $R^5{}_nSb[(R^1R^2)N(CH_2)_mSi(R^1R^2)]_{3-n}$

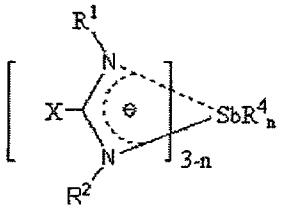
(iii): $R^5{}_nSb[(R^1R^2)N(CH_2)_mO]_{3-n}$

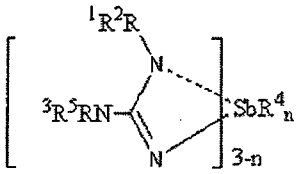
where each of R^1 and R^2 is independently selected from among H, C_1-C_6 alkyl, C_5-C_{10} cycloalkyl, C_6-C_{10} aryl, and -$Si(R^3)_3$ wherein each R^3 is independently selected from C_1-C_6 alkyl;

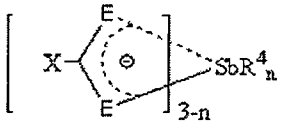
each R^5 is independently selected from among guanidinates, aminidates, isoureates, beta-diketonates, diketoiminates, diketiiminates, C_1-C_6 alkoxy, –NR^6R^7, and -$C(R^8)_3$, wherein each of R^6, R^7 and R^8 is independently selected from H, C_1-C_6 alkyl, C_5-C_{10} cycloalkyl, C_6-C_{10} aryl, -$Si(R^3)_3$,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

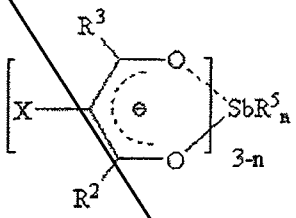
n is an integer from 0 to 3;

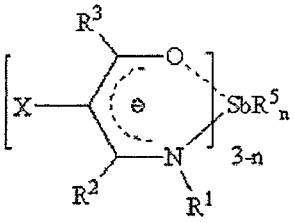
m is integer from 0 to 4.

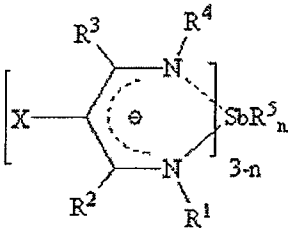


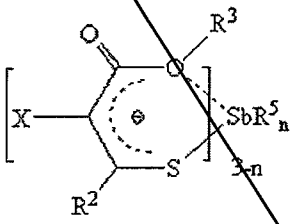


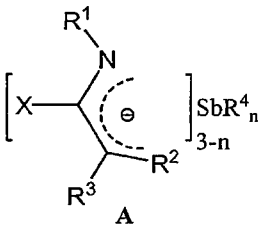




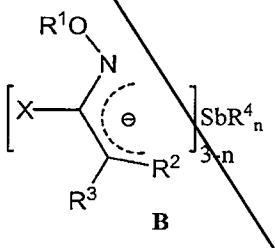




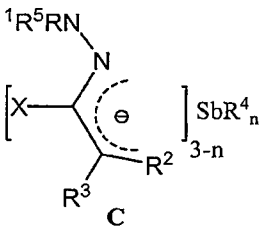




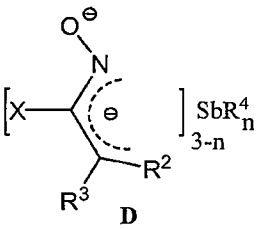
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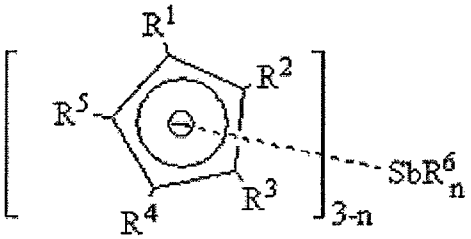
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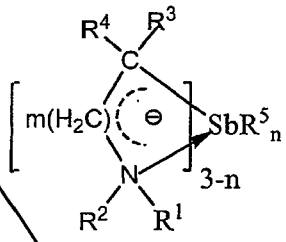


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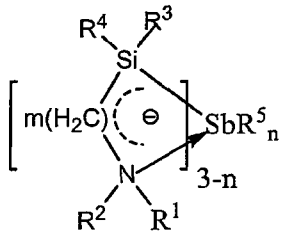


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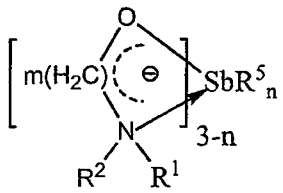




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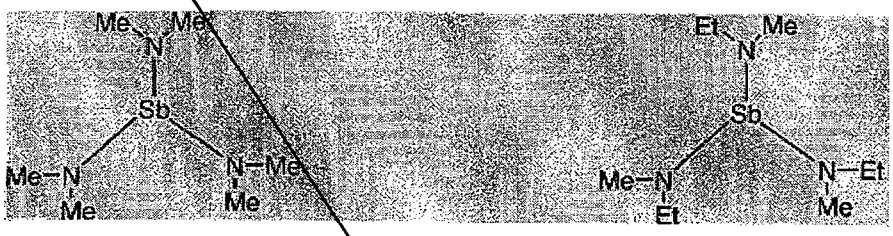


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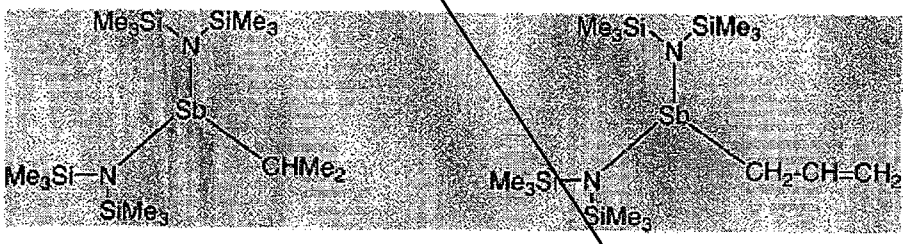


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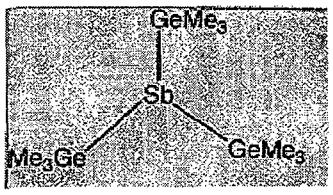
antimony amides of the formulae

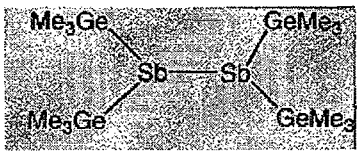


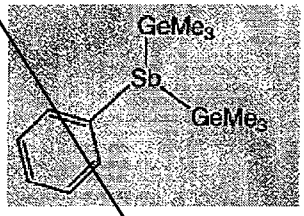
antimony (III) alkyl/amino precursors of the formulae:



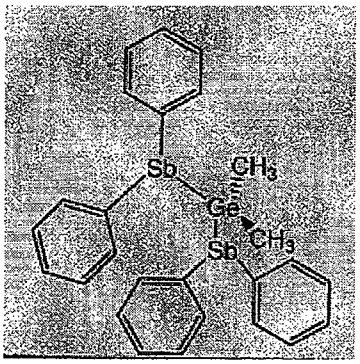
and stibenes with germanium anions, of the formulae:







and



.

6. The method of claim 1, comprising combining the precursor vapor with a component selected from the group consisting of ammonia, hydrogen, helium, argon, and nitrogen.

7. The method of claim 1, wherein the substrate is also contacted with precursor vapor of an antimony precursor and with precursor vapor of a tellurium precursor, so that the germanium-containing film comprises a GeSbTe film, and wherein the method is carried out so as to combat precursor pre-reaction of at least one of said germanium, antimony and tellurium precursors.

8. The method of claim 1, wherein the film is a smooth, amorphous GeTe or a GeSbTe film.

9. The method of claim 2, wherein the tellurium precursor comprises a dialkyl tellurium compound selected from among di-tert-butyl tellurium and diisopropyl tellurium.

10. The method of claim 1, wherein said film is deposited in a fill trench or via structure on the substrate.

11. The method of claim 1, comprising forming a phase change random access memory device including a germanium- and tellurium-containing film of smooth, amorphous character.

12. The method of claim 1, comprising combating pre-reaction of precursor by introducing to said process a pre-reaction-combating agent selected from the group consisting of (i) (O, N, S) organo Lewis base compounds, (ii) free radical inhibitors, and (iii) deuterium-containing reagents.

13. The method of claim 1, for forming a smooth amorphous germanium telluride film, comprising volatilizing the germanium precursor and a diakyl tellurium precursor to form the precursor vapor and contacting the precursor vapor with the substrate to form the smooth amorphous germanium telluride film on the substrate.

14. The method of claim 1, for forming a phase change random access memory device, comprising forming a germanium telluride film of smooth, amorphous character, including vapor deposition of germanium from said germanium precursor, wherein said vapor deposition comprises use of a dialkyl tellurium precursor, and is carried out with a co-reactant comprising ammonia.

15. The method of claim 14, wherein said dialkyl tellurium precursor is selected from the group consisting of di-tert-butyl tellurium and diisopropyl tellurium.

16. The method of claim 1, wherein said germanium precursor is contacted with said substrate in manufacturing a phase change random access memory device.

17. The method of claim 16, comprising contacting the substrate with vapor of an antimony precursor comprising a trialkyl or triamido antimony compound.

18. The method of claim 17, wherein the trialkyl or triamido antimony compound comprises tris(dimethylamino)antimony.

19. The method of claim 16, further comprising the use of a pre-reaction-combating agent selected from the group consisting of (i) (O, N, S) organo Lewis base compounds, (ii) free radical inhibitors, and (iii) deuterium-containing reagents.

20. The method of claim 16, wherein said germanium precursor is contacted with said substrate at temperature not exceeding 350°C.

CLAIMS

1. A method of forming a smooth, amorphous germanium telluride or germanium antimony telluride film on a substrate by a vapor deposition process, comprising volatilizing a germanium amidinate precursor to form a germanium precursor vapor, volatilizing a tellurium precursor to form a tellurium-containing precursor vapor, and when the film is a germanium antimony telluride film, volatilizing an antimony precursor to form an antimony-containing precursor vapor, optionally combining the germanium-containing precursor vapor with a component selected from the group consisting of ammonia, hydrogen, helium, argon, and nitrogen, and contacting the germanium-containing precursor vapor, the tellurium-containing precursor vapor, and when the film is a germanium antimony telluride film, the antimony-containing precursor vapor, with a substrate at conditions producing formation of the smooth amorphous film, and depositing the smooth, amorphous film on the substrate.

2. The method of claim 1, wherein the tellurium precursor is selected from the group consisting of tellurium compositions of the formulae:

R_1TeR_2

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 -$Si(R^3)_3$ wherein each R^3 is independently selected from C_1-C_6 alkyl;

$R_1Te(NR_2R_3)$

wherein:

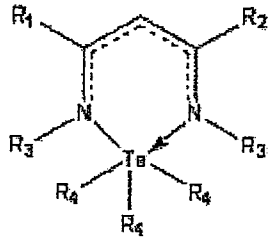
R_1, R_2 and R_3 may be the same as or different from one another, and are independently selected from among H, C_1-C_6 alkyl, C_5-C_{10} cycloalkyl, C_6-C_{10} aryl, and -$Si(R_3)_3$ wherein each R_3 is independently selected from C_1-C_6 alkyl;

R_1Te-TeR_2

wherein:

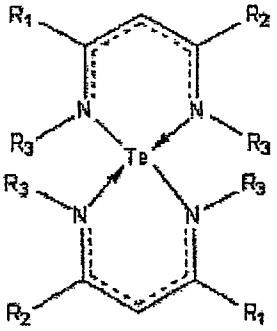
R_1 and R_2 may be the same as or different from one another, and are independently selected from among H, C_1-C_6 alkyl, C_5-C_{10} cycloalkyl, C_6-C_{10} aryl, and -$Si(R^3)_3$ wherein each R^3 is independently selected from C_1-C_6 alkyl;

tellurium complexes with beta-diketiminate ligands,



(I)

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



(II)

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

3. The method of claim 1, wherein the smooth, amorphous film is a germanium antimony telluride film.

4. The method of claim 3, wherein the antimony precursor is selected from the group consisting of antimony compositions of the formulae:

$$Sb(NR^1R^2)(R^3N(CR^5R^6)_mNR^4)$$

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, 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;

$$Sb(R^1)(R^2N(CR^4R^5)_mNR^3)$$

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;

$$Sb(R^1)_{3-n}(NR^2R^3)_n$$

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.

$$(R^4)_nSb(E(R^1R^2R^3))_{3-n}$$

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 alylsilyl, 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;

aminidates, guanidates and isoureates of the formula:

$$R^7_nSb[R^1NC(X)NR^2]_{3-n}$$

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;

tetra-alkyl guanidates of the formula:

$$R^5_nSb[(R^1R^2)NC(NR^3R^4)N)]_{3-n}$$

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 -$Si(R^9)_3$ 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, –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, -$Si(R^9)_3$, and -$Ge(R^9)_3$ wherein each R^9 is independently selected from C_1-C_6 alkyl; and

n is an integer from 0 to 3;

carbamates and thiocarbamates of the formula:

$R^4_nSb[(EC(X)E]_{3-n}$

wherein:

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 -$Si(R^5)_3$ 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, –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 -$Si(R^5)_3$, -$Ge(R^5)_3$ 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;

beta-diketonates, diketoiminates, and diketiiminates, of the formulae:

$[OC(R^3)C(X)C(R^2)O]_{3-n}Sb(R^5)_n$

$[OC(R^3)C(X)C(R^2)N(R^1)]_{3-n}Sb(R^5)_n$

$[R^4NC(R^3)C(X)C(R^2)N(R^1)]_{3-n}Sb(R^5)_n$

$[(R^3)OC(=O)C(X)C(R^2)S]_{3-n}Sb(R^5)_n$

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.

allyls of the formulae:

(i): $R^4{}_nSb[R^1NC(X)C(R^2R^3)]_{3-n}$

(ii): $R^4{}_nSb[(R^1O)NC(X)C(R^2R^3))]_{3-n}$

(iii): $R^4{}_nSb[(R^1R^5)NC(X)C(R^2R^3))]_{3-n}$

(iv): $R^4Sb[(ONC(X)C(R^2R^3))]$

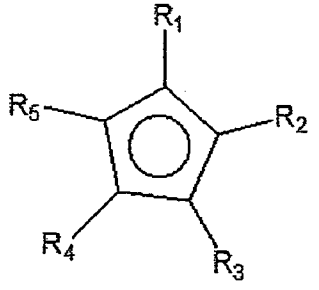
where each R^1,R^2, R^3 and R^5 is independently selected from among H, C_1-C_6 alkyl, C_5-C_{10} cycloalkyl, C_6-C_{10} aryl, and $-Si(R^6)_3$ wherein each R^6 is independently selected from C_1-C_6 alkyl;

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;

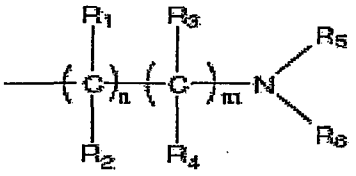
each R^4 is independently selected from among guanidinates, aminidates, isoureates, beta-diketonates, diketoiminates, diketiiminates, C_1-C_6 alkoxy, $-NR^7R^8$, and $-C(R^9)_3$, wherein each of R^7, R^8 and R^9 is independently selected from H, C_1-C_6 alkyl, C_5-C_{10} cycloalkyl, C_6-C_{10} aryl,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

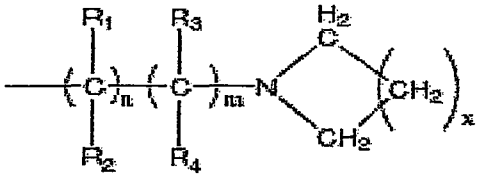
n is an integer from 0 to 3;

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



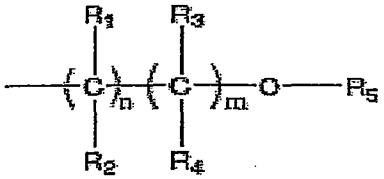
wherein each of R_1, R_2, R_3, R_4 and R_5 can be the same as or different from the others, and each is independently selected from among hydrogen, C_1-C_{12} alkyl, C_1-C_{12} alkylamino, C_6-C_{10} aryl, C_1-C_{12} alkoxy, C_3-C_6 alkylsilyl, C_2-C_{12} alkenyl, $R^1R^2NNR^3$, wherein R^1, R^2 and 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:





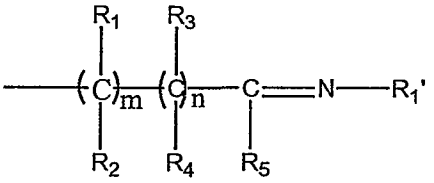
aminoalkyls

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;

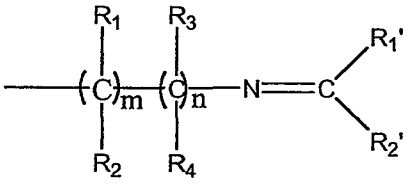


alkoxyalkyls and aryloxyalkyls

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;

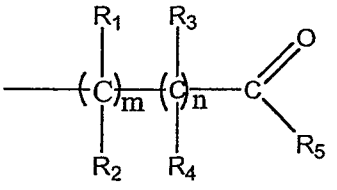


and



imidoalkyls

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 guanidinates, aminidates, isoureates, allyls, beta-diketonates, diketoiminates, and diketiiminates; and

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

(i): $R^5{}_nSb[(R^1R^2)N(CH_2)_mC(R^1R^2)]_{3-n}$

(ii): $R^5{}_nSb[(R^1R^2)N(CH_2)_mSi(R^1R^2)]_{3-n}$

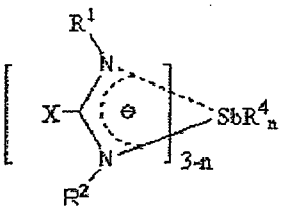
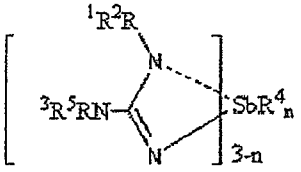
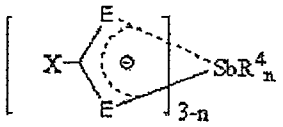
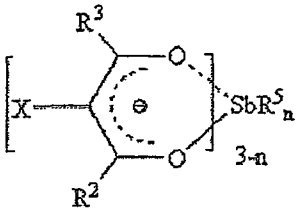
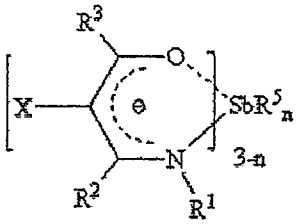
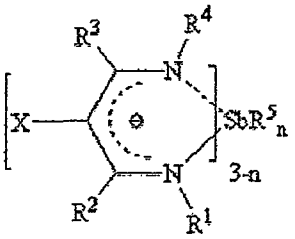
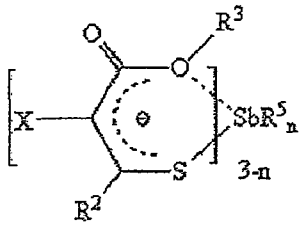
(iii): $R^5{}_nSb[(R^1R^2)N(CH_2)_mO]_{3-n}$

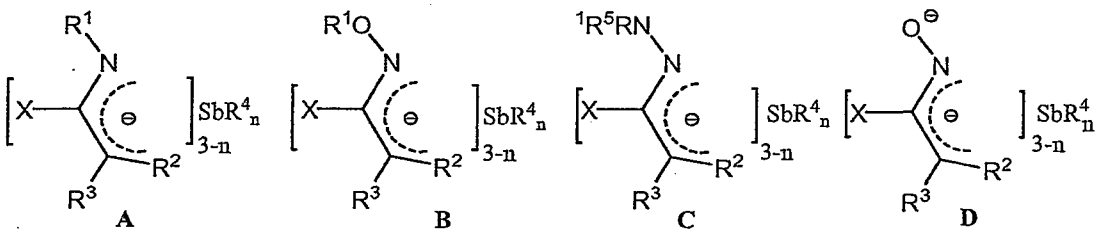
where each of R^1 and R^2 is independently selected from among H, C_1-C_6 alkyl, C_5-C_{10} cycloalkyl, C_6-C_{10} aryl, and -$Si(R^3)_3$ wherein each R^3 is independently selected from C_1-C_6 alkyl;

each R^5 is independently selected from among guanidinates, aminidates, isoureates, beta-diketonates, diketoiminates, diketiiminates, 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, -$Si(R^3)_3$, and -$Ge(R^3)_3$ wherein each R^3 is independently selected from C_1-C_6 alkyl;

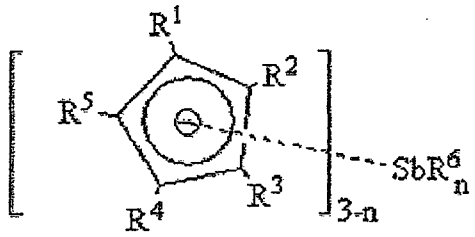
n is an integer from 0 to 3;

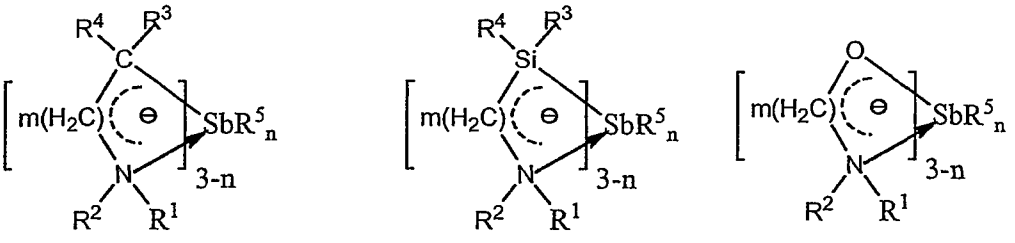
m is integer from 0 to 4.



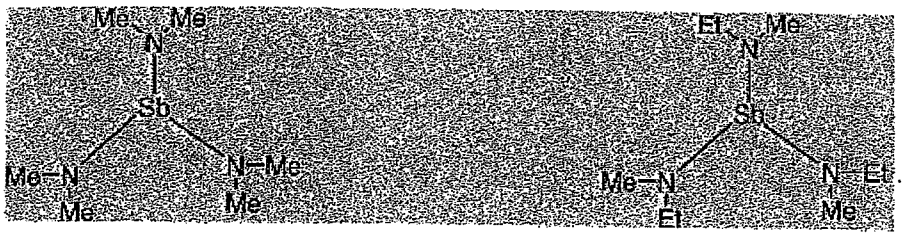
A B C D



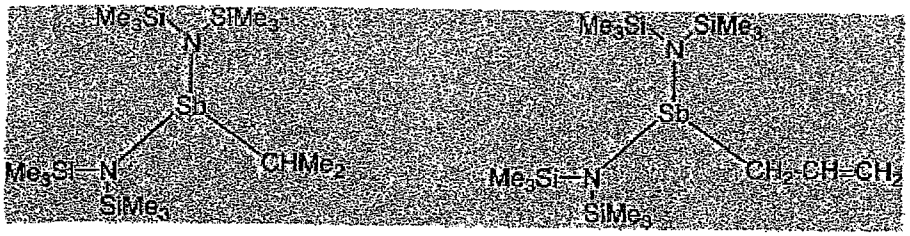


A B C

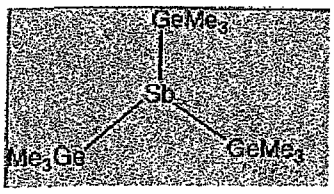
antimony amides of the formulae

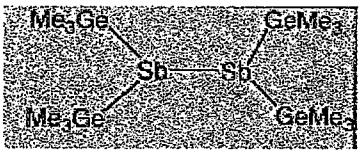


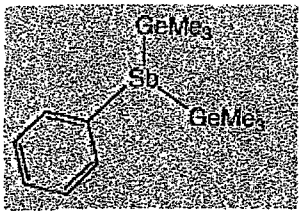
antimony (III) alkyl/amino precursors of the formulae:



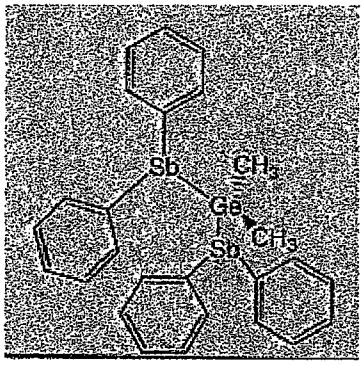
and stibenes with germanium anions, of the formulae:







and



.

5. The method of claim 1, comprising combining the germanium-containing precursor vapor with a component selected from the group consisting of ammonia, hydrogen, helium, argon, and nitrogen.

6. The method of claim 1, wherein the film is a germanium antimony telluride film, and wherein the method is carried out so as to combat precursor pre-reaction of at least one of said germanium, antimony and tellurium precursors.

7. The method of claim 1, wherein the tellurium precursor comprises a dialkyl tellurium compound selected from among di-tert-butyl tellurium and diisopropyl tellurium.

8. The method of claim 1, wherein said film is deposited in a fill trench or via structure on the substrate.

9. The method of claim 1, comprising forming a phase change random access memory device including the smooth, amorphous film.

10. The method of claim 1, comprising combating pre-reaction of precursor by introducing to said process a pre-reaction-combating agent selected from the group consisting of (i) (O, N, S) organo Lewis base compounds, (ii) free radical inhibitors, and (iii) deuterium-containing reagents.

11. The method of claim 1, wherein the smooth, amorphous film is a germanium telluride film.

12. The method of claim 1, comprising forming a phase change random access memory deviceincluding the smooth, amorphous film, wherein said tellurium precursor comprises a dialkyl tellurium precursor, and the film forming is carried out with a co-reactant comprising ammonia.