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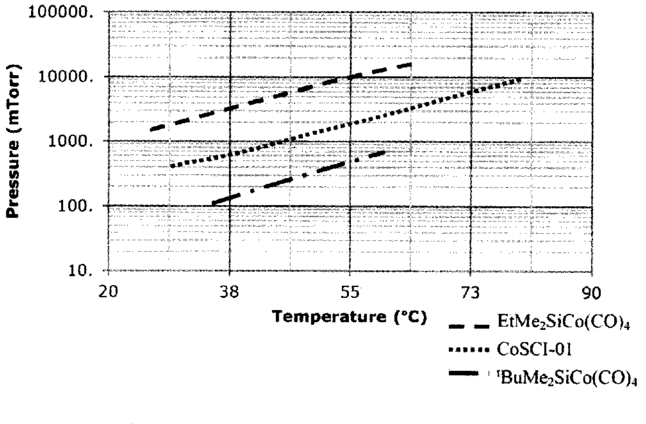
(54) Title: ORGANOMETALLIC COMPOUNDS USEFUL FOR CHEMICAL PHASE DEPOSITION

Fig. 1



(57) Abstract: Organometallic compounds useful in chemical phase deposition processes such as atomic layer deposition (ALD) and chemical vapor deposition (CVD).. The compounds correspond in structure to Formula 1 : $[\{R^1R^2R^3 (A))x\text{-}M(CO)y]z$ wherein R^1, R^2 and R^3 are independently selected from the group consisting of H, a lower alkyl group and a phenyl group optionally substituted with at least one independently selected lower alkyl group, with the proviso that at least one of R^1, R^2 and R^3 must be other than H; M is selected from the group consisting of the cobalt group metals, the iron group metals, the manganese group metals, and the chromium group metals; A is selected from the group consisting of Si, Ge, and Sn; and wherein: $x = 1$, $y = 4$, and $z = 1$ when M is selected from the group consisting of a cobalt group metal, $x = 1$, $y = 5$, and $z = 1$ when M is selected from the group consisting of a manganese group metal, $x = 2$, $y = 4$, and $z = 1$ when M is selected from the group consisting of a chromium group metal, and $x = 2$, $y = 4$, and $z = 1$ or, alternatively, $x = 1$, $y = 4$, and $z = 2$ when M is selected from the group consisting of an iron group metal. Methods of deposition are also provided which involve the reaction of at least one of the compounds of the invention, in the presence of co-reagents, to generate metal carbonyl hydrides which can decompose cleanly and thermally to form substantially pure metal films, metal oxide films, metal nitride films, metal phosphide films, metal boride films or metal sulphide films. Methods of selective deposition, such that metal or metal-containing films are deposited selectively on certain substrates and not on other substrate materials.

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- *with amended claims and statement (Art. 19(1))*

TITLE

Organometallic Compounds Useful for Chemical Phase Deposition

FIELD

[0001] The invention relates to compounds formed from metal carbonyl complexes with trialkyl silyl, germanyl or stannyl ligands, and to methods of preparing thin films of substantially pure metal, alternatively films of metal alloys, metal oxides, nitrides, phosphides, borides or sulphides by chemical vapor deposition (CVD) or atomic layer deposition (ALD) using such compounds. Methods of preparing thin films of substantially-pure metal alloys, mixed-metal oxides, mixed-metal nitrides, mixed-metal phosphides, mixed-metal borides or mixed-metal sulphides are also disclosed. Methods of substrate-selective deposition of metal films are also disclosed.

BACKGROUND

[0002] Various organometallic compounds are used to form thin metal films on a variety of substrates, and a variety of deposition techniques have been employed to do so. These include reactive sputtering, ion-assisted deposition, sol-gel deposition, CVD, and ALD, also known as atomic layer epitaxy. The CVD and ALD processes are increasingly used as they have the advantages of good compositional control, high film uniformity, good control of doping and, significantly, they give excellent conformal step coverage on highly non-planar microelectronics device geometries.

[0003] CVD (also referred to as metal-organic CVD or MOCVD) is a chemical process whereby compounds are used to form a thin film on a substrate. In a typical CVD process, the compounds are passed over a substrate (wafer) within a low pressure or ambient pressure reaction chamber. The compounds react and/or decompose on the substrate surface creating a thin film of deposited material. Volatile by-products are removed by gas flow through the reaction chamber. The deposited film thickness can be difficult to control because it depends on coordination of many parameters such as temperature, pressure, gas flow volumes and uniformity, chemical depletion effects and time.

[0004] ALD is a common method for the deposition of thin films. It is a self-limiting, sequential, unique film growth technique based on surface reactions that can provide atomic layer-forming control and deposit-conformal thin films of materials provided by compounds onto substrates of varying compositions. In ALD, the compounds are separated during the reaction. The first compound is passed over the substrate producing a monolayer on the substrate. Any excess unreacted compound is pumped out of the reaction chamber. A second compound is then passed over the substrate and reacts with the first compound, forming a second monolayer of film over the first-formed monolayer of film on the substrate surface. This cycle is repeated to create a film of desired thickness. ALD film growth is self-limited and based on surface reactions, creating uniform depositions that can be controlled at the nanometer-thickness scale.

[0005] Deposition of good quality metals by CVD and/or ALD is difficult either due to stability issues of the compounds or impurities in the final films. The stability of the compounds can impact the delivery of these materials to the growth chamber and thus the deposition rate or partial decomposition in the lines. If the compounds cannot decompose or react cleanly, then impurities such as C, N, O and H can incorporate into the film which causes the performance of the film to be less than optimum. The incorporation of impurities in the films may also have some impact on film adhesion to the underlying substrate and thus on the device performance.

[0006] The delivery of the compound and the lifetime of the compound in the bubbler are also important and this can be a challenge when solid compounds are involved, thus there is always a desire to use liquid compounds with good stability.

[0007] Current compounds for use in CVD and ALD do not provide the required performance to implement new processes for fabrication of next generation devices, such as semiconductors. For example, improved thermal stability, higher volatility, reduced vapor pressures, and increased deposition rates are needed.

[0008] This invention is related to compound engineering to meet some of the challenges highlighted above.

NOTATION AND NOMENCLATURE

[0009] Certain abbreviations, symbols, and terms are used throughout the following description and claims, and include the following.

[0010] As used herein, the term "lower alkyl group" refers to linear, branched, or cyclic alkyl groups having from 1 to 8 carbon atoms. Examples of linear alkyl groups include, without limitation, methyl groups, ethyl groups, propyl groups, and butyl groups. Examples of branched alkyl groups include, without limitation, isopropyl groups and t-butyl groups. Examples of cyclic alkyl groups include, without limitation, cyclopropyl groups, cyclopentyl groups, and cyclohexyl groups.

[0011] The term "lower alcohol" refers to a primary, secondary or tertiary alcohol having from 1 to 4 carbon atoms. Examples of such alcohols include, without limitation, methanol, ethanol, isopropanol and tertiary butanol.

[0012] The term "lower alkyl amine" refers to a primary or secondary amine having lower alkyl group(s) each having from 1 to 4 carbon atoms. Examples of such amines include, without limitation, methylamine, ethylamine, di-isopropylamine and tertiarybutylamine.

[0013] The term "substituted hydrazine" refers to hydrazines having from 1 to 4 substituents which are independently-selected lower alkyl groups, each having from 1 to 4 carbon atoms, or a phenyl group. Examples of such hydrazines include, without limitation, N,N-dimethyl hydrazine, tertiary-butyl hydrazine, methyl hydrazine and phenyl hydrazine.

[0014] The term "lower alkyl phosphine" refers to a primary or secondary phosphine having lower alkyl group(s) each having from 1 to 4 carbon atoms. Examples of such amines include, without limitation, methylphosphine, dimethylphosphine, ethylphosphine, and tertiary butylphosphine.

[0015] The term "lower alkyl thiol" refers to a primary, secondary or tertiary thiol having from 1 to 4 carbon atoms. Examples of such alcohols include, without limitation, methane thiol, ethane thiol, and tertiary-butyl thiol.

[0016] The term "lower alkyl borane" refers to a primary, secondary or tertiary borane, or a precursor thereof, having from 1 to 4 carbon atoms. Examples of such boranes include, without limitation, methyl borane, ethyl borane, and trimethyl borane.

[0017] The term "cobalt group metals" refers to the elements Co, Rh, and Ir.

[0018] The term "manganese group metals" refers to the elements Mn and Re.

[0019] The term "chromium group metals" refers to the elements Cr, Mo, and W.

[0020] The term "iron group metals" refers to the elements Fe, Ru, and Os.

[0021] As used herein, the term "compound" refers to an organometallic molecule, complex and/or compound which is deposited or delivered to or passed over a substrate to form a thin film by a vapor deposition process such as CVD or ALD.

[0022] As used herein, the term "metal-containing film" refers to a film of substantially pure metal, metal oxide, metal nitride, metal sulphide, metal boride or metal phosphide.

[0023] As used herein, the term "vapor deposition process" refers to any type of vapor deposition technique such as CVD or ALD. In various embodiments of the invention, CVD may take the form of conventional (pulsed) CVD, liquid injection CVD or photo-assisted CVD. In other embodiments, ALD may take the form of conventional (pulsed) ALD, liquid injection ALD, photo-assisted ALD, plasma-assisted ALD, or plasma-enhanced ALD. Such techniques are well-known in the art.

SUMMARY

[0024] In one aspect, the present invention provides an organometallic compound. The compound corresponds in structure to Formula 1:

$$[(R^1R^2R^3\,(A))_x\text{-}M(CO)_y]_z$$

wherein R^1, R^2 and R^3 are independently selected from the group consisting of H, a lower alkyl group and a phenyl group optionally substituted with at least one independently selected lower alkyl group, with the proviso that at least one of R^1, R^2 and R^3 must be other than H;

M is selected from the group consisting of the cobalt group metals, the iron group metals, the manganese group metals, and the chromium group metals;

A is selected from the group consisting of Si, Ge, and Sn; and wherein:

$x = 1$, $y = 4$, and $z = 1$ when M is selected from the group consisting of a cobalt group metal,

$x = 1$, $y = 5$, and $z = 1$ when M is selected from the group consisting of a manganese group metal,

$x = 2$, $y = 4$, and $z = 1$ when M is selected from the group consisting of a chromium group metal, and

$x = 2$, $y = 4$, and $z = 1$ or, alternatively, $x = 1$, $y = 4$, and $z = 2$ when M is selected from the group consisting of an iron group metal.

[0025] The compounds are useful in chemical phase deposition processes such as atomic layer deposition (ALD) and chemical vapor deposition (CVD)

[0026] Methods of deposition of metal-containing films are provided, which involve the reaction of the compound with at least one co-reagent to generate metal carbonyl hydrides which decompose cleanly and thermally to form substantially-pure metal films. Alternatively, substantially-pure metal oxide, nitride, phosphide, boride or sulphide films may be prepared by selection of appropriate co-reagents, as described herein.

[0027] Use of more than one compound of Formula 1 in the deposition processes disclosed herein results in the deposition of films of substantially-pure metal alloys, mixed-metal oxides, mixed-metal nitrides, mixed-metal phosphides, mixed-metal borides or mixed-metal sulphides.

[0028] Methods of selective deposition are also provided, such that metal or metal nitride films are deposited selectively on certain substrates and not on other substrate materials. One such method involves the use of substrate materials having a surface with a strong affinity for the silyl (or germanyl or tin) ligand component of the compound, such that after reaction of the compound with the co-reagent(s) the silyl ligand attaches to the surface having an affinity for Si, inhibiting the deposition of metal on that surface. Such substrate materials having an affinity include SiO_2, SiN, TiN, TaN.

[0029] An alternative method of selective deposition involves the use of substrate materials having an affinity for CO, such that after reaction of the compound with the co-reagent(s) the metal carbonyl is bound to the surface having such affinity. The metal carbonyl is subsequently dissociated thermally, leaving the metal coating the surface while the CO is removed as gas. Such substrate materials having an affinity for CO include the nickel group metals Ni, Pd, Pt, cobalt group metals Co, Rh, Ir, and iron group metals Fe, Ru, and Os.

BRIEF DESCRIPTION OF THE DRAWINGS

[0030] Fig. 1 shows the vapour pressures of compounds of the invention compared to a compound of the art.

[0031] Fig. 2 shows the thermal stability of $^tBuMe_2SiCo(CO)_4$.

[0032] Fig. 3 shows the thermal stability of a compound of the art CCTBA (3,3-Dimethyl-1-butyne)dicobalthexacarbonyl).

[0033] Fig. 4 shows a schematic of a CVD system used for exemplary thin film deposition.

[0034] Fig. 5 shows the binding energies of $^tBuMe_2SiCo(CO)_4$ on different surfaces.

[0035] Fig. 6 shows the TGA of $EtMe_2SiCo(CO)_4$.

[0036] Fig. 7 shows the vapor pressure of $EtMe_2SiCo(CO)_4$.

[0037] Fig. 8 shows the NMR spectrum of $Et_3SiCo(CO)_4$.

[0038] Fig. 9 shows the NMR spectrum of $^tBuMe_2SiCo(CO)_4$.

[0039] Fig. 10 shows the TGA of $^tBuMe_2SiCo(CO)_4$.

[0040] Fig. 11 shows the vapour pressure of $^tBuMe_2SiCo(CO)_4$.

[0041] Fig. 12 shows the thermal growth rate as a function of temperature for deposition using $^tBuMe_2SiCo(CO)_4$.

[0042] Fig. 13 shows the NMR of $PhMe_2SiCo(CO)_4$.

[0043] Fig. 14 shows the resistivity of a cobalt film deposited using $^tBuMe_2SiCo(CO)_4$.

[0044] Fig. 15 shows the growth rate as a function of pressure and the hydrogen to ammonia ratio for deposition using $tBuMe_2SiCo(CO)_4$.

[0045] Fig. 16 shows a demonstration of the process of selective deposition using a compound of the invention.

DETAILED DESCRIPTION

[0046] An organometallic compound is provided. The compound corresponds in structure to Formula 1:

$$[(R^1R^2R^3(A))_x\text{-}M(CO)_y]_z$$

wherein R^1, R^2 and R^3 are independently selected from the group consisting of H, a lower alkyl group and a phenyl group optionally substituted with at least one independently selected lower alkyl group, with the proviso that at least one of R^1, R^2 and R^3 must be other than H;

M is selected from the group consisting of the cobalt group metals, the iron group metals, the manganese group metals, and the chromium group metals;

A is selected from the group consisting of Si, Ge, and Sn; and wherein:

$x = 1$, $y = 4$, and $z = 1$ when M is selected from the group consisting of a cobalt group metal,

$x = 1$, $y = 5$, and $z = 1$ when M is selected from the group consisting of a manganese group metal,

$x = 2$, $y = 4$, and $z = 1$ when M is selected from the group consisting of a chromium group metal, and

$x = 2$, $y = 4$, and $z = 1$ or, alternatively, $x = 1$, $y = 4$, and $z = 2$ when M is selected from the group consisting of an iron group metal.

[0047] In various embodiments of the invention, metal carbonyl compounds with trialkyl silyl, germanyl or stannyl ligands, methods of making such compounds and methods of using such compounds, in the presence of appropriate co-reagents, to form substantially-pure metal-containing films, such as, but not limited to, metal, metal phosphide, metal sulphide, metal oxide, metal boride and metal nitride films, are provided.

[0048] The use of more than one compound of Formula 1, each having a different value of M, in the deposition processes disclosed herein results in the formation of films of substantially-pure metal alloys, mixed-metal oxides, mixed-metal nitrides, mixed-metal phosphides, mixed-metal borides or mixed-metal sulphides, the nature of the film formed being dependent upon the nature of the co-reagent used, as described herein.

[0049] In a first embodiment of the invention the compound corresponds to Formula 1 wherein M is a cobalt group metal and A is Si. Exemplary compounds include $EtMe_2SiCo(CO)_4$, $Et_3SiCo(CO)_4$, $Me_2SiCo(CO)_4$ and $PhMe_2SiCo(CO)_4$.

[0050] In a second embodiment of the invention the compound corresponds to Formula 1 wherein M is an iron group metal, A is Si, $x = 2$, $y = 4$, and $z = 1$. Exemplary compounds include $(Et_3Si)_2Fe(CO)_4$.

[0051] In a third embodiment of the invention the compound corresponds to Formula 1 wherein M is an iron group metal, A is Si, $x = 1$, $y = 4$, and $z = 2$.

[0052] In a fourth embodiment of the invention the compound corresponds to Formula 1 wherein M is a manganese group metal and A is Si. Exemplary compounds include $Et_3SiMn(CO)_5$.

[0053] In a fifth embodiment of the invention the compound corresponds to Formula 1 wherein M is a chromium group metals and A is Si. Exemplary compounds include $(PhMe_2Si)_2W(CO)_4$.

[0054] Embodiments of the invention include those in which R^1, R^2 and R^3 are independently selected from the group consisting of a lower alkyl group and a phenyl group optionally substituted with at least one independently selected lower alkyl group.

[0055] Exemplary compounds include those in which R^1, R^2 and R^3 are independently selected from the group consisting of a lower alkyl group having from 1 to 5 carbon atoms. Other exemplary compounds include those in which at least one of R^1, R^2 and R^3 is a methyl group.

[0056] Other exemplary compounds include those in which R^1, R^2 and R^3 are independently selected from the group consisting of a lower alkyl group having from 1 to 4 carbon atoms. Other exemplary compounds include those in which at least one of R^1, R^2 and R^3 is a methyl group

[0057] Other exemplary compounds include those in which R^1, R^2 and R^3 are independently selected from the group consisting of a lower alkyl group having from 1 to 4 carbon atoms, two of which are methyl group, the third of which is a lower alkyl group having from 3 to 4 carbon atoms.

[0058] Compounds of the invention have improved properties compared to compounds of the art. For example, as shown in Fig. 1, certain compounds of the invention have been shown to be more volatile than a representative compound of the art.

[0059] Further, as shown in Fig. 2, below, certain compounds of the invention have been shown to be more stable than a representative compound of the art (shown in Fig. 3, below), thus permitting better use (longer lifetime of the material in the container) and also allows for the use of higher temperatures in deposition processes such as CVD and ALD.

[0060] The compounds of Formula 1 are useful in chemical phase deposition processes such as atomic layer deposition (ALD) and chemical vapor deposition (CVD).

[0061] In further embodiments of the invention, methods of forming metal-containing films by vapor deposition processes are provided. The methods comprise using at least one compound of Formula 1 together with one or more co-reagents, as disclosed herein.

[0062] Fig. 4 shows a schematic of a CVD system used for exemplary thin film deposition. An inert carrier gas (1), such as Ar, is passed through a mass flow controller (2) at a controlled flow rate to bubbler (6), which contains a compound of Formula 1 (7) and carries the vaporized compound of Formula 1 to the reaction chamber (15). A liquid co-reagent (14) is delivered to the reaction chamber in a similar fashion, whereas a gaseous co-reagent is delivered directly to the reaction chamber at a controlled flow rate without going through the bubbler. The bubbler may be heated or cooled to obtain a suitable vapor pressure in the desired range. Typically, the temperature of the delivery line is higher than that of the bubbler by about 20 C°, so that the vapor does not condense before reaching reaction chamber. The compound of Formula 1 and the co-reagent are delivered simultaneously. In the reaction chamber, substrate(s) (16) rest on a preheated graphite holder (17) at a set temperature controlled by a heater (18) and a thermocouple (19). The pressure in the reaction chamber is controlled by a pressure regulating valve (20), which is connected to a vacuum pump. The delivered compound of Formula 1 and co-reagent react in the reaction chamber, deposit on substrate(s), and so form a thin film. The by-products of the reaction are pumped off under reduced pressure.

[0063] For example, in a sixth embodiment of the invention the reaction of a compound of Formula 1 with co-reagents generates metal carbonyl hydrides, which can decompose cleanly and thermally to form substantially pure metal films, while the volatile carbonyl and hydrolyzed trialkyl silyl ligands evaporate and are removed.

[0064] For the deposition of substantially pure metal films co-reagents include, but are not limited to, H2, ammonia, a lower alkyl amine, a lower alcohol, hydrazine and a substituted hydrazine.

[0065] In a seventh embodiment of the invention the reaction of a compound of Formula 1 with co-reagents generates metal carbonyl oxides, which can decompose cleanly and thermally to form metal oxide films, while the volatile carbonyl and trialkyl silyl ligands evaporate and are removed.

[0066] For the deposit of metal oxide films co-reagents include, but are not limited to, H_2O, O_2, O_3, and a lower alcohol.

[0067] In an eighth embodiment of the invention the reaction of a compound of Formula 1 with co-reagents generates metal carbonyl amides, which can decompose cleanly and thermally to form metal nitride films, while the volatile carbonyl and trialkyl silyl ligands evaporate and are removed.

[0068] For the deposit of metal nitride films co-reagents include, but are not limited to, ammonia, a lower alkyl amine, a lower alcohol, hydrazine and a substituted hydrazine.

[0069] In a ninth embodiment of the invention the reaction of a compound of Formula 1 with co-reagents generates metal carbonyl phosphide, which can decompose cleanly and thermally to form metal phosphide films, while the volatile carbonyl and trialkyl silyl ligands evaporate and are removed.

[0070] For the deposit of metal phosphide films co-reagents include, but are not limited to, PH_3 and a lower alkyl phosphine.

[0071] In a tenth embodiment of the invention the reaction of a compound of Formula 1 with co-reagents generates metal carbonyl sulphide, which can decompose cleanly and thermally to form metal sulphide films, while the volatile carbonyl and trialkyl sily ligands evaporate and are removed.

[0072] For the deposit of metal sulphide films co-reagents include, but are not limited to, H_2S and a lower alkyl thiol.

[0073] In an eleventh embodiment of the invention the reaction of a compound of Formula 1 with co-reagents generates metal carbonyl borides, which can decompose cleanly and thermally to form metal boride films, while the volatile carbonyl and trialkyl silyl ligands evaporate and are removed.

[0074] For the deposit of metal boride films co-reagents include, but are not limited to, borane and a lower alkyl borane.

[0075] In a further embodiment of the invention, the use of more than one compound of Formula 1, each having a different value of M, in the deposition processes disclosed herein results in the formation of films of substantially-pure metal alloys, mixed-metal oxides, mixed-metal nitrides, mixed-metal phosphides, mixed-metal borides or mixed-metal sulphides, the nature of the film formed being dependent upon the nature of the co-reagent used, as described herein.

[0076] For example, in a twelfth embodiment of the invention the use of a cobalt-containing compound of Formula 1 together with a chromium-containing compound of Formula 1 will result in the deposition of a cobalt-chromium alloy.

[0077] In further embodiments of the invention, methods of selective deposition are provided such that metal or metal nitride films are deposited selectively on certain substrates and not on other substrate materials.

[0078] For example, a thirteenth embodiment of the invention involves the use of substrate materials having a surface with a strong affinity for the silyl (or germanyl or tin, as appropriate) ligand component of the compound of Formula 1 such that, after reaction of the compound of Formula 1 with the co-reagent, the silyl (or germanyl or tin, as appropriate) ligand attaches to the surface having such affinity, inhibiting the deposition of metal on that surface.

[0079] Such substrate materials having an affinity include, but are not limited to, SiO_2, SiN, TiN, and TaN.

[0080] A fourteenth embodiment of the invention involves the use of substrate materials having an affinity for CO such that, after reaction of the compound of Formula 1 with the co-reagent, the metal carbonyl is bound to the surface having such affinity. The metal carbonyl is subsequently dissociated thermally, leaving the metal coating the surface whilst the CO is removed as gas.

[0081] Such substrate materials having an affinity for CO include, but are not limited to, the nickel group metals Ni, Pd, Pt, cobalt group metals Co, Rh, Ir, and iron group metals Fe, Ru, and Os.

[0082] Fig. 5 shows the binding energies of $^{t}BuMe_2SiCo(CO)_4$ to different surfaces. The more negative the energy, the better binding, meaning that the molecule will bind preferentially to Co or Cu, and thus the deposition will preferentially take place on that surface compared to silicon oxide where the binding is weak.

EXAMPLES

Example 1: Synthesis of $EtMe_2SiCo(CO)_4$

[0083] 3 g of $Co_2(CO)_8$ and 40 mL of dry pentane were charged into a 100 mL flask under N_2, followed by the addition of 1.7 g of $EtMe_2SiH$. After stirring for 1 hr, pentane and excess $EtMe_2SiH$ were removed under reduced pressure. The liquid product was purified by distillation under reduced pressure. NMR confirmed the product to be $EtMe_2SiCo(CO)_4$. TGA analysis and vapor pressure measurements showed that the material has a good volatility for vapor deposition applications, as shown in Fig. 6 and Fig. 7, respectively.

Example 2: Synthesis of $Et_3SiCo(CO)_4$

[0084] 5 g of $Co_2(CO)_8$ and 60 mL of dry pentane were charged into a 100 mL flask under N_2, followed by the addition of 3.7 g of Et_3SiH. After stirring for 1 hr, pentane and excess Et_3SiH were removed under reduced pressure. The liquid product was purified by distillation under reduced pressure. NMR confirmed the product to be $Et_3SiCo(CO)_4$, as shown in Fig. 8.

Example 3: Synthesis of $^{t}BuMe_2SiCo(CO)_4$

[0085] 3 g of $Co_2(CO)_8$ and 40 mL of dry pentane were charged into a 100 mL flask under N_2, followed by the addition of 2 g of $tBuMe_2SiH$. After stirring for 4 hr, pentane and excess $tBuMe_2SiH$ were removed under reduced pressure. The liquid product was purified by distillation under reduced pressure. As shown in Fig. 9, NMR confirmed the product to be $^{t}BuMe_2SiCo(CO)_4$. TGA analysis and vapor pressure measurements showed that the material had good volatility for vapor deposition applications, as shown in Fig. 10 and Fig. 11.

[0086] Fig. 12 shows that $^{t}BuMe_2SiCo(CO)_4$ has good thermal stability up to about 150°C, making it suitable for use in deposition.

Example 4: Synthesis of $(Et_3Si)_2Fe(CO)_4$

[0087] 35 g of Et_3SiH and 5 g of $Fe_3(CO)_{12}$ were charged in a bubbler. The bubbler was then heated at 120 °C for 36 hrs. Excess Et_3SiH was removed under reduced pressure, followed by filtration to collect the product. NMR confirmed the product to be $(Et_3Si)_2Fe(CO)_4$.

Example 5. Synthesis of $Et_3SiMn(CO)_5$

[0088] 2.5 g $Mn_2(CO)_{10}$ and 30 g of Et_3SiH were charged in a bubbler. The bubbler was then heated at 170 C for 36 hrs. Excess Et_3SiH was removed under reduced pressure, followed by distillation under reduced pressure to collect the product. NMR confirmed the product to be $Et_3SiMn(CO)_5$.

Example 6. Synthesis of $(DimethylphenylSi)_2W(CO)_4$

[0089] 6.73 g of $W(CO)_6$ was suspended in 60 mL of dry dichloromethane. The suspension was cooled in a dry ice/acetone bath, followed by the addition of 1 mL Br_2 diluted in 10 mL dichloromethane. The mixture was stirred for another 20 minutes. Dichloromethane was then pumped off in an ice/water bath to yield $W_2Br_4(CO)_8$.

[0090] In another reaction flask, 10 g of $PhMe_2SiH$ was mixed with 60 mL of dimethoxyethane, followed by the addition of 6 g of potassium hydride. The reaction mixture was refluxed for 8 hrs, and then filtered to collect the liquid. The obtained liquid was then mixed with $W_2Br_4(CO)_8$ and stirred for 8 hrs in ice bath. Volatile solvent was pumped off. Sublimation was then carried out to collect $(PhMe_2Si)_2W(CO)_4$.

Example 7: Synthesis of $PhMe_2SiCo(CO)_4$

[0091] 5 g of $Co_2(CO)_8$ and 40 mL of dry pentane were charged into a 100 mL flask under N_2, followed by the addition of 4.38 g of $PhMe_2SiH$. After stirring for 1 hr, pentane and excess PhMe2SiH were removed under reduced pressure. The liquid product was purified by distillation under reduced pressure. NMR confirmed the product to be $PhMe_2SiCo(CO)_4$, as shown in Fig. 13.

Example 8: Deposition of Co thin film using $EtMe_2SiCo(CO)_4$ compound and NH_3 gas as co-reagent.

[0092] $EtMe_2SiCo(CO)_4$ compound in a bubbler was heated at 60 °C, while the NH_3 gas was at room temperature. The temperature of the substrate holder was 200 °C. The carrier gas for Co reagent was Ar containing 5% H_2. The flow rate of both was ca. 200 sccm. The pressure in the reaction chamber was 500 mbar. Substrates used were glass slide, Cu slide and TiN slide. Deposition was carried out for 6 minutes. All substrates were coated with shining Co thin film.

Example 9. Deposition of Co thin film using $Et_3SiCo(CO)_4$ compound and methanol as co-reagent.

[0093] $Et_3SiCo(CO)_4$ compound in a bubbler was heated at 60 °C, while methanol was cooled to 0 °C. The temperature of the substrate holder was 200 °C. The carrier gas for Co reagent was Ar containing 5% H_2. The flow rate of both was ca. 200 sccm. The pressure in the reaction chamber was 500 mbar. Substrates used were glass slide, Cu slide and TiN slide. Deposition was carried out for 10 minutes. All substrates were coated with shining Co thin film.

Example 10. Deposition of Fe thin film using $(Et_3Si)_2Fe(CO)_4$ compound and NH_3 as co-reagent

[0094] $(Et_3Si)_2Fe(CO)_4$ compound in a bubbler was heated at 80 °C, while the NH_3 gas was at room temperature. The temperature of the substrate holder was 250 °C. The carrier gas for Co reagent was Ar containing 5% H_2. The flow rate of both was ca. 200 sccm. The pressure in the reaction chamber was 500 mbar. Substrates used were glass slide, Cu slide and TiN slide. Deposition was carried out for 10 minutes. Fe deposition was confirmed by EDX.

Example 11. Deposition of CoO thin film using $EtMe_2SiCo(CO)_4$ compound and O_2 gas as co-reagent.

[0095] $EtMe_2SiCo(CO)_4$ compound in bubbler was heated at 60 °C while the methanol was at room temperature. The temperature of the substrate holder was 200 °C. The carrier gas for Co reagent was N_2. The flow rate of both was ca. 200 sccm. The pressure in the reaction chamber was 500 mbar. Substrates used were glass slide, and TiN slide. Deposition was carried out for 6 minutes. All substrates were coated with CoO thin film. During the deposition air was present in the reactor system, resulting in higher oxygen content in the Co film that was deposited. This shows that CoO can be grown with O_2 as co-reagent.

Example 12. Deposition of Co thin film using $^{t}BuMe_2SiCo(CO)_4$ compound and NH_3/H_2 gas mixture as co-reagent.

[0096] $^{t}BuMe_2SiCo(CO)_4$ compound in a bubbler was heated at 40 °C, while the NH_3/H_2 gas mixture containing 25% H_2 was kept at room temperature. The temperature of the reactor was 200 °C. The carrier gas for Co reagent was N_2. The flow rate of both was 200 sccm. The pressure in the reaction chamber was 100 Torr. Deposition was carried out for 30 minutes. A resistivity of 6.09×10^{-5} µΩcm was achieved.

[0097] Fig. 14 shows the conductivity of the cobalt films obtained as a function of hydrogen/ammonia mixture, demonstrating that good quality films with high conductivities can be prepared using a hydrogen/ammonia mixture with greater than about 25% hydrogen.

[0098] Fig. 15 shows that the growth rate flattens out when about 25-80% hydrogen is used with ammonia, confirming the conductivity data from Fig. 14. Film growth stability is observed.

Example 13. Selective deposition of Co thin film on Co seed layers using $EtMe_2SiCo(CO)_4$ compound and NH_3 gas as co-reagent.

[0099] $EtMe_2SiCo(CO)_4$ compound in bubbler was heated at 40 °C while the NH_3 gas was at room temperature. The temperature of the substrate holder was 200 °C. The carrier gas for Co reagent was N_2. The flow rate of both was ca. 200 sccm. The pressure in the reaction chamber was 90 torr. Initially low pressure CVD was carried out to deposit seed layers of Co metal on Cu Substrate. This was then followed with selective ALD growth of cobalt on the seed cobalt layers. During the CVD of cobalt seed, there was induction period on the SiO_2 surface compared to Cu which allows for selective deposition of cobalt on copper as compared to silicon oxide, as shown in Fig. 16.

[00100] The following reference characters are used in Fig. 4: 1 Inert carrier gas input; 2 Mass flow controller; 3 Valve controlling direct input of inert carrier gas to reaction chamber; 4 Valve controlling input of inert carrier gas to bubbler; 5 Valve controlling input of inert carrier gas containing vaporized precursor to reaction chamber; 6 Bubbler containing compound; 7 Compound; 8 Input of gaseous co-reagent or inert carrier gas for liquid co-reagent; 9 Mass flow controller; 10

Valve controlling direct input of gaseous co-reagent or inert carrier gas; 11 Valve controlling input of inert carrier gas to bubbler; 12 Valve controlling input of inert carrier gas containing vaporized co-reagent to reaction chamber; 13 Bubbler containing co-reagent; 14 Liquid co-reagent; 15 Quartz tube wall of reaction chamber; 16 Substrate; 17 Graphite substrate holder with heater and thermocouple; 18 Heater; 19 Thermocouple; 20 Pressure regulating valve to vacuum pump controlling gas pressure in reaction chamber; and 21 Metal flanges for reaction chamber.

[00101] The scope of the claims should not be limited by the illustrated embodiments set forth as examples, but should be given the broadest interpretation consistent with a purposive construction of the claims in view of the description as a whole.

CLAIMS

What is claimed is:

1. An organometallic compound corresponding in structure to Formula 1:

$$[(R^1R^2R^3\ (A))_x\text{-}M(CO)_y]_z$$

wherein R^1, R^2 and R^3 are independently selected from the group consisting of H, a lower alkyl group and a phenyl group optionally substituted with at least one independently selected lower alkyl group, with the proviso that at least one of R^1, R^2 and R^3 must be other than H;

M is selected from the group consisting of the cobalt group metals, the iron group metals, the manganese group metals, and the chromium group metals;

A is selected from the group consisting of Si, Ge, and Sn; and wherein:

$x = 1$, $y = 4$, and $z = 1$ when M is selected from the group consisting of a cobalt group metal,

$x = 1$, $y = 5$, and $z = 1$ when M is selected from the group consisting of a manganese group metal,

$x = 2$, $y = 4$, and $z = 1$ when M is selected from the group consisting of a chromium group metal, and

$x = 2$, $y = 4$, and $z = 1$ or, alternatively, $x = 1$, $y = 4$, and $z = 2$ when M is selected from the group consisting of an iron group metal.

2. The compound of claim 1, wherein A is Si.
3. The compound of claim 1, wherein A is Ge.
4. The compound of claim 1, wherein A is Sn.
5. The compound of claim 2, wherein M is a cobalt group metal.
6. The compound of claim 2, wherein M is an iron group metal.
7. The compound of claim 2, wherein M is a manganese group metal.
8. The compound of claim 2, wherein M is a chromium group metal.
9. The compound of claim 3, wherein M is a cobalt group metal.
10. The compound of claim 3, wherein M is an iron group metal.
11. The compound of claim 3, wherein M is a manganese group metal.
12. The compound of claim 3, wherein M is a chromium group metal.
13. The compound of claim 4, wherein M is a cobalt group metal.
14. The compound of claim 4, wherein M is an iron group metal.
15. The compound of claim 4, wherein M is a manganese group metal.

16. The compound of claim 4, wherein M is a chromium group metal.
17. The compound of claim 5, wherein M is Co.
18. The compound of claim 17, wherein R^1, R^2 and R^3 are independently selected from the group consisting of lower alkyl groups having from 1 to 5 carbon atoms.
19. The compound of claim 18, wherein at least one of R^1, R^2 and R^3 is a methyl group.
20. The compound of claim 19, wherein at least two of R^1, R^2 and R^3 are methyl groups.
21. The compound of claim 20, wherein one of R^1, R^2 and R^3 is a lower alkyl group having from 2 to 4 carbon atoms.
22. A compound selected from the group consisting of $EtMe_2SiCo(CO)_4$, $Et_3SiCo(CO)_4$, $^{t}BuMe_2SiCo(CO)_4$, $(Et_3Si)_2Fe(CO)_4$, $Et_3SiMn(CO)_5$, $(PhMe_2Si)_2W(CO)_4$ and $PhMe_2SiCo(CO)_4$.
23. The compound of claim 22 wherein the compound is $^{t}BuMe_2SiCo(CO)_4$.
24. A method for forming a metal-containing film by a vapor deposition process, the method comprising:
    a) providing at least one substrate,
    b) delivering to said substrate at least one compound of Formula 1 in the gaseous phase,
    c) simultaneously with or subsequently to step b), delivering to said substrate at least one co-reagent in the gaseous phase, and
    d) removing gaseous reaction products.
25. The method of claim 24 wherein A is Si.
26. The method of claim 25 wherein M is a cobalt group metal.
27. The method of claim 26 wherein M is cobalt.
28. The method of claim 27 wherein R^1, R^2 and R^3 are independently selected from the group consisting of lower alkyl groups having from 1 to 5 carbon atoms.
29. The method of claim 28 wherein the compound is selected from the group consisting of $(Me_2Et)SiCo(CO)_4$, $(Et)_3Si\ Co(CO)_4$ and $^{t}BuMe_2SiCo(CO)_4$.
30. The method of claim 29 wherein the compound is $^{t}BuMe_2SiCo(CO)_4$.
31. The method of claim 28 wherein the metal containing film is substantially pure metal and the co-reagent is selected from the group consisting of H_2, ammonia, a lower alkyl amine, a lower alcohol, hydrazine and a substituted hydrazine.
32. The method of claim 31 wherein the co-reagent is selected from the group consisting of H_2, ammonia and methanol.
33. The method of claim 32, wherein the co-reagent is ammonia.

34. The method of claim 32, wherein the co-reagent is a mixture of ammonia and H_2.
35. The method of claim 29, wherein the co-reagent is ammonia.
36. The method of claim 29, wherein the co-reagent is a mixture of ammonia and H_2.
37. The method of claim 30, wherein the co-reagent is ammonia.
38. The method of claim 30, wherein the co-reagent is a mixture of ammonia and H_2.
39. The method of claim 24 wherein the metal containing film is metal oxide and the co-reagent is selected from the group consisting of H_2O, O_2, O_3, and a lower alcohol.
40. The method of claim 39, wherein the compound of Formula 1 is a compound of claim 21.
41. The method of claim 24 wherein the metal containing film is metal nitride and the co-reagent is selected from the group consisting of ammonia, a lower alkyl amine, a lower alcohol, hydrazine and a substituted hydrazine.
42. The method of claim 41, wherein the compound of Formula 1 is a compound of claim 21.
43. The method of claim 24 wherein the metal containing film is metal phosphide and the co-reagent is selected from the group consisting of PH_3 and a lower alkyl phosphine.
44. The method of claim 24 wherein the metal containing film is metal sulphide and the co-reagent is selected from the group consisting of H_2S and a lower alkyl thiol.
45. The method of claim 24 wherein the vapor deposition process is chemical vapor deposition.
46. The method of claim 24 wherein the vapor deposition process is atomic layer deposition.
47. A method of selectively depositing a metal-containing film on one or more of a plurality of substrates, the method comprising:
    a) providing at least two substrates comprising different materials, one of said substrate materials having an affinity for ligand component A of a compound of Formula 1,
    b) delivering to said substrates at least one compound of Formula 1 in the gaseous phase,
    c) simultaneously with or subsequently to step b), delivering to said substrate at least one co-reagent in the gaseous phase, and
    d) removing gaseous reaction products.
48. The method of claim 47 wherein the substrate material having an affinity is an oxide.
49. The method of claim 48 wherein the substrate material is SiO_2.
50. The method of claim 49, wherein the compound of Formula 1 is a compound of claim 21.
51. The method of claim 47 wherein the substrate material having an affinity is a nitride.
52. The method of claim 51 wherein the substrate material is SiN.
53. The method of claim 52, wherein the compound of Formula 1 is a compound of claim 21.

54. A method of selectively depositing a metal-containing film on one or more of a plurality of substrates, the method comprising:
    - a) providing at least two substrates comprising different materials, one of said substrate materials having an affinity for CO,
    - b) delivering to said substrate at least one compound of Formula 1 in the gaseous phase,
    - c) simultaneously with or subsequently to step b), delivering to said substrate at least one co-reagent in gaseous phase, and
    - d) removing gaseous reaction products.
55. The method of claim 54 wherein the substrate material having an affinity is an elemental metal.
56. The method of claim 55 wherein the substrate material having an affinity is selected from the group consisting of Ni, Pd, Pt, Co, Rh, Ir, Fe, Ru, and Os.
57. The method of claim 56 wherein the metal containing film is Co.
58. The method of claim 57 in which the compound of Formula 1 is a compound of claim 21.

AMENDED CLAIMS

received by the International Bureau on 15 September 2016 (15.09.2016)

What is claimed is:

1. An organometallic compound corresponding in structure to Formula 1:

(R1R2R3 (Si))-Co(CO)4

wherein R1, R2 and R3 are independently selected from the group consisting of a lower alkyl group and a phenyl group optionally substituted with at least one independently selected lower alkyl group, with the proviso that at least two of R1, R2 and R3 are methyl groups.

2. The compound of claim 1, wherein one of R1, R2 and R3 is a lower alkyl group having from 2 to 4 carbon atoms.

3. A compound selected from the group consisting of EtMe2SiCo(CO)4, tBuMe2SiCo(CO)4, and PhMe2SiCo(CO)4.

4. The compound of claim 2 wherein the compound is tBuMe2SiCo(CO)4.

5. A method for forming a metal-containing film by a vapor deposition process, the method comprising:

a) providing at least one substrate,

b) delivering to said substrate at least one compound of Formula 1 in the gaseous phase,

c) simultaneously with or subsequently to step b), delivering to said substrate at least one co-reagent in the gaseous phase, and

d) removing gaseous reaction products.

6. The method of claim 5 wherein one of R1, R2 and R3 is a lower alkyl group having from 2 to 4 carbon atoms.

7. The method of claim 6 wherein the compound is selected from the group consisting of (Me2Et)SiCo(CO)4, (Et)3Si Co(CO)4 and tBuMe2SiCo(CO)4.

8. The method of claim 7 wherein the compound is tBuMe2SiCo(CO)4.

9. The method of claim 5 wherein the metal containing film is substantially pure metal and the co-reagent is selected from the group consisting of H2, ammonia, a lower alkyl amine, a lower alcohol, hydrazine and a substituted hydrazine.

10. The method of claim 9 wherein the co-reagent is selected from the group consisting of H2, ammonia and methanol.

11. The method of claim 6, wherein the co-reagent is ammonia.

12. The method of claim 6, wherein the co-reagent is a mixture of ammonia and H2.

13. The method of claim 7, wherein the co-reagent is ammonia.

14. The method of claim 7, wherein the co-reagent is a mixture of ammonia and H2.

15. The method of claim 8, wherein the co-reagent is ammonia.

16. The method of claim 8, wherein the co-reagent is a mixture of ammonia and H2.

17. The method of claim 5 wherein the metal containing film is metal oxide and the co-reagent is selected from the group consisting of H2O, O2, O3, and a lower alcohol.

18. The method of claim 17, wherein the compound of Formula 1 is a compound of claim 2.

19. The method of claim 5 wherein the metal containing film is metal nitride and the co-reagent is selected from the group consisting of ammonia, a lower alkyl amine, a lower alcohol, hydrazine and a substituted hydrazine.

20. The method of claim 19, wherein the compound of Formula 1 is a compound of claim 2.

21. The method of claim 5 wherein the metal containing film is metal phosphide and the co-reagent is selected from the group consisting of PH3 and a lower alkyl phosphine.

22. The method of claim 5 wherein the metal containing film is metal sulphide and the co-reagent is selected from the group consisting of H2S and a lower alkyl thiol.

23. The method of claim 5 wherein the vapor deposition process is chemical vapor deposition.

24. The method of claim 5 wherein the vapor deposition process is atomic layer deposition.

25. A method of selectively depositing a metal-containing film on one or more of a plurality of substrates, the method comprising:

a) providing at least two substrates comprising different materials, one of said substrate materials having an affinity for Si,

b) delivering to said substrates at least one compound of Formula 1 in the gaseous phase,

c) simultaneously with or subsequently to step b), delivering to said substrate at least one co-reagent in the gaseous phase, and

d) removing gaseous reaction products.

26. The method of claim 25 wherein the substrate material having an affinity is an oxide.

27. The method of claim 26 wherein the substrate material is SiO2.

28. The method of claim 27, wherein the compound of Formula 1 is a compound of claim 2.

29. The method of claim 27, wherein the compound of Formula 1 is a compound of claim 3.

30. The method of claim 27, wherein the compound of Formula 1 is the compound of claim 4.

31. The method of claim 25 wherein the substrate material having an affinity is a nitride.

32. The method of claim 29 wherein the substrate material is SiN.

33. The method of claim 30, wherein the compound of Formula 1 is a compound of claim 2.

34. The method of claim 30, wherein the compound of Formula 1 is a compound of claim 3.

35. The method of claim 30, wherein the compound of Formula 1 is the compound of claim 4.

36. A method of selectively depositing a metal-containing film on one or more of a plurality of substrates, the method comprising:

a) providing at least two substrates comprising different materials, one of said substrate materials having an affinity for CO,

b) delivering to said substrate at least one compound of Formula 1 in the gaseous phase,

c) simultaneously with or subsequently to step b), delivering to said substrate at least one co-reagent in gaseous phase, and

d) removing gaseous reaction products.

37. The method of claim 36 wherein the substrate material having an affinity is an elemental metal.

38. The method of claim 37 wherein the substrate material having an affinity is selected from the group consisting of Ni, Pd, Pt, Co, Rh, Ir, Fe, Ru, and Os.

39. The method of claim 38 wherein the metal containing film is Co.

40. The method of claim 39 in which the compound of Formula 1 is a compound of claim 2.

41. The method of claim 39 in which the compound of Formula 1 is a compound of claim 3.

42. The method of claim 39 in which the compound of Formula 1 is the compound of claim 4.

STATEMENT UNDER ARTICLE 19 (1)

Responsive to the International Search Report, Claim 1 has been amended to recite subject matter neither disclosed in, nor obvious in view of, the cited prior art. Claim 1, as amended, incorporate the limitations of original claims 2, 5, 17, 18, 19 and 20. It is believed that the revised set of claims can be distinguished over the art. With respect to the composition-of-matter claims 1-4, the compounds so-claimed are, unexpectedly, more thermally stable and more volatile than compounds of the art. Certain compounds encompassed by claim 1 have been disclosed, but have never actually been synthesized and, therefore, their properties have never been determined. As such, these compounds can be considered as a selection from a broader family of compounds generically disclosed in the art. Compounds of the invention contain two types of R groups attached to the Si atom. This results in a compound which is liquid in nature, enabling better and more consistent delivery during the deposition process. Further, by having two different R groups, control of the second group may be used to increase the thermal stability of the compound, such that delivery of the compound to the deposition chamber is achieved without decomposition in the delivery lines or decomposition in the reaction chamber (which results in the generation of impurities in the final film).Thus, the use of a compound of the invention in the vapour deposition processes disclosed results in the deposition of a better quality of film compared to films prepared according to methods of the art. Compounds of the invention are also useful for the selective deposition of metal-containing films on one substrate in the presence of other substrates.

Fig. 1

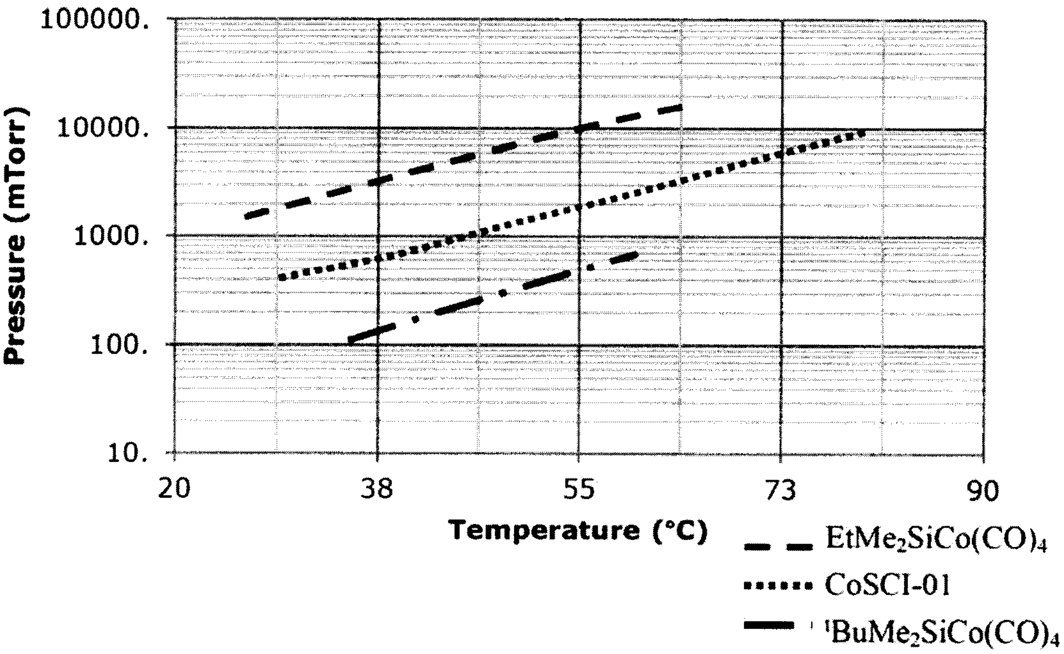

100000.
10000.
1000.
100.
10.
Pressure (mTorr)
20
38
55
73
90
Temperature (°C)
$EtMe_2SiCo(CO)_4$
CoSCI-01
$^tBuMe_2SiCo(CO)_4$

Fig. 2

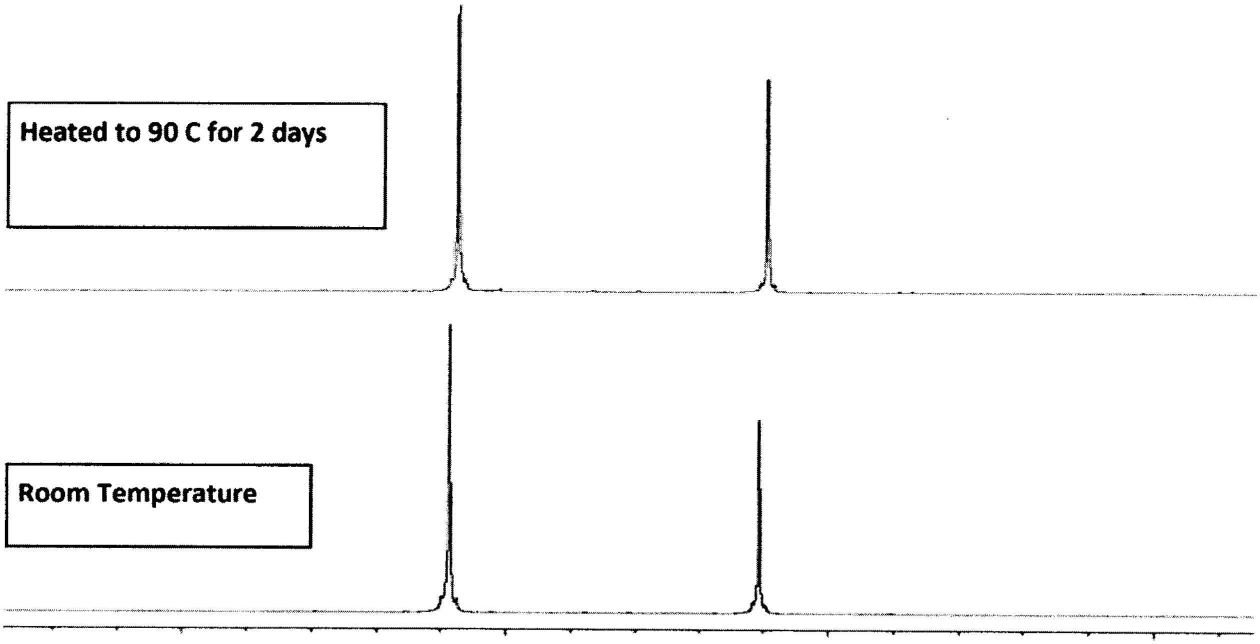

Heated to 90 C for 2 days
Room Temperature

Fig. 3

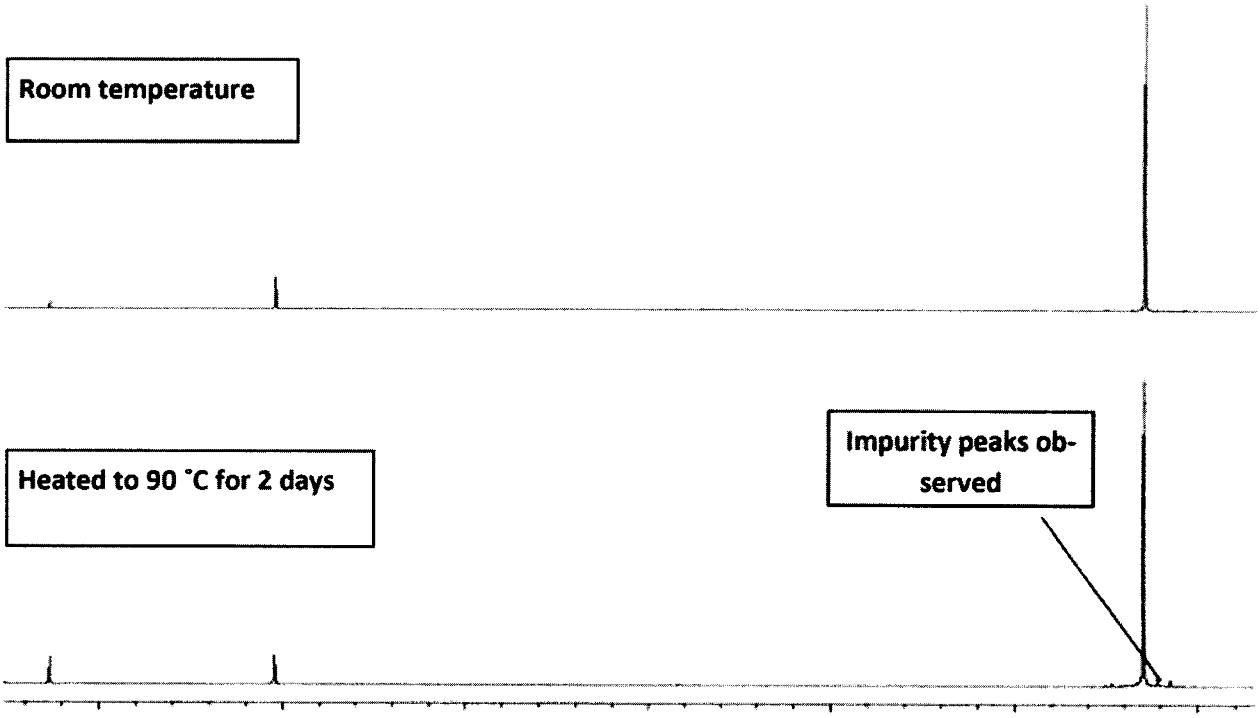

Room temperature
Heated to 90 ˚C for 2 days
Impurity peaks observed

Fig. 4

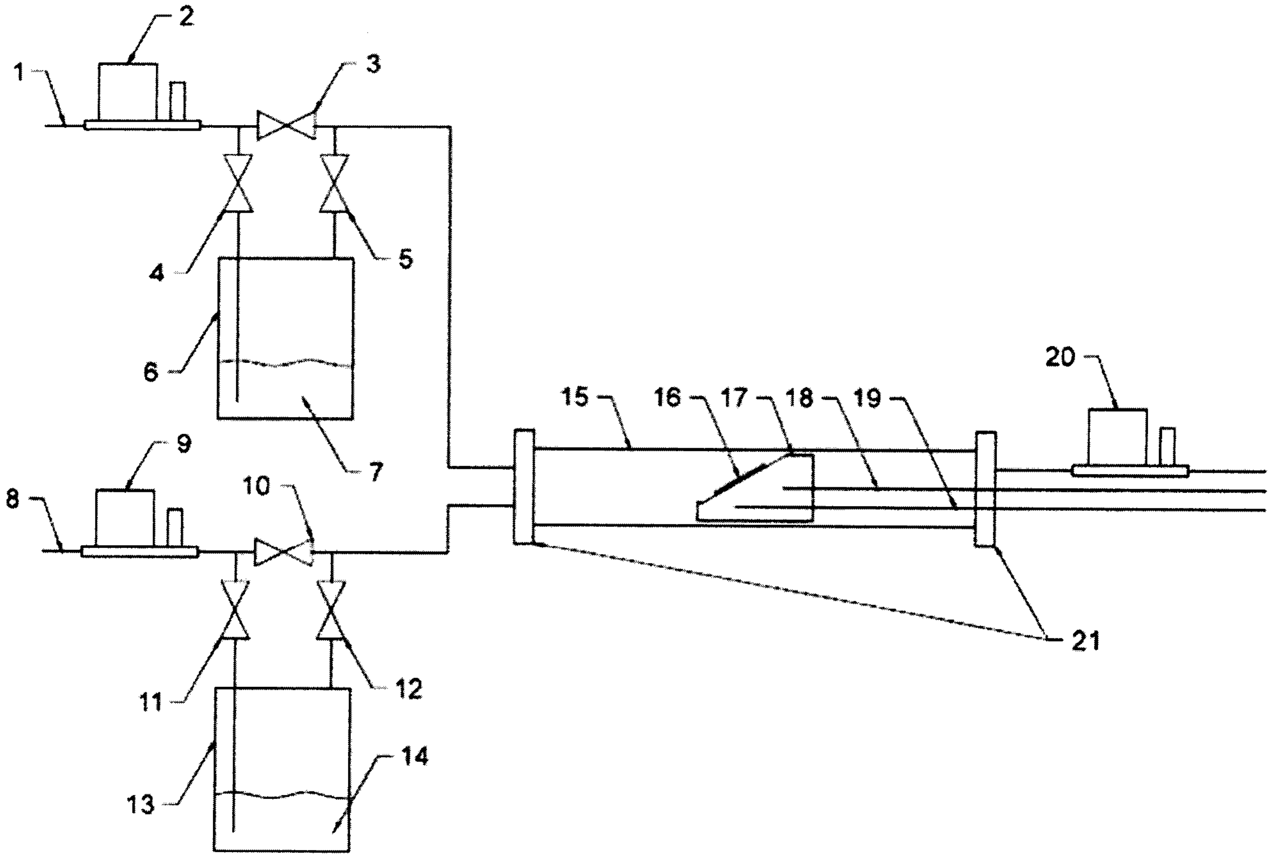
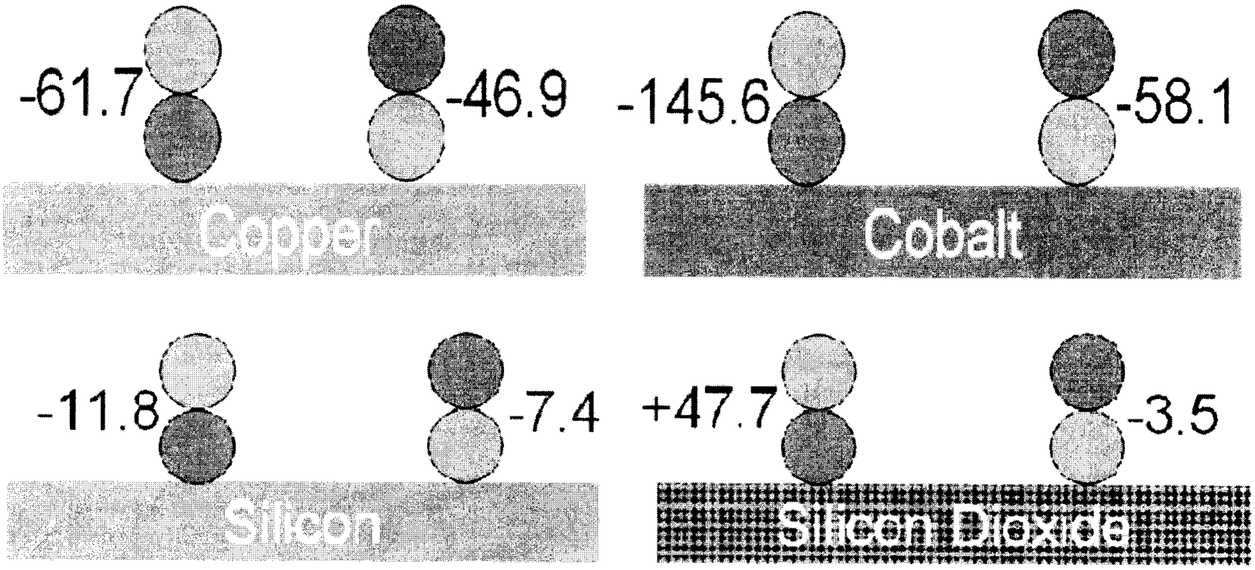

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21

Fig. 5



Binding energies in kcal/mol

Figure 6

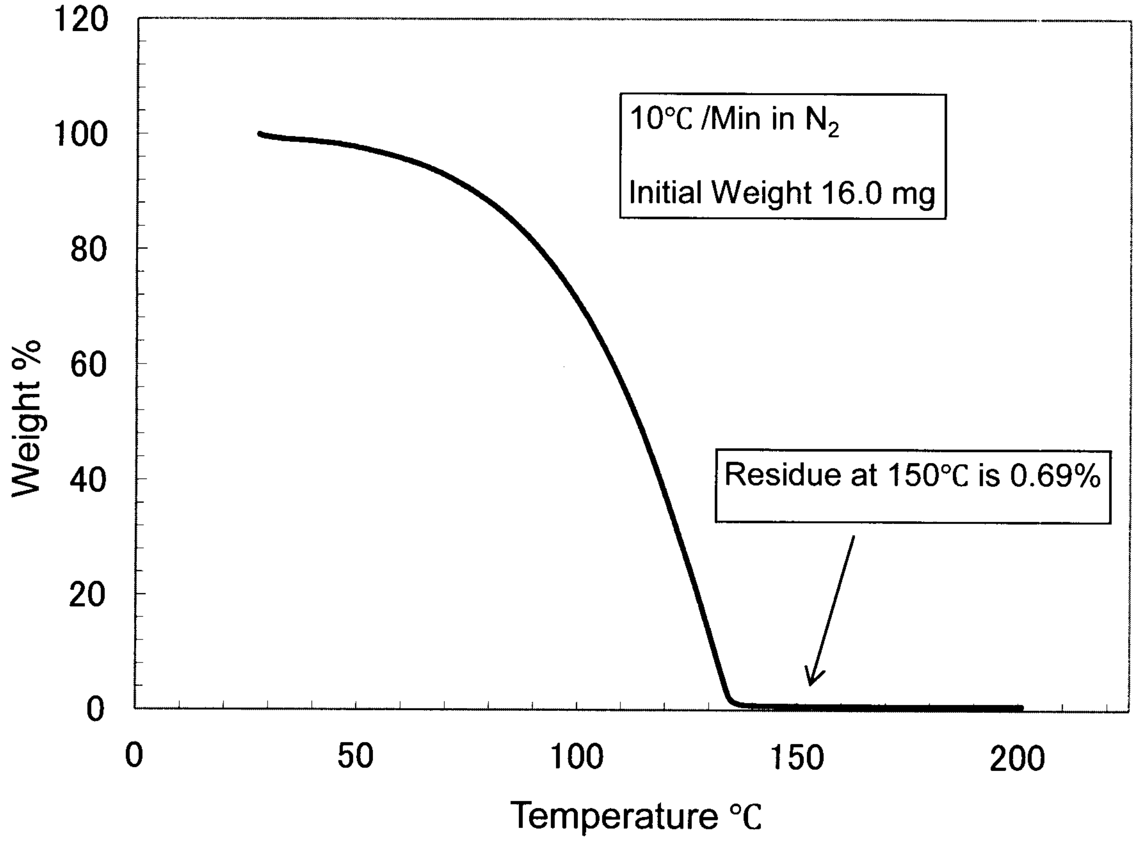

120
100
80
60
40
20
0
Weight %
0
50
100
150
200
Temperature °C
10°C /Min in N2
Initial Weight 16.0 mg
Residue at 150°C is 0.69%

Fig. 7

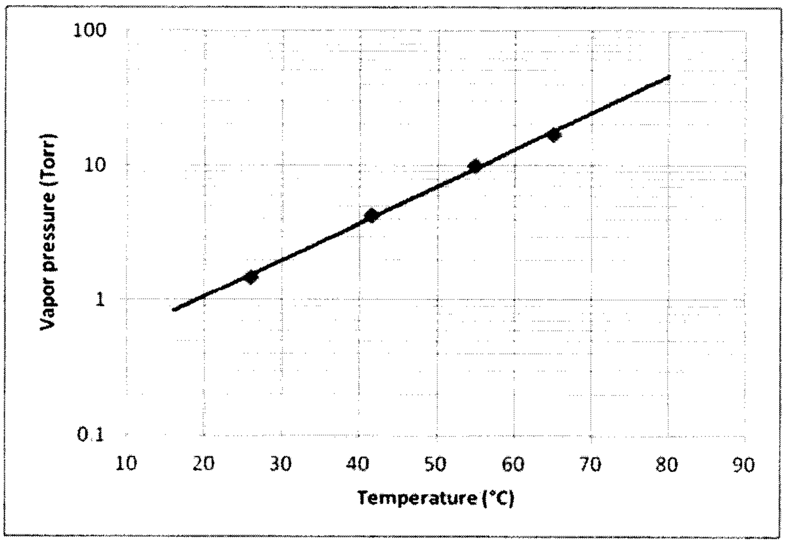

100
10
1
0.1
Vapor pressure (Torr)
10
20
30
40
50
60
70
80
90
Temperature (°C)

Figure 8

Figure 9

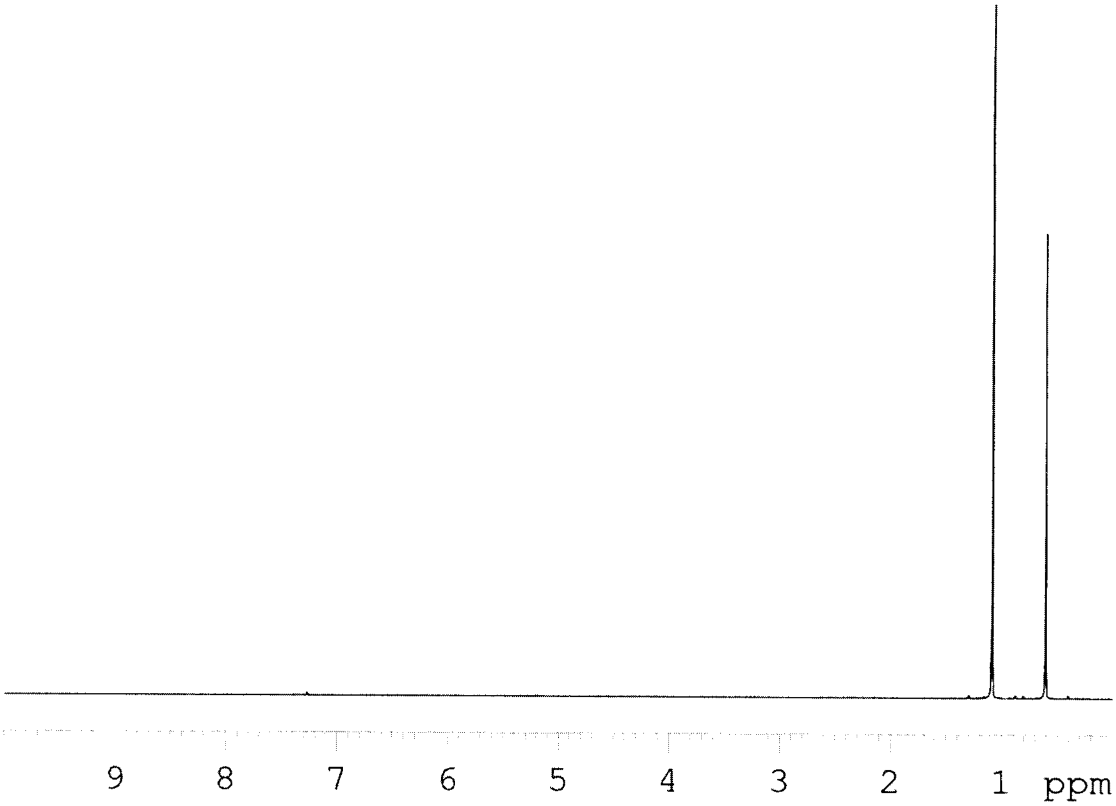


Fig. 10

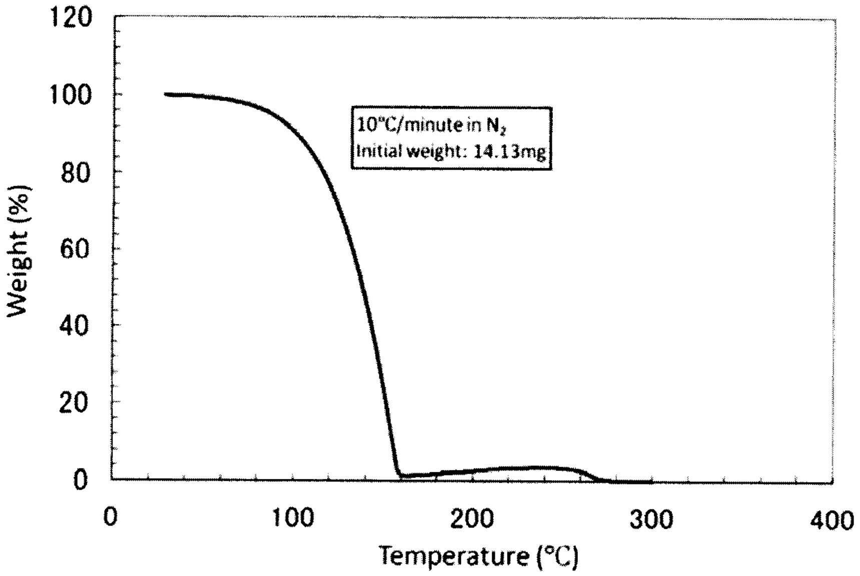

120
100
80
60
40
20
0
Weight (%)
10°C/minute in N_2
Initial weight: 14.13mg
0
100
200
300
400
Temperature (°C)

Fig. 11

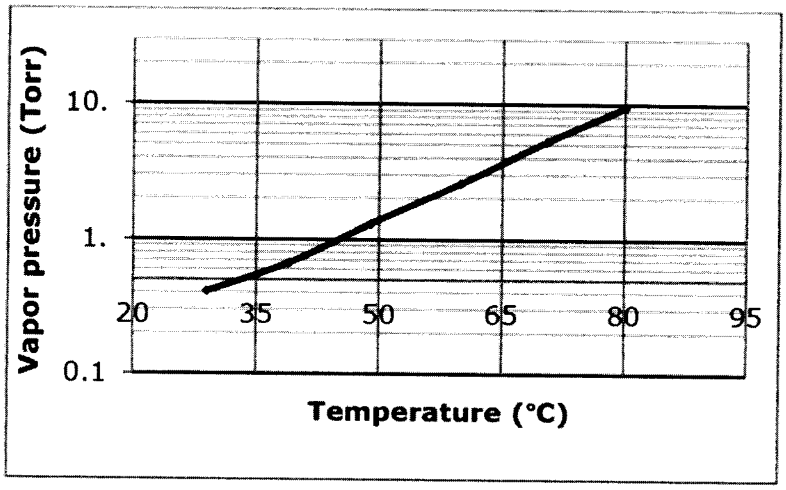

Vapor pressure (Torr)
10.
1.
0.1
20
35
50
65
80
95
Temperature (°C)

Fig. 12

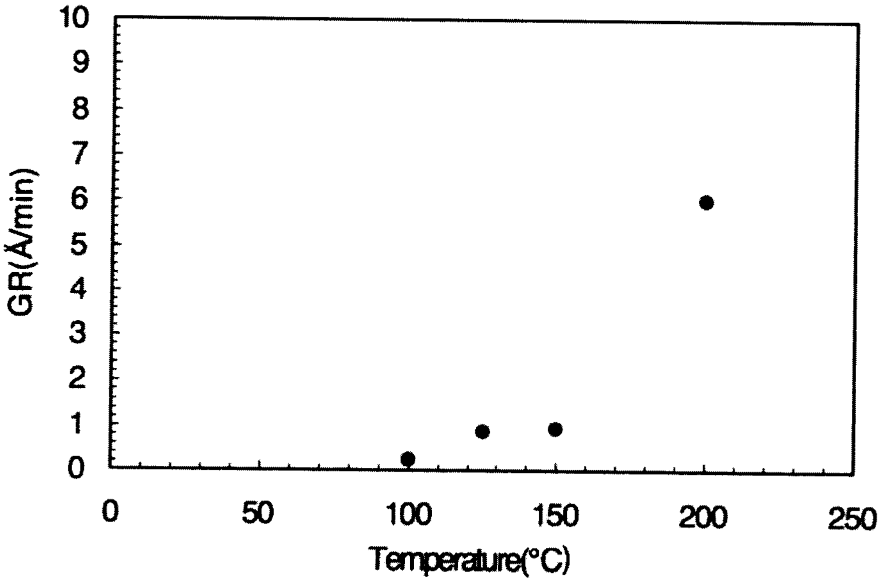

GR(Å/min)
10
9
8
7
6
5
4
3
2
1
0
0
50
100
150
200
250
Temperature(°C)

Figure 13

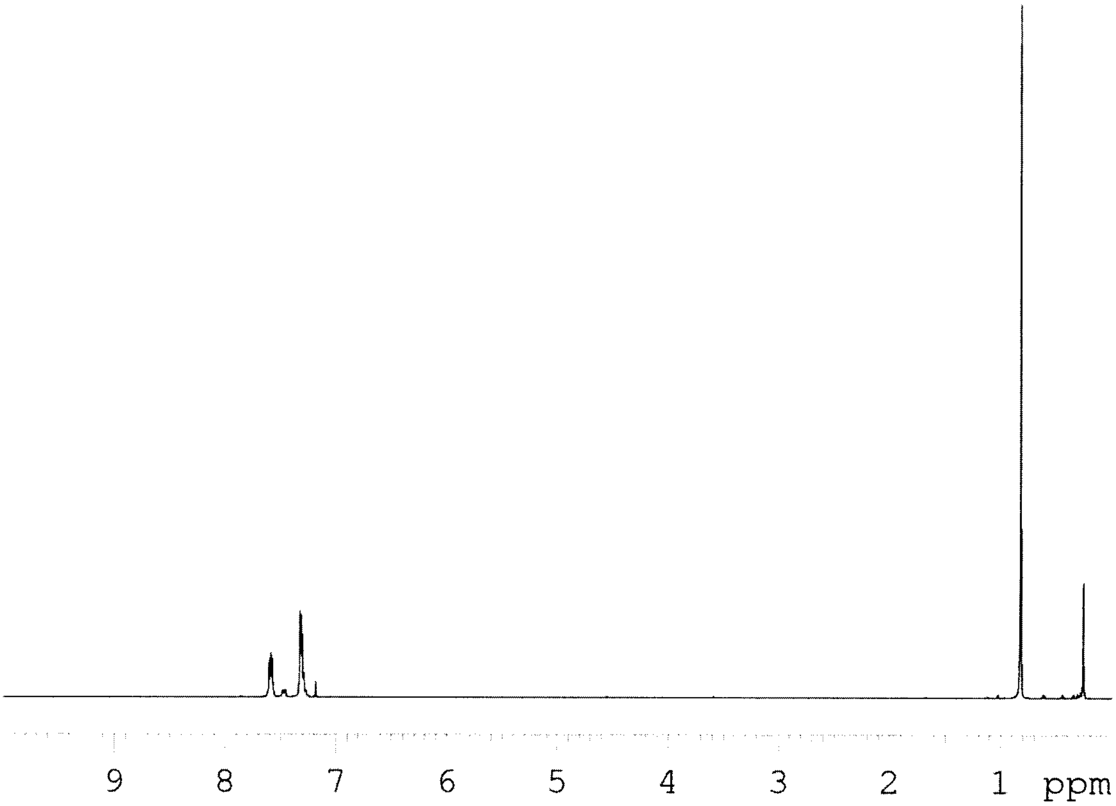


Fig. 14

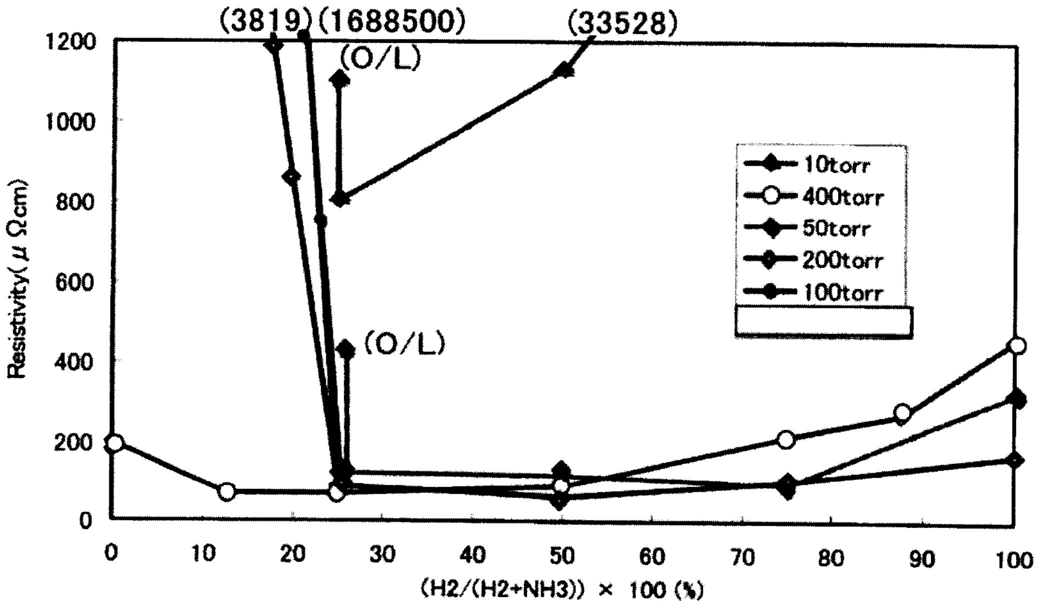

(3819)
(1688500)
(33528)
(O/L)
(O/L)
Resistivity(μ Ωcm)
1200
1000
800
600
400
200
0
0
10
20
30
40
50
60
70
80
90
100
(H2/(H2+NH3)) × 100 (%)
10torr
400torr
50torr
200torr
100torr

Fig. 15

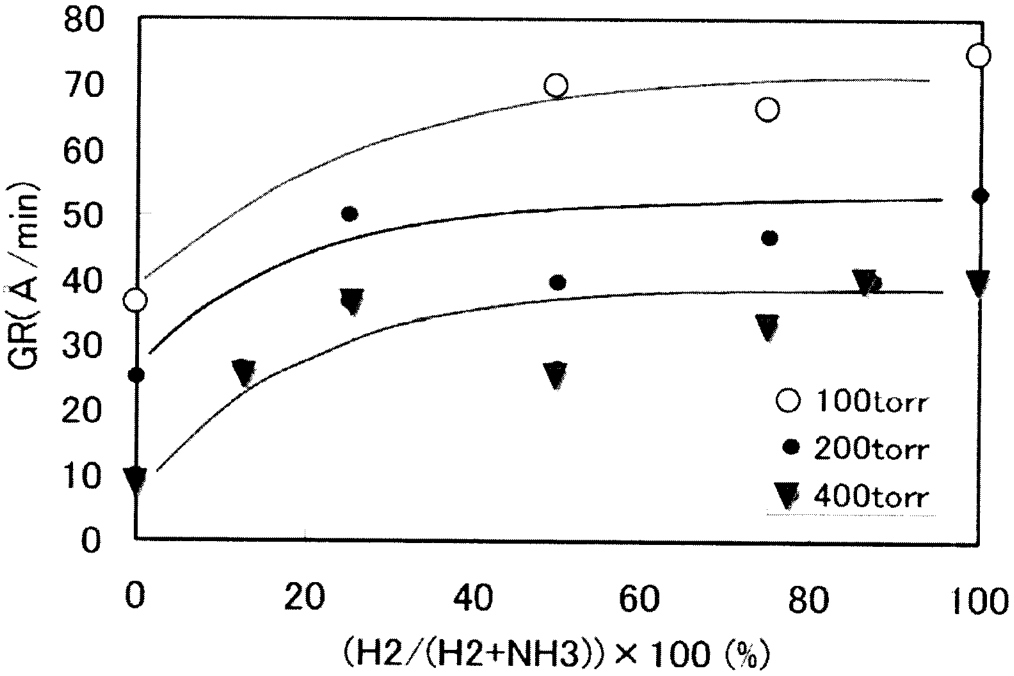
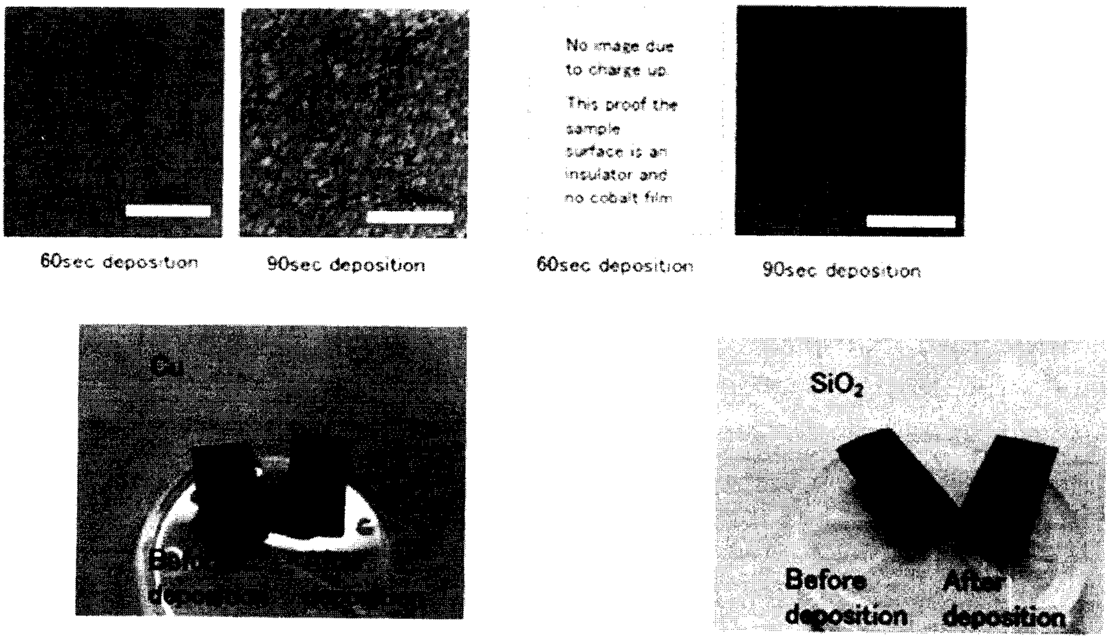


Fig. 16


60sec deposition

90sec deposition

No image due to charge up.

This proof the sample surface is an insulator and no cobalt film

60sec deposition

90sec deposition

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2016/050481

A. CLASSIFICATION OF SUBJECT MATTER
IPC: ***C07F 7/08*** (2006.01) , ***C07F 7/22*** (2006.01) , ***C07F 7/30*** (2006.01) , ***C23C 16/18*** (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC (2006.01): ***C07F 7/08***, ***C07F 7/22***, ***C07F 7/30***, ***C23C 16/18***

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
STN (Registry, CAPlus), Canadian Patent Database (CPD)
Keywords: cvd, vapor deposition, ald, layer deposition

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	WO 2014/118748 A1 (GATINEAU et al.) 07 August 2014 (07-08-2014) *see page 12, lines 16-31, page 13, lines 3-13 and claims 1, 3-5, 7, 11, 13-21*	1, 2, 5, 17-42, 45, 46, 54-56 43, 44, 47-53, 57, 58
X Y	WO2014/118750 A1 (GATINEAU et al.) 07 August 2014 (07-08-2014) *see page11, lines 2-12, page 13, lines 10-25 and claims 1, 2, 6, 8, 9 and 11-17*	1, 2, 7, 18-22, 24, 39-42, 45, 46,54-56 43, 44, 47-53, 57, 58
X	VEERANA et al., "Synthesis and characterization of bimetallic nickel and cobalt carbonyl complexes containing stannyl groups", *Journal of Cluster Science* (2010), 21(3), 417-426 *see compound 3*	1, 4, 13
X	WEBB et al., "Novel carbene complexes from triphenyl- and trimethylgermylpentacarbonyl manganese", *Journal of Organometallic Chemistry* (1973), 59, C21-C23 *see 2nd paragraph*	1, 3, 9

☑ Further documents are listed in the continuation of Box C.

☑ See patent family annex.

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Date of the actual completion of the international search
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INTERNATIONAL SEARCH REPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CAREY et al. “Reactivity of metal-metal bonds. IV. Reaction of sulfur dioxide with compounds containing tin-tin and tin-manganese bonds”, *Canadian Journal of Chemistry* (1968), 46(4), 643-7 *see the abstract*	1, 4, 15
X	ABAKUMOV et al., “Infrared study of the interaction between carbonyl complexes of manganese, iron, cobalt, and rhenium and bisorganometallic derivatives of mercury”, *Metalloorganicheskaya Khimiya* (1992), 5(4), 941-5 *see table 1*	1, 3, 11
X	DELBEKE et al., “Transition metal chemistry. VI. Calculation of force constants in the CO stretching region of cis-disubstituted Group VI metal carbonyls and iron carbonyl complexes with C2v symmetry”, *Journal of Organometallic Chemistry* (1970), 25(1), 219-22 *see abstract and table 1*	1-4, 6, 10, 14, 22
X	AUDET(née Christie) et al., “Transition-metal carbonyl derivatives of the germanes. Part 18. Tetracarbonylbis(permethylgermyl)iron compounds [Fe(CO)4(GeMe3-xHx)(GeMe3-yHy)] for x,y = 0-3”, *Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry* (1972-1999) (1988), (10), 2635-43 *see scheme 2*	1, 3, 11

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
WO2014118748A1	07 August 2014 (07-08-2014)	WO2014118748A1 JP2016513086A KR20150111359A US2016010204A1	07 August 2014 (07-08-2014) 12 May 2016 (12-05-2016) 05 October 2015 (05-10-2015) 14 January 2016 (14-01-2016)
WO2014118750A1	07 August 2014 (07-08-2014)	WO2014118750A1 JP2016513087A	07 August 2014 (07-08-2014) 12 May 2016 (12-05-2016)