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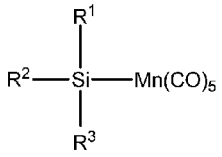
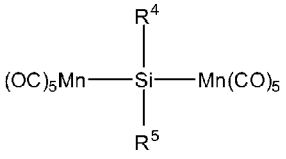


(I)



(II)

(57) Abstract: Manganese-containing compounds, their synthesis, and their use for the deposition of manganese containing films are disclosed. The disclosed manganese-containing compounds have one of the formulae (I) and (II) wherein each of R^1, R^2, R^3 R^4, and R^5 is independently selected from the group consisting of Hydrogen; halogen; linear, cyclic or branched hydrocarbons;; primary amino ligands (-NHR); and secondary amino ligands (-NRR?), with R and R' independently being H or a linear, cyclic or branched hydrocarbon, provided at least one of R^1, R^2, or R^3 in Formula (I) and R^4 or R^5 in Formula (II) is an amino ligand.

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MANGANESE-CONTAINING COMPOUNDS, THEIR SYNTHESIS, AND USE IN MANGANESE-CONTAINING FILM DEPOSITION

Cross Reference to Related Applications

This application claims the benefit under 35 U.S.C. § 119(e) to U.S. provisional application No. 61/759,175 filed January 31, 2013, the entire contents of each being incorporated herein by reference.

Technical Field

Manganese-containing compounds, their synthesis, and their use for the deposition of manganese-containing films are disclosed.

Background

Chemical Vapor Deposition (CVD) and Atomic Layer Deposition (ALD) have been applied as main deposition techniques for producing thin films for semiconductor devices. These methods enable the achievement of conformal films (metal, oxide, nitride, silicide, etc.) through fine tuning of parameters during the deposition processes. Mainly the film growth is controlled by chemical reactions of metal-containing compounds (precursors) and the development of optimum precursors is essential under prediction of their properties and reaction processes.

Manganese-containing films are becoming important for a variety of electronics and electrochemical applications. For example, manganese silicate ($MnSiO_x$) was found to be an excellent barrier to the diffusion of copper, O_2, and H_2O vapor. The adhesion strength of copper and $MnSiO_x$ was found to be strong enough to meet semiconductor industry requirement for interconnections. Deposited manganese dissolves into the copper surface and diffuses to increase adhesion to capping layer. Also manganese-metal alloys like Mn-Cu, Mn-Pt may serve as seed layers.

Synthesis methods of alkyl or halide silyl manganese pentacarbonyl complexes ($R_3SiMn(CO)_5$) are known. See, e.g., MacDiarmid et al., Properties of

silicon derivatives of cobalt, manganese and iron carbonyls, pp. 431-448; Xu et al., Photochemical synthesis of silyl manganese pentacarbonyls $(CO)_5MnSiR_3$, Huaxue Xuebao, 67(20) pp. 2355-2362 (2009); Xu et al., Study on the photochemical silyl exchange reactions of $(CO)_5MnSiR_3$ with R'_3SiH, Xuebao, 69(8), pp. 999-1006 (2011); Deshong et al., Regioselective opening of epoxides and ethers by (trialkylsilyl)manganese pentacarbonyl complexes. A general strategy for the synthesis of spiroketal lactone and cyclopentenone derivatives, Journal of organic chemistry, 53(20), pp. 4892-4894 (1988); Schmitt et al., Synthesis and applications of metal silicide nanowires, Journal of material chemistry, 20, pp. 223-235 (2010); Higgins et al., Higher manganese silicide nanowires of nowotny chimney ladder phase, Journal of American chemical society 130, pp. 16086-16094 (2008).

Deposition using alkyl or halide silyl manganese pentacarbonyl are also known as precursors for forming manganese-containing films. See, e.g., Kodas et al., The chemistry of metal CVD, 9.2 Classification of precursors pp. 431-433; Aylett et al., Chemical vapor deposition of transition-metal silicides by pyrolysis of silyl transition-metal carbonyl compound, J.C.S. Dalton, pp.2058-2061 (1977); Schmitt et al., Synthesis and applications of metal silicide nanowires, Journal of material chemistry, 20, pp. 223-235 (2010); Higgins et al., Higher manganese silicide nanowires of nowotny chimney ladder phase, Journal of American chemical society 130, pp. 16086-16094 (2008).

A need remains for manganese compounds suitable for deposition of manganese-containing films.

Notation and Nomenclature

Certain abbreviations, symbols, and terms are used throughout the following description and claims, and include:

As used herein, the indefinite article “a” or “an” means one or more.

As used herein, the term “alkyl group” refers to saturated functional groups containing exclusively carbon and hydrogen atoms. Further, the term “alkyl group” refers to linear, branched, or cyclic alkyl groups. Examples of linear alkyl groups

include without limitation, methyl groups, ethyl groups, propyl groups, butyl groups, etc. Examples of branched alkyls groups include without limitation, t-butyl. Examples of cyclic alkyl groups include without limitation, cyclopropyl groups, cyclopentyl groups, cyclohexyl groups, etc.

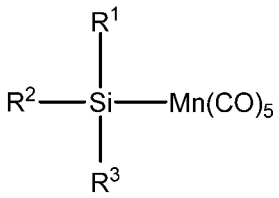
As used herein, the term “hydrocarbon” means a functional group containing exclusively hydrogen and carbon atoms. The functional group may be saturated (containing only single bonds) or unsaturated (containing double or triple bonds).

As used herein, the abbreviation “Me” refers to a methyl group; the abbreviation “Et” refers to an ethyl group; the abbreviation “Pr” refers to any propyl group (i.e., n-propyl or isopropyl); the abbreviation “iPr” refers to an isopropyl group; the abbreviation “Bu” refers to any butyl group (n-butyl, iso-butyl, t-butyl, sec-butyl); the abbreviation “tBu” refers to a tert-butyl group; the abbreviation “sBu” refers to a sec-butyl group; the abbreviation “iBu” refers to an iso-butyl group; the abbreviation “ph” refers to a phenyl group; and the abbreviation “Cp” refers to cyclopentadienyl group.

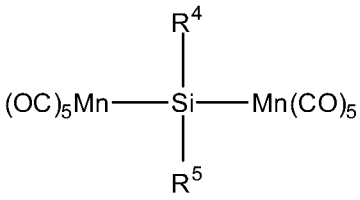
The standard abbreviations of the elements from the periodic table of elements are used herein. It should be understood that elements may be referred to by these abbreviations (e.g., Mn refers to manganese, Si refers to silicon, C refers to carbon, etc.).

Summary

Compounds having one of the following formulae are disclosed:



Formula I



Formula II

wherein each of R^1, R^2, R^3, R^4, and R^5 is independently selected from the group consisting of Hydrogen; a halogen; and linear, cyclic or branched hydrocarbons;

primary amino ligands (-NHR); and secondary amino ligands (-NRR'), with R and R' independently being H or a linear, cyclic or branched hydrocarbon, provided at least one of R^1, R^2, or R^3 in Formula I and R^4 or R^5 in Formula II is an amino ligand. The disclosed compounds may have one or more of the following aspects:

- the Formula I compound including one or two neutral adduct ligands selected from the group consisting of NMe_3, NEt_3, $NiPr_3$, $NMeEt_2$, NC_5H_5, OC_4H_8, Me_2O, and Et_2O;
- the compound having Formula I,
- the compound being $(NMe_2)_3SiMn(CO)_5$,
- the compound being $SiH(NMe_2)_2Mn(CO)_5$,
- the compound being $SiH_2(NMe_2)Mn(CO)_5$,
- the compound being $Si(NEt_2)_3Mn(CO)_5$,
- the compound being $SiH(NEt_2)_2Mn(CO)_5$,
- the compound being $SiH_2(NEt_2)Mn(CO)_5$,
- the compound being $Si(N\text{-}iPr_2)_3Mn(CO)_5$,
- the compound being $SiH(N\text{-}iPr_2)_2Mn(CO)_5$,
- the compound being $SiH_2(N\text{-}iPr_2)Mn(CO)_5$,
- the compound being $Si(NHtBu)_3Mn(CO)_5$,
- the compound being $SiH(NHtBu)_2Mn(CO)_5$,
- the compound being $SiH_2(NHtBu)Mn(CO)_5$,
- the compound being $(CH_2{=}CH)Si(Me)(NMe_2)Mn(CO)_5$,
- the compound being $(CH_2{=}CH)Si(Me)(NEt_2)Mn(CO)_5$,
- the compound being $(CH_2{=}CH)Si(Me)(NiPr_2)Mn(CO)_5$,
- the compound being $(CH_2{=}CH)Si(NEt_2)_2Mn(CO)_5$,
- the compound being $(NHSiMe_3)Si(Me)(H)Mn(CO)_5$,
- the compound being $(CH_2{=}CH)Si(Me)(NMe_2)Mn(CO)_5$,
- the compound being $(CH_2{=}CH)Si(Me)(NEt_2)Mn(CO)_5$,
- the compound being $(CH_2{=}CH)Si(Me)(NiPr_2)Mn(CO)_5$,
- the compound being $(CH_2{=}CH)Si(NEt_2)_2Mn(CO)_5$,
- the compound being $(NHSiMe_3)Si(Me)(H)Mn(CO)_5$,
- the compound having Formula II,

- the compound being $(CO)_5MnSi(NMe_2)_2Mn(CO)_5$,
- the compound being $(CO)_5MnSi(NEt_2)_2Mn(CO)_5$,
- the compound being $(CO)_5MnSi(N\text{-}iPr_2)_2Mn(CO)_5$,
- the compound being $(CO)_5MnSi(NMe_2)(H)Mn(CO)_5$,
- the compound being $(CO)_5MnSi(NEt_2)(H)Mn(CO)_5$,
- the compound being $(CO)_5MnSi(N\text{-}iPr_2)(H)Mn(CO)_5$,
- the compound being $(CO)_5MnSi(NHtBu)(H)Mn(CO)_5$,
- the compound being $(CO)_5MnSi(NHSiMe_3)(Me)Mn(CO)_5$,
- the compound being $(CO)_5MnSi(NHSiMe_3)(Et)Mn(CO)_5$,
- the compound being $(CO)_5MnSi(NHSiMe_3)(iPr)Mn(CO)_5$,
- the compound being $(CO)_5MnSi(NHSiMe_3)(tBu)Mn(CO)_5$,
- the compound being $(CO)_5MnSi(CH{=}CH_2)(NMe_2)Mn(CO)_5$,
- the compound being $(CO)_5MnSi(CH{=}CH_2)(NEt_2)Mn(CO)_5$,
- the compound being $(CO)_5MnSi(CH{=}CH_2)(N\text{-}iPr_2)Mn(CO)_5$, and
- the compound being $(CO)_5MnSi(CH{=}CH_2)(NHtBu)Mn(CO)_5$.

Methods of depositing manganese-containing films are also disclosed. One of the manganese-containing compounds disclosed above is introduced into a reactor having a substrate disposed therein. At least part of the manganese-containing compound is deposited onto the substrate to form the manganese-containing film. The disclosed methods may have one or more of the following aspects:

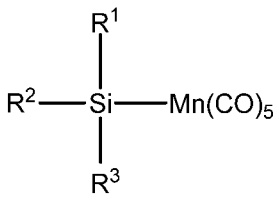
- The depositing step being chemical vapor deposition (CVD);
- The depositing step being atomic layer deposition (ALD);
- The depositing step being plasma enhanced chemical vapor deposition (PECVD);
- The depositing step being plasma enhanced atomic layer deposition (PEALD);
- The depositing step being pulsed chemical vapor deposition (PCVD);
- The depositing step being low pressure chemical vapor deposition (LPCVD);

- The depositing step being sub-atmospheric chemical vapor deposition (SACVD);
- The depositing step being atmospheric pressure chemical vapor deposition (APCVD);
- The depositing step being spatial ALD;
- The depositing step being radicals incorporated deposition;
- The depositing step being super critical fluid deposition;
- The depositing step being a combination of two or more of CVD, ALD, PECVD, PEALD, PCVD, LPCVD, SACVD, APCVD, spatial ALD, radicals incorporated deposition, or super critical deposition;
- the method being performed at a temperature between about 20°C and about 800°C;
- the method being performed at a temperature between about 25°C and about 600°C;
- the reactor having a pressure between approximately 0.1Pa and approximately 10^5Pa;
- the reactor having a pressure between between approximately 2.5Pa and approximately 10^3 Pa;
- the manganese-containing film being pure manganese;
- the manganese-containing film being manganese nitride (Mn_xN_y), wherein x and y are each integers ranging inclusively from 1 to 3;
- the manganese-containing film being manganese silicide (Mn_xSi_y), wherein x and y are each integers ranging inclusively from 1 to 3;
- the manganese-containing film being manganese silicide nitride ($Mn_xSi_yN_z$), wherein x, y, and z are each integers ranging inclusively from 1 to 3;
- the manganese-containing film being manganese oxide (Mn_xO_y), wherein x and y are each integers ranging inclusively from 1 to 3;
- the manganese-containing film being manganese silicate ($MnSiO_x$), wherein x is an integer ranging inclusively from 1 to 3;
- the manganese-containing film being manganese-doped indium arsenide (In, Mn)As;

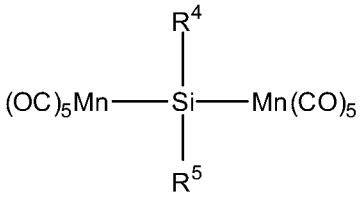
- the manganese-containing film being manganese-doped gallium arsenide (Ga, Mn)As;
- the manganese-containing film being manganese-doped zinc oxide (Mn)ZnO;
- the manganese-containing film being manganese-doped tin dioxide (Mn)SnO_2;
- introducing a reaction gas into the reactor at the same time or at an alternate time as the introduction of the manganese-containing compound;
- the reaction gas being a reducing agent selected from the group consisting of N_2, H_2, NH_3, SiH_4 , Si_2H_6, Si_3H_8, $(CH_3)_2SiH_2$, $(C_2H_5)_2SiH_2$, $(CH_3)_3SiH$, $(C_2H_5)_3SiH$, $[N(C_2H_5)_2]_2SiH_2$, $N(CH_3)_3$, $N(C_2H_5)_3$, $(SiMe_3)_2NH$, $(CH_3)HNNH_2$, $(CH_3)_2NNH_2$, phenyl hydrazine, B_2H_6, $(SiH_3)_3N$, radical species of these reducing agents, and mixtures of these reducing agents; and
- the reaction gas being an oxidizing reagent selected from the group consisting of O_2, O_3, H_2O, H_2O_2, NO, NO_2, acetic acid, radical species of these oxidizing agents, and mixtures of these oxidizing agents.

Detailed Description of Preferred Embodiments

Manganese-containing compounds having the following formula are disclosed:



Formula I



Formula II

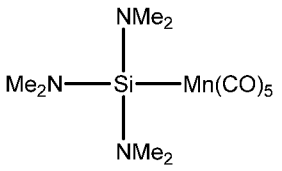
wherein each of R^1, R^2, R^3 , R^4 and R^5 is independently selected from the group consisting of Hydrogen (H); a halogen (I, Br, Cl, or F); linear, cyclic or branched hydrocarbons; primary amino ligands (-NHR); and secondary amino ligands (-NRR'), with R and R' independently being H or a linear, cyclic or branched hydrocarbon, provided at least one of R^1, R^2, or R^3 in Formula I and R^4 or R^5 in

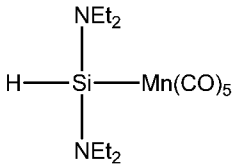
Formula II is an amino ligand. The compound of Formula I may alternatively be referred to as $(NR'_2)_xR_{3-x}SiMn(CO)_5$ compounds, wherein x=1-3, each R is independently selected from Hydrogen; a halogen; or a linear, cyclic or branched hydrocarbons; and each R' is independently selected from Hydrogen or a linear, cyclic or branched hydrocarbon.

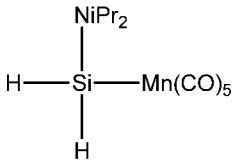
The Formula I compound may include one or two neutral adduct ligands selected from the group consisting of NMe_3, NEt_3, $NiPr_3$, $NMeEt_2$, NC_5H_5, OC_4H_8, Me_2O, and Et_2O. Preferably, the ligand is NMe_3 or NEt_3.

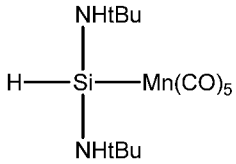
Exemplary compounds of Formula I include, but are not limited to, $(NMe_2)_3SiMn(CO)_5$, $SiH(NMe_2)_2Mn(CO)_5$, $SiH_2(NMe_2)Mn(CO)_5$, $Si(NEt_2)_3Mn(CO)_5$, $SiH(NEt_2)_2Mn(CO)_5$, $SiH_2(NEt_2)Mn(CO)_5$, $Si(N\text{-}iPr_2)_3Mn(CO)_5$, $SiH(N\text{-}iPr_2)_2Mn(CO)_5$, $SiH_2(N\text{-}iPr_2)Mn(CO)_5$, $Si(NHtBu)_3Mn(CO)_5$, $SiH(NHtBu)_2Mn(CO)_5$, $SiH_2(NHtBu)Mn(CO)_5$, $(CH_2{=}CH)Si(Me)(NMe_2)Mn(CO)_5$, $(CH_2{=}CH)Si(Me)(NEt_2)Mn(CO)_5$, $(CH_2{=}CH)Si(Me)(NiPr_2)Mn(CO)_5$, $(CH_2{=}CH)Si(NEt_2)_2Mn(CO)_5$, and $(NHSiMe_3)Si(Me)(H)Mn(CO)_5$, preferably $(NMe_2)_3SiMn(CO)_5$ or $Si(NEt_2)_3Mn(CO)_5$.

Preferably, the compound may be selected from $Si(NMe_2)_3Mn(CO)_5$, $SiH(NEt_2)_2Mn(CO)_5$, $SiH_2(N\text{-}iPr_2)Mn(CO)_5$, or $SiH(NHtBu)_2Mn(CO)_5$, illustrated below:









Exemplary compounds of Formula II include, but are not limited to, $(CO)_5MnSi(NMe_2)_2Mn(CO)_5$, $(CO)_5MnSi(NEt_2)_2Mn(CO)_5$, $(CO)_5MnSi(N\text{-}iPr_2)_2Mn(CO)_5$, $(CO)_5MnSi(NMe_2)(H)Mn(CO)_5$, $(CO)_5MnSi(NEt_2)(H)Mn(CO)_5$, $(CO)_5MnSi(N\text{-}iPr_2)(H)Mn(CO)_5$, $(CO)_5MnSi(NHtBu)(H)Mn(CO)_5$, $(CO)_5MnSi(NHSiMe_3)(Me)Mn(CO)_5$, $(CO)_5MnSi(NHSiMe_3)(Et)Mn(CO)_5$, $(CO)_5MnSi(NHSiMe_3)(iPr)Mn(CO)_5$, $(CO)_5MnSi(NHSiMe_3)(tBu)Mn(CO)_5$, $(CO)_5MnSi(CH{=}CH_2)(NMe_2)Mn(CO)_5$, $(CO)_5MnSi(CH{=}CH_2)(NEt_2)Mn(CO)_5$, $(CO)_5MnSi(CH{=}CH_2)(N\text{-}iPr_2)Mn(CO)_5$, and

$(CO)_5MnSi(CH=CH_2)(NHtBu)Mn(CO)_5$, preferably $(CO)_5MnSi(NMe_2)_2Mn(CO)_5$ or $(CO)_5MnSi(NEt_2)_2Mn(CO)_5$.

The manganese-containing compounds may be synthesized by reacting $Mn_2(CO)_{10}$ with an excess amount of aminosilane at -78°C. These reactants are commercially available or may be synthesized by general methods known in the art using mono-, di-, or tri-chlorosilane and corresponding amine. The mixture, with stirring, is warmed to room temperature or heated to complete reaction. During reaction, hydrogen generation is observed. After several hours stirring, excess aminosilane is removed under vacuum. A dark color oil or solid is purified by vacuum distillation or sublimation.

The adduct may be synthesized by adding the manganese-containing compound to a solvent, such as toluene or dichloromethane. The resulting mixture is cooled to approximately -15°C. The adduct ligand is slowly added to the cooled mixture. The cooled adduct mixture is allowed to warm to room temperature (approximately 20°C), with continuous stirring. Excess adduct ligand is removed under vacuum. The resulting adduct product may be purified by distillation or sublimation.

At least part of the disclosed manganese-containing compounds may deposited onto a substrate to form the manganese-containing films by chemical vapor deposition (CVD), atomic layer deposition (ALD), or other types of depositions that are related to vapor coating such as a plasma enhanced CVD (PECVD), plasma enhanced ALD (PEALD), pulsed CVD (PCVD), low pressure CVD (LPCVD), sub-atmospheric CVD (SACVD) or atmospheric pressure CVD (APCVD), hot-wire CVD (HWCVD, also known as catCVD, in which a hot wire seres as a catalyst for the deposition process), spatial ALD, hot-wire ALD (HWALD), radicals incorporated deposition, and super critical fluid deposition or combinations thereof. Preferably, the deposition method is CVD, ALD or PE-ALD.

The disclosed methods may be useful in the manufacture of semiconductor, photovoltaic, LCD-TFT, or flat panel type devices. The method includes introducing the vapor of at least one manganese-containing compound disclosed above into a reactor having at least one substrate disposed therein. and depositing

at least part of the manganese-containing compound onto the at least one substrate to form a manganese-containing layer using a vapor deposition process. The temperature and the pressure within the reactor and the temperature of the substrate are held at conditions suitable for formation of the manganese-containing layer on at least one surface of the substrate. A reaction gas may also be used to help in formation of the manganese-containing layer.

The reactor may be any enclosure or chamber of a device in which deposition methods take place, such as, without limitation, a parallel-plate type reactor, a cold-wall type reactor, a hot-wall type reactor, a single-wafer reactor, a multi-wafer reactor, or other such types of deposition systems. All of these exemplary reactors are capable of serving as an ALD or CVD reactor. The reactor may be maintained at a pressure ranging from about 0.5 mTorr to about 20 Torr. In addition, the temperature within the reactor may range from about room temperature (20°C) to about 600°C. One of ordinary skill in the art will recognize that the temperature may be optimized through mere experimentation to achieve the desired result.

The temperature of the reactor may be controlled by either controlling the temperature of the substrate holder (called a cold wall reactor) or controlling the temperature of the reactor wall (called a hot wall reactor) or a combination of both methods. Devices used to heat the substrate are known in the art.

The reactor wall may be heated to a sufficient temperature to obtain the desired film at a sufficient growth rate and with desired physical state and composition. A non-limiting exemplary temperature range to which the reactor wall may be heated includes from approximately 20°C to approximately 600°C. When a plasma deposition process is utilized, the deposition temperature may range from approximately 20°C to approximately 550°C. Alternatively, when a thermal process is performed, the deposition temperature may range from approximately 100°C to approximately 600°C.

Alternatively, the substrate may be heated to a sufficient temperature to obtain the desired manganese-containing layer at a sufficient growth rate and with desired physical state and composition. A non-limiting exemplary temperature

range to which the substrate may be heated includes from 100°C to 600°C. Preferably, the temperature of the substrate remains less than or equal to 500°C.

The type of substrate upon which the manganese-containing layer will be deposited will vary depending on the final use intended. In some embodiments, the substrate may be chosen from oxides which are used as dielectric materials in MIM, DRAM, or FeRam technologies (for example, ZrO_2 based materials, HfO_2 based materials, TiO_2 based materials, rare earth oxide based materials, ternary oxide based materials, etc.) or from nitride-based layers (for example, TaN) that are used as an oxygen barrier between copper and the low-k layer. Other substrates may be used in the manufacture of semiconductors, photovoltaics, LCD-TFT, or flat panel devices. Examples of such substrates include, but are not limited to, solid substrates such as copper and copper based alloy, metal nitride-containing substrates (for example, TaN, TiN, WN, TaCN, TiCN, TaSiN, and TiSiN); insulators (for example, SiO_2, Si_3N_4, SiON, HfO_2, Ta_2O_5, ZrO_2, TiO_2, Al_2O_3, and barium strontium titanate); or other substrates that include any number of combinations of these materials. The actual substrate utilized may also depend upon the specific compound embodiment utilized. In many instances though, the preferred substrate utilized will be selected from Si and SiO_2 substrates.

The disclosed manganese-containing compounds may be supplied either in neat form or in a blend with a suitable solvent, such as ethyl benzene, xylene, mesitylene, decane, dodecane, to form a precursor mixture. The disclosed compounds may be present in varying concentrations in the solvent.

One or more of the neat compounds or precursor mixtures are introduced into a reactor in vapor form by conventional means, such as tubing and/or flow meters. The vapor form of the neat compound or precursor mixture may be produced by vaporizing the neat compound or precursor mixture through a conventional vaporization step such as direct vaporization, distillation, by bubbling, or by using a sublimator such as the one disclosed in PCT Publication WO2009/087609 to Xu et al. The neat compound or precursor mixture may be fed in liquid state to a vaporizer where it is vaporized before it is introduced into the reactor. Alternatively, the neat compound or precursor mixture may be vaporized

by passing a carrier gas into a container containing the neat compound or precursor mixture or by bubbling the carrier gas into the neat compound or precursor mixture. The carrier gas may include, but is not limited to, Ar, He, N_2,and mixtures thereof. The carrier gas and compound are then introduced into the reactor as a vapor.

If necessary, the container of the neat compound or precursor mixture may be heated to a temperature that permits the neat compound or precursor mixture to be in its liquid phase and to have a sufficient vapor pressure. The container may be maintained at temperatures in the range of, for example, approximately 0°C to approximately 200°C. Those skilled in the art recognize that the temperature of the container may be adjusted in a known manner to control the amount of precursor vaporized.

In addition to the optional mixing of the manganese-containing compound with solvents, second precursors, and stabilizers prior to introduction into the reactor, the manganese-containing compound may be mixed with a reaction gas inside the reactor.

The reaction gas may include a reducing reagent which is selected from, but not limited to, N_2, H_2, NH_3, SiH_4 , Si_2H_6, Si_3H_8, $(CH_3)_2SiH_2$, $(C_2H_5)_2SiH_2$, $(CH_3)_3SiH$, $(C_2H_5)_3SiH$, $[N(C_2H_5)_2]_2SiH_2$, $N(CH_3)_3$, $N(C_2H_5)_3$, $(SiMe_3)_2NH$, $(CH_3)HNNH_2$, $(CH_3)_2NNH_2$, phenyl hydrazine, B_2H_6, $(SiH_3)_3N$, radical species of these reducing agents, and mixtures of these reducing agents. Preferably, when an ALD process is performed, the reducing reagent is H_2.

When the desired manganese-containing layer also contains oxygen, such as, for example and without limitation, Mn_xO_y, the reaction gas may include an oxidizing reagent which is selected from, but not limited to, O_2, O_3, H_2O, H_2O_2, acetic acid, formalin, para-formaldehyde, radical species of these oxidizing agents, and mixtures of these oxidizing agents. Preferably, when an ALD process is performed, the oxidizing reagent is H_2O.

The reaction gas may be treated by plasma in order to decompose the reaction gas into its radical form. The plasma may be generated or present within the reaction chamber itself. Alternatively, the plasma may generally be at a

location removed from the reaction chamber, for instance, in a remotely located plasma system. One of skill in the art will recognize methods and apparatus suitable for such plasma treatment.

For example, the reaction gas may be introduced into a direct plasma reactor, which generates plasma in the reaction chamber, to produce the plasma-treated reaction gas in the reaction chamber. Exemplary direct plasma reactors include the Titan™ PECVD System produced by Trion Technologies. The reaction gas may be introduced and held in the reaction chamber prior to plasma processing. Alternatively, the plasma processing may occur simultaneously with the introduction of the reaction gas. In-situ plasma is typically a 13.56 MHz RF capacitively coupled plasma that is generated between the showerhead and the substrate holder. The substrate or the showerhead may be the powered electrode depending on whether positive ion impact occurs. Typical applied powers in in-situ plasma generators are from approximately 50W to approximately 1000 W. The disassociation of the reaction gas using in-situ plasma is typically less than achieved using a remote plasma source for the same power input and is therefore not as efficient in reaction gas disassociation as a remote plasma system, which may be beneficial for the deposition of metal-nitride-containing films on substrates easily damaged by plasma.

Alternatively, the plasma-treated reaction gas may be produced outside of the reaction chamber. The MKS Instruments' ASTRON®i reactive gas generator may be used to treat the reaction gas prior to passage into the reaction chamber. Operated at 2.45 GHz, 7kW plasma power, and a pressure ranging from approximately 3 Torr to approximately 10 Torr, the reaction gas O_2 may be decomposed into two O^- radicals. Preferably, the remote plasma may be generated with a power ranging from about 1 kW to about 10 kW, more preferably from about 2.5 kW to about 7.5 kW.

When the desired manganese-containing layer also contains another element, such as, for example and without limitation, Ta, Hf, Nb, Mg, Al, Sr, Y, Ba, Ca, As, In, Sb, Bi, Sn, Pb, Co, lanthanides (such as Er), or combinations thereof, the reaction gas may include a second precursor which is selected from, but not

limited to, metal alkyls, such as $(CH_3)_3Al$, metal amines, such as $Nb(Cp)(NtBu)(NMe_2)_3$, and any combination thereof.

The manganese-containing compound and one or more reaction gases may be introduced into the reactor simultaneously (chemical vapor deposition), sequentially (atomic layer deposition), or in other combinations. For example, the manganese-containing compound may be introduced in one pulse and two additional precursors may be introduced together in a separate pulse [modified atomic layer deposition]. Alternatively, the reactor may already contain the reaction gas prior to introduction of the manganese-containing compound. Alternatively, the manganese-containing compound may be introduced to the reactor continuously while other reaction gases are introduced by pulse (pulsed-chemical vapor deposition). The reaction gas may be passed through a plasma system localized or remotely from the reactor, and decomposed to radicals. In each example, a pulse may be followed by a purge or evacuation step to remove excess amounts of the component introduced. In each example, the pulse may last for a time period ranging from about 0.01 s to about 30 s, alternatively from about 0.3 s to about 3 s, alternatively from about 0.5 s to about 2 s. In another alternative, the manganese-containing compound and one or more reaction gases may be simultaneously sprayed from a shower head under which a susceptor holding several wafers is spun (spatial ALD).

In one non-limiting exemplary atomic layer deposition type process, the vapor phase of a manganese-containing compound is introduced into the reactor, where it is contacted with a suitable substrate. Excess manganese-containing compound may then be removed from the reactor by purging and/or evacuating the reactor. An oxidizing reagent is introduced into the reactor where it reacts with the absorbed manganese-containing compound in a self-limiting manner. Any excess oxidizing reagent is removed from the reactor by purging and/or evacuating the reactor. If the desired layer is a manganese oxide layer, this two-step process may provide the desired layer thickness or may be repeated until a layer having the necessary thickness has been obtained.

The manganese-containing layers resulting from the processes discussed above may include pure manganese, manganese nitride (Mn_xN_y), manganese silicide (Mn_xSi_y), manganese silicide nitride ($Mn_xSi_yN_z$), manganese oxide (Mn_xO_y), manganese silicate ($MnSiO_x$), manganese-doped indium arsenide {(In,Mn)As}, manganese-doped gallium arsenide {(Ga,Mn)As}, manganese-doped zinc oxide {(Mn)ZnO}, and manganese-doped tin dioxide {(Mn)SnO_2}, wherein x and y are integers which each inclusively ranges from 1 to 3. One of ordinary skill in the art will recognize that by judicial selection of the appropriate manganese-containing compound and reaction gases, the desired manganese-containing layer composition may be obtained.

Upon obtaining a desired film thickness, the film may be subject to further processing, such as thermal annealing, furnace-annealing, rapid thermal annealing, UV or e-beam curing, and/or plasma gas exposure. Those skilled in the art recognize the systems and methods utilized to perform these additional processing steps. For example, the manganese-containing film may be exposed to a temperature ranging from approximately 200°C to approximately 1000°C for a time ranging from approximately 0.1 second to approximately 7200 seconds under an inert atmosphere, a H-containing atmosphere, a N-containing atmosphere, an O-containing atmosphere, or combinations thereof. Most preferably, the temperature is 400°C for 3600 seconds under a H-containing atmosphere. The resulting film may contain fewer impurities and therefore may have an improved density resulting in improved leakage current. The annealing step may be performed in the same reaction chamber in which the deposition process is performed. Alternatively, the substrate may be removed from the reaction chamber, with the annealing/flash annealing process being performed in a separate apparatus. Any of the above post-treatment methods, but especially thermal annealing, is expected to effectively reduce any carbon and nitrogen contamination of the manganese-containing film. This in turn is expected to improve the resistivity of the film.

In another alternative, the disclosed manganese-containing compounds may be used as doping or implantation agents. The disclosed

manganese-containing precursors may be deposited on top of the film to be doped, such as an indium arsenide (InAs) film, a gallium arsenide (GaAs) film (a zinc oxide (ZnO) film, or a tin dioxide (SnO_2) film. The manganese then diffuses into the film during an annealing step to form the manganese-doped films {(In,Mn)As, (Ga,Mn)As, (Mn)ZnO, or (Mn)SnO_2}. See, e.g., US2008/0241575 to Lavoie et al., the doping method of which is incorporated herein by reference in its entirety. Alternatively, high energy ion implantation using a variable energy radio frequency quadrupole implanter may be used to dope the manganese of the manganese-containing compound into a film. See, e.g., Kensuke et al., JVSTA 16(2) Mar/Apr 1998, the implantation method of which is incorporated herein by reference in its entirety. In another alternative, plasma doping, pulsed plasma doping or plasma immersion ion implantation may be performed using the disclosed manganese-containing compounds. See, e.g., Felch et al., Plasma doping for the fabrication of ultra-shallow junctions Surface Coatings Technology, 156 (1-3) 2002, pp. 229-236, the doping method of which is incorporated herein by reference in its entirety.

Examples

The following non-limiting examples are provided to further illustrate embodiments of the invention. However, the examples are not intended to be all inclusive and are not intended to limit the scope of the inventions described herein.

Prophetic Synthesis of $(CO)_5MnSiH(NEt_2)_2$

$Mn_2(CO)_{10}$ will be added to a 100 mL flask. $SiH_2(NEt_2)_2$ will slowly be dropped into the flask at a cooled temperature, -78°C. The mixture will be allowed to warm to room temperature or will be heated with continuous stirring to complete reaction. Hydrogen gas will be generated after 5 min stirring. After 2 hours of stirring, excess $SiH_2(NEt_2)_2$ will be removed as a gas under vacuum. The product may be purified under vacuum.

Prophetic Synthesis of $(CO)_5MnSi(NMe_2)_3$

$Mn_2(CO)_{10}$ will be added to a 100 mL flask. $SiH(NMe_2)_3$ will slowly be dropped into the flask at a cooled temperature, -78°C. The mixture will be allowed to warm to room temperature or will be heated with continuous stirring to complete reaction. Hydrogen gas will be generated during stirring. After 2 hours of stirring, excess $SiH(NMe_2)_3$ will be removed as a gas under vacuum. The product may be purified under vacuum.

Prophetic Synthesis of $(CO)_5MnSiH(NHtBu)_2$

$Mn_2(CO)_{10}$ will be added to a 100 mL flask. $SiH_2(NHtBu)_2$ will slowly be dropped into the flask at a cooled temperature, -78°C. The mixture will be allowed to warm to room temperature or will be heated with continuous stirring to complete reaction. Hydrogen gas will be generated during stirring. After 2 hours of stirring, excess $SiH_2(NHtBu)_2$ will be removed as a gas under vacuum. The product may be purified under vacuum.

Prophetic Synthesis of $(CO)_5MnSiH_2(NHiPr)$

$Mn_2(CO)_{10}$ will be added to a 100 mL flask. $SiH_3(NHiPr)$ will slowly be dropped into the flask at a cooled temperature, -78°C. The mixture will be allowed to warm to room temperature or will be heated with continuous stirring to complete reaction. Hydrogen gas will be generated during stirring. After 2 hours of stirring, excess $SiH_3(NHiPr)$ will be removed as a gas under vacuum. The product may be purified under vacuum.

Prophetic Synthesis of $(Et_2N)_2HSiMn(CO)_5 \cdot 2\ NEt_3$

$(Et_2N)_2HSiMn(CO)_5$ will be added to a 100mL flask with toluene or dichloromethane. The solution will be cooled at -15°C and liquid triethylamine will be added slowly. After addition of the amine, the mixture will be allowed to warm to room temperature with continuous stirring to complete reaction. After overnight reaction, excess triethylamine will be removed under vacuum. The product may be purified by distillation or sublimation under vacuum.

Prophetic Synthesis of $(CO)_5MnSi(NEt_2)_2Mn(CO)_5$

$Mn_2(CO)_{10}$ will be added to a 100 mL flask. $SiH_2(NEt_2)_2$ will slowly be dropped into the flask at a cooled temperature, -78°C. The mixture will be allowed to warm to room temperature with continuous stirring. Hydrogen gas will be generated during stirring. After 1 hour stirring, excess $SiH_2(NEt_2)_2$ will be removed as a gas under vacuum at room temperature. This method is the same method used to synthesize $(CO)_5MnSiH(NEt_2)_2$ in the example above. $(CO)_4CoSi(NEt_2)Co(CO)_4$ will also be produced.

Prophetic ALD Deposition of MnSi Film

Applicants believe that any of the disclosed compounds may be used to deposit Mn_xSi_y films using ALD techniques known in the art and H_2 as a reaction gas.

Prophetic ALD Deposition of Mn Film

Applicants believe that any of the disclosed compounds may be used to deposit Mn films using plasma enhanced ALD techniques known in the art and H_2 or NH_3 as reaction gas.

Prophetic CVD Deposition of Mn_xO_y Film

Applicants believe that any of the disclosed compounds may be used to deposit Mn_xO_y films using CVD techniques known in the art and O_2 or H_2O as a reaction gas.

Prophetic CVD Deposition of $MnSiO_x$ Film

Applicants believe that any of the disclosed compounds may be used to deposit $MnSiO_x$ films using CVD techniques known in the art using O_2 or H_2O as a reaction gas.

Prophetic CVD Deposition of Mn_xN_y Film

Applicants believe that any of the disclosed compounds may be used to deposit Mn_xN_y films using CVD techniques known in the art using NH_3 as a reaction gas.

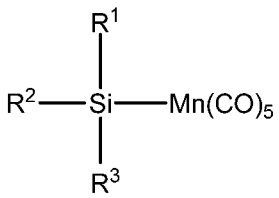
Prophetic CVD Deposition of $Mn_xSi_yN_z$ Film

Applicants believe that any of the disclosed compounds may be used to deposit $Mn_xSi_yN_z$ films using CVD techniques known in the art using NH_3 as a reaction gas.

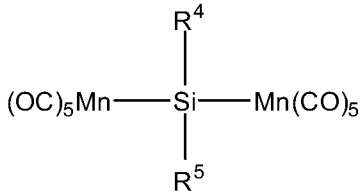
It will be understood that many additional changes in the details, materials, steps, and arrangement of parts, which have been herein described and illustrated in order to explain the nature of the invention, may be made by those skilled in the art within the principle and scope of the invention as expressed in the appended claims. Thus, the present invention is not intended to be limited to the specific embodiments in the examples given above and/or the attached drawings.

We claim:

1. A compound having the formula:



Formula I



Formula II

wherein each of R^1, R^2, R^3, R^4 and R^5 is independently selected from the group consisting of Hydrogen; a halogen; linear, cyclic or branched hydrocarbons; primary amino ligands (-NHR); and secondary amino ligands (-NRR'), with R and R' independently being H or a linear, cyclic or branched hydrocarbon, provided at least one of R^1, R^2, or R^3 in Formula I and R^4 or R^5 in Formula II is an amino ligand.

2. The compound of claim 1, wherein the Formula I compound includes one or two neutral adduct ligands selected from the group consisting of NMe_3, NEt_3, $NiPr_3$, $NMeEt_2$, NC_5H_5, OC_4H_8, Me_2O, and Et_2O.

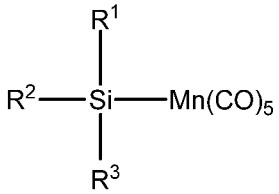
3. The compound of claim 1 or 2, wherein the compound has Formula I and is selected from the group consisting of $(NMe_2)_3SiMn(CO)_5$, $SiH(NMe_2)_2Mn(CO)_5$, $SiH_2(NMe_2)Mn(CO)_5$, $Si(NEt_2)_3Mn(CO)_5$, $SiH(NEt_2)_2Mn(CO)_5$, $SiH_2(NEt_2)Mn(CO)_5$, $Si(N\text{-}iPr_2)_3Mn(CO)_5$, $SiH(N\text{-}iPr_2)_2Mn(CO)_5$, $SiH_2(N\text{-}iPr_2)Mn(CO)_5$, $Si(NHtBu)_3Mn(CO)_5$, $SiH(NHtBu)_2Mn(CO)_5$, $SiH_2(NHtBu)Mn(CO)_5$, $(CH_2{=}CH)Si(Me)(NMe_2)Mn(CO)_5$, $(CH_2{=}CH)Si(Me)(NEt_2)Mn(CO)_5$, $(CH_2{=}CH)Si(Me)(NiPr_2)Mn(CO)_5$, $(CH_2{=}CH)Si(NEt_2)_2Mn(CO)_5$, $(NHSiMe_3)Si(Me)(H)Mn(CO)_5$, $(CH_2{=}CH)Si(Me)(NMe_2)Mn(CO)_5$, $(CH_2{=}CH)Si(Me)(NEt_2)Mn(CO)_5$, $(CH_2{=}CH)Si(Me)(N\text{-}iPr_2)Mn(CO)_5$, $(CH_2{=}CH)Si(NEt_2)_2Mn(CO)_5$, and $(NHSiMe_3)Si(Me)(H)Mn(CO)_5$.

4. The compound of claim 3, wherein the compound is selected from the group consisting of $SiH(NEt_2)_2Mn(CO)_5$, $Si(NMe_2)_3Mn(CO)_5$, $SiH_2(NiPr_2)Mn(CO)_5$, and $SiH(NHtBu)_2Mn(CO)_5$.

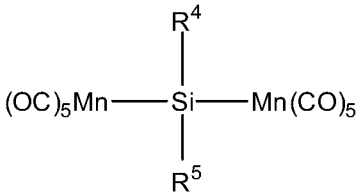
5. The compound of claim 1, wherein the compound has Formula II and is selected from the group consisting of $(CO)_5MnSi(NMe_2)_2Mn(CO)_5$, $(CO)_5MnSi(NEt_2)_2Mn(CO)_5$, $(CO)_5MnSi(N\text{-}iPr_2)_2Mn(CO)_5$, $(CO)_5MnSi(NMe_2)(H)Mn(CO)_5$, $(CO)_5MnSi(NEt_2)(H)Mn(CO)_5$, $(CO)_5MnSi(N\text{-}iPr_2)(H)Mn(CO)_5$, $(CO)_5MnSi(NHtBu)(H)Mn(CO)_5$, $(CO)_5MnSi(NHSiMe_3)(Me)Mn(CO)_5$, $(CO)_5MnSi(NHSiMe_3)(Et)Mn(CO)_5$, $(CO)_5MnSi(NHSiMe_3)(iPr)Mn(CO)_5$, $(CO)_5MnSi(NHSiMe_3)(tBu)Mn(CO)_5$, $(CO)_5MnSi(CH{=}CH_2)(NMe_2)Mn(CO)_5$, $(CO)_5MnSi(CH{=}CH_2)(NEt_2)Mn(CO)_5$, $(CO)_5MnSi(CH{=}CH_2)(N\text{-}iPr_2)Mn(CO)_5$, and $(CO)_5MnSi(CH{=}CH_2)(NHtBu)Mn(CO)_5$.

6. A method of depositing a manganese-containing film, the method comprising:

introducing a manganese-containing compound into a reactor having a substrate disposed therein, wherein the manganese-containing compound has the formula:



Formula I



Formula II

wherein each of R^1, R^2, R^3, R^4 and R^5 is independently selected from the group consisting of Hydrogen; a halogen; linear, cyclic or branched hydrocarbons; primary amino ligands (-NHR); and secondary amino ligands (-NRR'), with R and R' independently being H or a linear, cyclic or branched hydrocarbon, provided at least one of R^1, R^2, or R^3 in Formula I and R^4 or R^5 in Formula II is an amino ligand;

depositing at least part of the manganese-containing compound onto the substrate to form the manganese-containing film.

7. The method of claim 6, wherein the Formula I manganese-containing compound includes one or two neutral adduct ligands selected from the group consisting of NMe_3, NEt_3, $NiPr_3$, $NMeEt_2$, NC_5H_5, OC_4H_8, Me_2O, and Et_2O.

8. The method of claim 6 or 7, wherein the depositing step is selected from the group consisting of chemical vapor deposition (CVD), atomic layer deposition (ALD), plasma enhanced chemical vapor deposition (PECVD), plasma enhanced atomic layer deposition (PEALD), pulsed chemical vapor deposition (PCVD), low pressure chemical vapor deposition (LPCVD), sub-atmospheric chemical vapor deposition (SACVD), atmospheric pressure chemical vapor deposition (APCVD), spatial ALD, radicals incorporated deposition, super critical fluid deposition, and combinations thereof.

9. The method of any one of claims 6 to 8, wherein the method is performed at a temperature between about 20°C and about 800°C, preferably between about 25°C and about 600°C.

10. The method of any one of claims 6 to 9, wherein the reactor has a pressure between approximately 0.1Pa and approximately 10^5Pa, preferably between approximately 2.5Pa and approximately 10^3 Pa.

11. The method of any one of claims 6 to 10, wherein the manganese-containing film is selected from the group consisting of pure manganese, manganese nitride (Mn_xN_y), manganese silicide (Mn_xSi_y), manganese silicide nitride ($Mn_xSi_yN_z$), manganese oxide (Mn_xO_y), and manganese silicate ($MnSiO_x$), wherein x, y, and z are each integers ranging inclusively from 1 to 3.

12. The method of any one of claims 6 to 11, wherein the manganese-containing film is selected from the group consisting of manganese-doped indium arsenide {(In,Mn)As}, manganese-doped gallium arsenide {(Ga,Mn)As}, manganese-doped zinc oxide {(Mn)ZnO}, and manganese-doped tin dioxide {(Mn)SnO_2}.

13. The method of any one of claims 6 to 12, further comprising introducing a reaction gas into the reactor at the same time or at an alternate time as the introduction of the manganese-containing compound.

14. The method of claim 13, wherein the reaction gas is a reducing agent selected from the group consisting of N_2, H_2, NH_3, SiH_4, Si_2H_6, Si_3H_8, $(CH_3)_2SiH_2$, $(C_2H_5)_2SiH_2$, $(CH_3)_3SiH$, $(C_2H_5)_3SiH$, $[N(C_2H_5)_2]_2SiH_2$, $N(CH_3)_3$, $N(C_2H_5)_3$, $(SiMe_3)_2NH$, $(CH_3)HNNH_2$, $(CH_3)_2NNH_2$, phenyl hydrazine, B_2H_6, $(SiH_3)_3N$, radical species of these reducing agents, and mixtures of these reducing agents.

15. The method of claim 13, wherein the reaction gas is an oxidizing reagent selected from the group consisting of O_2, O_3, H_2O, H_2O_2, NO, NO_2, acetic acid, radical species of these oxidizing agents, and mixtures of these oxidizing agents.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2014/058715

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C07F19/00(2006.01)i, C07F7/02(2006.01)i, C07F13/00(2006.01)i, C23C16/18(2006.01)i, H01L21/285(2006.01)i

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)

Int.Cl. C07F19/00, C07F7/02, C07F13/00, C23C16/18, H01L21/285

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

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2014
Registered utility model specifications of Japan 1996-2014
Published registered utility model applications of Japan 1994-2014

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAplus/REGISTRY(STN), Thomson Innovation, JSTPlus(JDreamIII), JST7580(JDreamIII), JSTChina(JDreamIII), Scopus

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	AYLETT,B.J. et al, Chemical vapor deposition of metal silicides from organometallic compounds with silicon-metal bonds, Vacuum, 1985, Vol.35, No.10-11, p.435-9	1-15
A	BRAUNSTEIN,P. et al, New Mono- and Polynuclear Iron Silylene and Stannylene Complexes, Organometallics, 2001, Vol.20, No.4, p.627-633	1-15
A	SCHMID,G. et al, Base-Stabilized Silyleneiron Complexes, Angewandte Chemie International Edition, 1977, Vol.16, No.11, p.785-6	1-15

☑ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18.04.2014	28.04.2014

Name and mailing address of the ISA/JP	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2014/058715

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Roland A Fischer, Metal-organic chemical vapour deposition of manganese gallium alloys from the novel mixed metal single-source precursors $(CO)_5Mn\text{-}Ga(C_2H_5)_2[N(CH_3)_3]$, $(CO)_5Mn\text{-}Ga(C_2H_5)_2(NC_7H_{13})$ and $[(CO)_5Mn]_2Ga[(CH_2)_3NMe_2]$, Thin Solid Films, 1996, Vol.289, Nos.1-2, p.147-152	1-15
P,A	WO 2013/048417 A1 (INTEL CORPORATION) 2013.04.04, whole document (No Family)	1-15