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(54) Title: ORGANOMETALLIC COMPOUND AND METHOD

(A)x-M-(OR3)4-x (I)

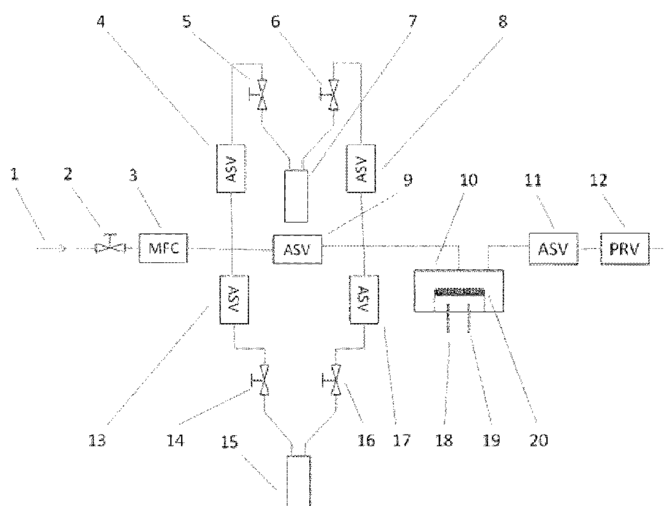

Figure 1 . Sketch of ALD system for thin film deposition.

(57) Abstract: A class of organometallic compounds is provided. The compounds correspond in structure to Formula 1 (A)x-M-(OR3)4-x wherein: A is selected from the group consisting of -NR1R2, -N(R4)(CH2)nN(R5R6), -N=C(NR4R5)(NR6R7), OCOR1, halo and Y; R1 and R2 are independently selected from the group consisting of H and a cyclic or acyclic alkyl group having from 1 to 8 carbon atoms, with the proviso that at least one of R1 and R2 must be other than H; R4, R5, R6 and R7 are independently selected from the group consisting of H and an acyclic alkyl group having from 1 to 4 carbon atoms; Y is selected from the group consisting of a 3- to 13-membered heterocyclic radical containing at least one nitrogen atom; R3 is a cyclic or acyclic alkyl group having from 1 to 6 carbon atoms; M is selected from the group consisting of Si, Ge, Sn, Ti, Zr and Hf; x is an integer from 1 to 3; and n is an integer from 1 to 4. Compounds of the invention may be useful as precursors in chemical phase deposition processes such as atomic layer deposition (ALD), chemical vapour deposition (CVD), plasma assisted ALD and plasma assisted CVD. Methods of low temperature vapour phase deposition of metal oxide films, such as SiO2 films, are also provided.

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TITLE

Organometallic compound and method

FIELD OF THE INVENTION

The invention relates to organometallic compounds which may be useful as precursors for metal oxide vapour phase deposition. The organometallic compounds of the invention comprise one or more ligands which are strong Lewis bases. The invention also relates to the low temperature vapour phase deposition of metal oxides using such compounds as a catalyst, in the presence of an oxidant.

BACKGROUND OF THE INVENTION

As the size of transistors keeps decreasing, challenges arise with the use of standard methods for the thermal deposition of SiO_2 and other metal oxides at high temperature. The use of high temperature causes diffusion of some elements. This diffusion changes the basic properties of transistors. Consequently, the devices are damaged. Therefore, low temperature thermal deposition of good quality SiO_2 and metal oxides for high k applications is preferred. However, in general, thermal (i.e. high temperature) deposition of SiO_2 is preferred as plasma-assisted deposition can damage the underlying device structures. Silicon dioxide (SiO_2) is a common dielectric material in silicon microelectronic devices. High quality SiO_2 has been formed by the thermal oxidation of silicon between 700-900°C. SiO_2 has also been deposited by chemical vapour deposition (CVD); some such approaches have utilized plasma techniques. However, CVD is not conformal in high aspect ratio structures and displays void formation in trenches and vias.

Atomic layer deposition (ALD) methods can be used to obtain conformality and atomic layer control of thin film growth. Atomic layer deposition (ALD) is a growth method based on sequential, self-limiting surface reactions. A variety of materials, including oxides, nitrides, and various metals have been deposited using ALD.

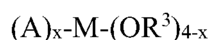
Despite its importance, SiO_2 ALD has been difficult to achieve. SiO_2 ALD using $SiCl_4$ and H_2O requires high temperatures (>325 °C) and large reactant exposures (>109 L (1 L) 10^{-6} Torr s). The use of NH_3 or pyridine permits the use of temperatures close to room temperature and exposures of ~103-104 L. However, the by-products generated by these methods may cause blockage of the vacuum lines, incorporation of the amine hydrochloride salts into the films and, thus, the final quality of the films are very poor.

However, the use of halides in these methods results in the release of corrosive HCl during deposition. In addition, the HCl liberated can react with the amine catalyst to form chloride salts, leading to film contamination and thus poor film quality.

To avoid using halides, SiO_2 ALD has been attempted using a variety of reactants such as alkoxysilanes, aminosilanes and isocyanates, using a variety of different catalysts and reaction conditions. These methods suffer from a number of disadvantages, such as requiring large reactant exposures, long deposition times or resulting in contamination of the deposited film.

SUMMARY OF THE INVENTION

A class of organometallic compounds is provided. The compounds correspond in structure to Formula 1:



$$(A)_x\text{-}M\text{-}(OR^3)_{4-x}$$

wherein:

A is selected from the group consisting of $-NR^1R^2$, $-N(R^4)(CH_2)_nN(R^5R^6)$,

$-N{=}C(NR^4R^5)(NR^6R^7)$, $OCOR^1$, halo and Y;

R^1 and R^2 are independently selected from the group consisting of H and a cyclic or acyclic alkyl group having from 1 to 8 carbon atoms, with the proviso that at least one of R^1 and R^2 must be other than H;

R^4, R^5, R^6 and R^7 are independently selected from the group consisting of H and an acyclic alkyl group having from 1 to 4 carbon atoms;

Y is selected from the group consisting of a 3- to 13-membered heterocyclic radical containing at least one nitrogen atom;

R^3 is a cyclic or acyclic alkyl group having from 1 to 6 carbon atoms;

M is selected from the group consisting of Si, Ge, Sn, Ti, Zr and Hf;

x is an integer from 1 to 3; and

n is an integer from 1 to 4.

Such compounds may be useful as precursors for metal oxide vapour phase deposition. The compounds of the invention comprise one or more ligands which are strong Lewis bases. Exemplary bases comprise acetates, halides and neutral, nitrogen-containing species with high proton affinity such as phosphazenes, amidines and guanidines.

These compounds may have utility as precursors for vapour deposition processes such as CVD, ALD, plasma assisted ALD and plasma assisted CVD.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic representation of an ALD system for thin film deposition.

Figure 2 shows the NMR spectrum of (pyrrolodinyl)$Si(OMe)_3$

Figure 3 shows the NMR spectrum of $(pyrrolodinyl)_2Si(OMe)_2$

Figure 4 shows the TGA of $(pyrrolodinyl)_2Si(OMe)_2$

Figure 5 shows the vapour pressure of $(pyrrolodinyl)_2Si(OMe)_2$

Figure 6 shows the thermal stability of $(pyrrolodinyl)_2Si(OMe)_2$

Figure 7 shows the NMR spectrum of $(pyrrolodinyl)_3Si(OMe)$

Figure 8 shows the TGA of $(pyrrolodinyl)_3Si(OMe)$

Figure 9 shows the vapour pressure of $(pyrrolodinyl)_3Si(OMe)$

Figure 10 shows the NMR spectrum of (Tetramethylguanidinyl)$Si(OMe)_3$

Figure 11 shows the NMR spectrum of $(Tetramethylguanidinyl)_2Si(OMe)_2$

Figure 12 shows the NMR spectrum of $(Et_2N)Si(OMe)_3$

Figure 13 shows the NMR spectrum of $ClSi(OMe)_3$

Figure 14 shows the NMR spectrum of $Cl_2Si(OMe)_2$

Figure 15 shows the NMR spectrum of $(AcO)Si(OMe)_3$

Figure 16 shows the NMR spectrum of $(Me_2N)_2Si(OMe)_2$

Figure 17 shows the vapour pressure of $(Me_2N)_2Si(OMe)_2$

Figure 18 shows the thermal stability of $(Me_2N)_2Si(OMe)_2$

Figure 19 shows the CVD growth rate *vs.* temperature of of SiO_2 using $(pyrrolodinyl)_2Si(OMe)_2$ and H_2O at 80 Torr.

Figure 20 shows the CVD growth rate *vs.* temperature and pressure of of SiO_2 using $(pyrrolodinyl)_2Si(OMe)_2$ and O_3.

Figure 21 shows the ALD of SiO_2 using $(pyrrolodinyl)_2Si(OMe)_2$ and O_3, showing linear film thickness with number of ALD cycles.

Figure 22 shows the ALD of SiO_2 using (pyrrolodinyl)$_2$Si(OMe)$_2$ and O_3, showing the temperature effect on the growth rate.

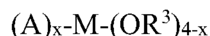
Figure 23 shows the wet etching rate of SiO_2 films in dilute HF acid (0.1%), films prepared by CVD at 250°C and various pressures using (pyrrolodinyl)$_2$Si(OMe)$_2$ and O_3.

Figure 24 shows the wet etching rate of SiO_2 films in dilute HF acid (0.1%), films prepared by CVD and ALD at various temperatures using (pyrrolodinyl)$_2$Si(OMe)$_2$ and O_3.

Figure 25 Table showing the wet etching rate comparison of the new material with commercially available material used to carry out deposition of silicon oxide films using the same conditions

DETAILED DESCRIPTION OF THE INVENTION

A class of organometallic compounds is provided. The compounds correspond in structure to Formula 1:



$$(A)_x\text{-}M\text{-}(OR^3)_{4-x}$$

wherein:

A is selected from the group consisting of $-NR^1R^2$, $-N(R^4)(CH_2)_nN(R^5R^6)$,

$-N{=}C(NR^4R^5)(NR^6R^7)$, $OCOR^1$, halo and Y;

R^1 and R^2 are independently selected from the group consisting of H and a cyclic or acyclic alkyl group having from 1 to 8 carbon atoms, with the proviso that at least one of R^1 and R^2 must be other than H;

R^4, R^5, R^6 and R^7 are independently selected from the group consisting of H and an acyclic alkyl group having from 1 to 4 carbon atoms;

Y is selected from the group consisting of a 3- to 13-membered heterocyclic radical containing at least one nitrogen atom;

R^3 is a cyclic or acyclic alkyl group having from 1 to 6 carbon atoms;

M is selected from the group consisting of Si, Ge, Sn, Ti, Zr and Hf;

x is an integer from 1 to 3; and

n is an integer from 1 to 4.

Such compounds may be useful as precursors for metal oxide vapour phase deposition. The compounds of the invention comprise one or more ligands which are strong Lewis bases. Exemplary bases comprise acetates, halides and neutral, nitrogen-containing species with high proton affinity such as phosphazenes, amidines and guanidines.

Strong bases catalyze the formation of SiO_2 much more effectively and more efficiently than a base such as NH_3, which is a typical example of a base used in the art. The use of a strongly basic catalyst allows for CVD and ALD deposition of SiO_2 at a low temperature. It also results in a good quality SiO_2 film.

Compounds of the invention may be useful as precursors in chemical phase deposition processes such as atomic layer deposition (ALD), chemical vapour deposition (CVD), plasma assisted ALD and plasma assisted CVD.

The use of a compound of the invention in the process outlined above has the advantage that deposition may be carried out at lower temperatures (0- 500° C) than processes previously known in the art.

The temperature range at which the reaction proceeds may be adjusted by changing the number of $(NR^1R^2)_x$ groups attached to a compound of Formula 1 (i.e. changing x), and by changing the nature of the (NR^1R^2) group.

The reaction temperature may be in the range of from 0 – 500°C, more preferably from 100 – 350°C.

Incorporation of a strongly basic ligand into a compound of Formula 1 also allows for simpler process compared to processes of the art, which use two components (Si precursor plus catalyst), improving uniformity of exposure and film quality.

A compound of Formula 1 can be designed to provide desirable characteristics such as volatility and stability to facilitate application to the substrate. This can be affected by adjusting the number (x) and identity of the strongly basic ligand(s) A and of the alkyl group(s) (OR^3).

Compounds of the invention include those in which M is selected from the group consisting of Si, Ge, Sn, Ti, Hf and Zr. Preferred compound include those in which M is selected from the group consisting of Si, Ge and Sn. More preferred compounds include those in which M is Si.

Compounds of the invention also include those in which R^3 is a cyclic or acyclic alkyl group having from 1 to 6 carbon atoms. Preferred compounds are those in which R^3 is a linear or branched lower alkyl group having from 1 to 4 carbon atoms. Yet other preferred compounds are those in which R^3 is selected from the group consisting of methyl and ethyl.

Compounds of the invention also include those in which A is selected from the group consisting of $-NR^1R^2$, $-N(R^4)(CH_2)_nN(R^5R^6)$, $-N{=}C(NR^4R^5)(NR^6R^7)$, $OCOR^1$, halo and Y. Preferred compounds include those in which A is selected from the group consisting of acetate, tetraethylguanidinyl, dimethylethylenediaminyl, bromo, iodo and an $-NR^1R^2$ group. More preferred compounds include those in which A is an $-NR^1R^2$ group.

Other preferred compounds are those in which R^1 and R^2 are independently selected from the group consisting of H and a cyclic or acyclic alkyl group having from 1 to 8 carbon atoms.

More preferred compounds of the invention include those in which R^1 and R^2 are independently selected from the group consisting of an alkyl group having from 1 to 4 carbon atoms. Other referred compounds of the invention include those in which R^1 and R^2 are independently selected from the group consisting of methyl, ethyl and isobutyl.

Compounds of the invention also include those in which Y represents a 3- to 13-membered heterocyclic radical containing at least one nitrogen atom.

Preferred compounds of the invention include those in which Y is a radical such as aziridinyl, azetidinyl, pyrrolidinyl, pyrrolyl, piperidinyl, pyridinyl, azepanyl, or azepinyl.

Further compounds of the invention include those in which Y contains at least one other heteroatom, such as an oxaziridinyl, imidazolidinyl, pyrazolidinyl, oxazolidinyl, isoxazolidinyl, piperazinyl, morpholiny, imidazolyl, pyrazolyl, oxazolinyl, isoxazolyl, diazinyl, or oxazinyl radical.

Preferred compounds are those in which Y is selected from the group consisting of pyrrolidinyl, azetidinyl and aziridinyl.

Compounds of the invention also include those in which R^4, R^5, R^6 and R^7 are independently selected from the group consisting of H and an acyclic alkyl group having from 1 to 4 carbon atoms. Preferred compounds are those in which

are independently selected from the group consisting of methyl and ethyl.

Compounds of the invention may be useful as precursors for thin film deposition, using methods such as ALD or CVD. For example, one way in which the deposition of SiO_2 films by ALD may be carried out is as follows:

a) Providing at least one substrate having functional O-H groups covering the surface,

b) delivering to said substrate at least one compound of Formula 1 (wherein M = Si) in the gaseous phase,

c) purging substrate with purge gas;

d) delivering to said substrate an oxygen source in gaseous phase,

e) purging substrate with purge gas,

f) repeat steps b) through e) until a desired thickness of silicon oxide is deposited.

Suitable oxygen sources include, but are not limited to, compounds such as H_2O in gaseous phase, H_2O_2 in gaseous phase, O_2, O_3 and hydrazine

A typical schematic for an ALD system is shown in Figure 1.

For the half cycle of precursor A reaction, an inert carrier gas (1) such as Ar is passed through manual valve (2) and mass flow controller (3) at a controlled flow rate to bubbler 1 (7) containing precursor A and carries vaporized precursor A to the reaction chamber (10). The automatic switch valves (ASV) 4 and 8 for bubbler 1 open automatically for the period of time that is pre-set. ASV 4 and 8 then close automatically, followed by purging and vacuuming of the reaction chamber for a pre-set period of time. The half cycle reaction for precursor A is finished. Automatically, ASV 13 and 17 open up, an inert carrier gas (1) such as Ar is passed through manual valve (2) and mass flow controller (3) at a controlled flow rate to bubbler 2 (15) containing precursor B and carries vaporized precursor B to the reaction chamber (10). After the pre-set period of time, ASV 13 and 17 close automatically, followed by purging and vacuuming of the reaction chamber for a pre-set period of time. The half cycle reaction for precursor B is finished. A full reaction cycle is finished, i.e. one atomic layer of product is deposited on substrate (20). The cycle is repeated to obtain the desired thickness. The temperature is controlled by a heater (18) and thermocouple (19). The pressure in the reaction chamber is controlled by pressure regulating valve (12), which is connected to vacuum pump.

Compounds of the invention may be prepared by processes known in the art. The examples below are illustrative of such processes, but are not intended to be limiting.

Example 1

Synthesis of (pyrrolodinyl)$Si(OMe)_3$

Chemical formula: $[(CH_2)_4N]-Si(OCH_3)_3$

7.1 g pyrrolidine and 100 mL hexane were charged into a 250 mL flask under N_2, followed by the addition of 40 mL of 2.5M BuLi. After stirring for 1 hr, 15.2 g tetramethyl orthosilicate was added. After stirring overnight, the reaction mixture was filtered and a clear liquid

collected. Volatiles were removed under vacuum. The obtained liquid product was then purified by distillation. NMR analysis confirmed the product, as shown in Figure 2.

Example 2

Synthesis of $(pyrrolodinyl)_2Si(OMe)_2$

Chemical formula: $[(CH_2)_4N]_2$-$Si(OCH_3)_2$

7.1 g pyrrolidine and 100 mL hexane were charged into a 250 mL flask under N_2, followed by the addition of 40 mL of 2.5M BuLi. After stirring for 1 hr, 7.6 g tetramethyl orthosilicate was added. After stirring overnight, the reaction mixture was filtered to collect a clear liquid. Volatiles were removed under vacuum. The obtained liquid product was then purified by distillation. NMR analysis confirmed the product, as shown in Figure 3. As seen in Figure 4, the TGA curve shows a stable material with minimal residue. Vapour pressure measurements shown in Figure 5 demonstrate good volatility and Figure 6 demonstrates the thermal stability of the compound up to 450°C.

Example 3

Synthesis of $(pyrrolodinyl)_3Si(OMe)$

Chemical formula: $[(CH_2)_4N]_3$-$Si(OCH_3)$

7.1 g pyrrolidine and 100 mL hexane were charged into a 250 mL flask under N_2, followed by the addition of 40 mL of 2.5M BuLi. After stirring for 1 hr, 5.1 g tetramethyl orthosilicate was added. After stirring overnight, the reaction mixture was filtered to collect a clear liquid. Volatiles were removed under vacuum. The obtained liquid product was then purified by distillation. NMR analysis confirmed the product, as shown in Figure 7. As seen in Figure 8, the TGA curve shows a stable material with minimal residue. Vapour pressure measurements shown in Figure 9 demonstrate good volatility.

Example 4

Synthesis of $(Tetramethylguanidinyl)Si(OMe)_3$

Chemical formula: $[NC(N(CH_3)_2)_2]$ -$Si(OCH_3)_3$

10 g Tetramethylguanidine and 100 mL hexane were charged into a 250 mL flask under N_2, followed by the addition of 35 mL of 2.5M BuLi. After stirring for 1 hr, 13.2 g tetramethyl orthosilicate was added. After stirring overnight, the reaction mixture was filtered to collect a clear liquid. Volatiles were removed under vacuum. The obtained liquid product was then purified by distillation. NMR analysis confirmed the product, as shown in Figure 10.

Example 5

Synthesis of $(Tetramethylguanidinyl)_2Si(OMe)_2$

Chemical formula: $[NC(N(CH_3)_2)_2]_2-Si(OCH_3)_2$

10 g Tetramethylguanidine and 100 mL hexane were charged into a 250 mL flask under N_2, followed by the addition of 35 mL of 2.5M BuLi. After stirring for 1 hr, 6.6 g tetramethyl orthosilicate was added. After stirring overnight, the reaction mixture was filtered to collect a clear liquid. Volatiles were removed under vacuum. The obtained liquid product was then purified by distillation. NMR analysis confirmed the product, as shown in Figure 11.

Example 6

Synthesis of $(Tetramethylguanidinyl)_3Si(OMe)$

Chemical formula: $[NC(N(CH_3)_2)_2]_3-Si(OCH_3)$

10 g Tetramethylguanidine and 100 mL hexane were charged in a 250 mL flask under N_2, followed by the addition of 35 mL of 2.5M BuLi. After stirring for 1 hr, 4.4 g tetramethyl orthosilicate was added. After stirring overnight, the reaction mixture was filtered to collect a clear liquid. Volatiles were removed under vacuum. The obtained liquid product was then purified by distillation.

Example 7

Synthesis of $(Et_2N)Si(OMe)_3$

Chemical formula: $[(CH_3CH_2)_2N]-Si(OCH_3)_3$

3.7 g diethylamine and 100 mL hexane were charged in a 250 mL flask under N_2, followed by the addition of 20 mL of 2.5M BuLi. After stirring for 1 hour, 7.6 g tetramethyl orthosilicate was added. After stirring overnight, the reaction mixture was filtered to collect a clear liquid. Volatiles were removed under vacuum. The obtained liquid product was then purified by distillation. NMR analysis confirmed the product, as shown in Figure 12.

Example 8

Synthesis of $ClSi(OMe)_3$

Chemical formula: $Cl-Si(OCH_3)_3$

To a 250 mL flask were charged 5.1 g acetyl chloride, 7.6 g tetramethyl orthosilicate and 0.02 g aluminum trichloride, under N_2. The mixture was heated to reflux for 3 hours and then allowed to cool to room temperature. Volatiles were removed under vacuum. The obtained liquid product was then purified by distillation. NMR analysis confirmed the product, as shown in Figure 13.

Example 9

Synthesis of $Cl_2Si(OMe)_2$

Chemical formula: Cl_2-$Si(OCH_3)_2$

To a 250 mL flask were charged 4 g (pyrrolodinyl)$_2$Si(OMe)$_2$ and 50 mL diethyl ether, followed by the addition of 35 mL of 2M HCl in diethyl ether. After stirring for 1 hr the reaction mixture was filtered. Volatiles were removed from the filtrate under vacuum whilst cooling in an ice/acetone bath. NMR analysis confirmed the product, as shown in Figure `4.

Example 10

Synthesis of (AcO)Si(OMe)$_3$

Chemical formula: (AcO)-Si(OCH$_3$)$_3$

To a 100 mL flask were charged 22.8 g tetramethyl orthosilicate and 15.3 g acetic anhydride, under N_2. The mixture was heated at 120 °C for 4 hours and then allowed to cool to room temperature. Volatiles were removed under vacuum. Fractional distillation was then carried out to collect the desired product. NMR analysis confirmed the product, as shown in Figure 15.

Example 11

Synthesis of (Me$_2$N)$_2$Si(OMe)$_2$

Chemical formula: [(CH$_3$)$_2$N]$_2$ -Si(OCH$_3$)$_2$

40 mL of 2.5M BuLi in hexane was charged into a 250 mL flask under N_2, followed by the passing of dimethylamine gas till the completion of the reaction. After stirring for 1 hr, 7.6 g tetramethyl orthosilicate was added. After stirring overnight, the reaction mixture was filtered and a clear liquid collected. Volatiles were removed under vacuum. The obtained liquid product was then purified by distillation. NMR analysis confirmed the product, as shown in Figure 16. Vapour pressure measurements shown in Figure 17 demonstrate very good volatility. Thermal decomposition tests carried out in sealed ampoules shown in Figure 18 show that this material is thermally stable up to 450°C.

Example 12

SiO_2 deposition using (pyrrolidinyl)$_2$Si(OMe)$_2$

SiO_2 films have been prepared by CVD and ALD from the precursor (pyrrolidine)$_2$Si(OMe)$_2$ using O_3 or H_2O as an oxidant, at various temperatures and pressures. Data has been obtained on growth rate of the SiO_2 films, and film quality was measured by density and wet etching rate (WER) in dilute HF acid.

Growth rates of films prepared by CVD as a function of temperature and gas pressure are shown in Figures 19 and 20. These show that when H_2O is used as the oxidant the growth rate is relatively slow, 3A/min or less (the scale in Figure 19 is in nm/min which is 10A/min). Subsequent tests used O_3 as the oxidizing agent, resulting in approximately ten times higher growth rates, as shown in Figure 20. Growth rate is largely independent of deposition pressure and appears to be optimized in the 200 – 300°C temperature range.

Subsequent tests measured film growth per cycle using ALD. Figure 21 shows linear film thickness growth vs. number of cycles, and flat growth rate per cycle with increasing exposure time as expected if the single atomic layer per cycle deposition process is working correctly.

Figure 22 illustrates the temperature dependence of the growth rate per cycle as a function of temperature indicating an optimal temperature range of 250 – 400°C.

Quality of the produced films was measured by measuring density and the wet etching rate in 0.1% HF acid. Figure 23 shows the WER and density of films prepared by CVD at 250°C and various deposition pressures. Figure 24 compares WER for films prepared at various temperatures by CVD and ALD, showing the superior quality of ALD prepared films (lower WER is considered indicative of superior film quality).

For comparison WER for films prepared by various methods are referenced from literature. WER for Thermal SiO2 has been measured at 1.8A/min, this is the best quality film but required high temperatures incompatible with many applications. Films prepared by plama enhanced CVD and ALD using standard precursors were measured at 60 A/min and 40 A/min respectively. These are substantially higher than the WER for ALD films demonstrated here, as shown in Figure 25.

1. Inert carrier gas input

2. Manual valve controlling inert gas input

3. Mass flow controller controlling the inert gas input digitally

4. Automatic switch valve for input of inert carrier gas to bubbler 1

5. Manual valve on the bubbler for input of inert carrier gas

6. Manual valve on the bubbler for output of inert carrier gas containing vaporized precursor

7. Bubbler containing precursor A

8. Automatic switch valve for input of inert carrier gas containing vaporized precursor to reaction chamber

9. Automatic switch valve for removal of any residues in the line.

10. Reaction chamber

11. Automatic switch valve for removal of precursors and residues in the line

12. Pressure regulating valve to vacuum pump controlling gas pressure in reaction chamber

13. Automatic switch valve for input of inert carrier gas to bubbler 2

14. Manual valve on the bubbler for input of inert carrier gas

15. Bubbler containing precursor B

16. Manual valve on the bubbler for output of inert carrier gas containing vaporized precursor

17. Automatic switch valve for input of inert carrier gas containing vaporized precursor to reaction chamber

18. Heater

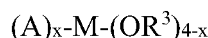
19. Thermocouple

20. Substrate

CLAIMS

What is claimed is:

1. An organometallic compound of Formula 1:



$$(A)_x\text{-}M\text{-}(OR^3)_{4-x}$$

wherein:

A is selected from the group consisting of $-NR^1R^2$, $-N(R^4)(CH_2)_nN(R^5R^6)$, $-N{=}C(NR^4R^5)(NR^6R^7)$, $OCOR^1$, halo and Y;

R^1 and R^2 are independently selected from the group consisting of H and a cyclic or acyclic alkyl group having from 1 to 8 carbon atoms, with the proviso that at least one of R^1 and R^2 must be other than H;

R^4, R^5, R^6 and R^7 are independently selected from the group consisting of H and an acyclic alkyl group having from 1 to 4 carbon atoms;

Y is selected from the group consisting of a 3- to 13-membered heterocyclic radical containing at least one nitrogen atom;

R^3 is a cyclic or acyclic alkyl group having from 1 to 6 carbon atoms;

M is selected from the group consisting of Si, Ge, Sn, Ti, Zr and Hf;

x is an integer from 1 to 3; and

n is an integer from 1 to 4.

2. The compound of claim 1, wherein M is selected from the group consisting of Si, Ge and Sn.

3. The compound of claim 2, wherein M is Si.

4. The compound of claim 3, wherein A is selected from the group consisting of $-NR^1R^2$, $-N(R^4)(CH_2)_nN(R^5R^6)$, $-N{=}C(NR^4R^5)(NR^6R^7)$, $OCOR^1$, halo and Y.

5. The compound of claim 4, wherein A is selected from the group consisting of acetate, tetraethylguanidinyl, dimethylethylenediaminyl, bromo, iodo, $-NR^1R^{2.}$ and Y.

6. The compound of claim 5, wherein A is $-NR^1R^{2.}$

7. The compound of claim 6, wherein R^1 and R^2 are independently selected from the group consisting of H and an acyclic alkyl group having from 1 to 4 carbon atoms.

8. The compound of claim 7, wherein wherein R^1 and R^2 are independently selected from the group consisting of methyl, ethyl and isobutyl.

9. The compound of claim 5, wherein A is Y.

10. The compound of claim 9, wherein Y is selected from the group consisting of aziridinyl, azetidinyl, pyrrolidinyl, pyrrolyl, piperidinyl, pyridinyl, azepanyl, and azepinyl.

11. The compound of claim 10, wherein Y is selected from the group consisting of aziridinyl, azetidinyl and pyrrolidinyl.

12. The compound of claim 8 or 11, wherein R^1 and R^2 are independently selected from the group consisting of H and a cyclic or acyclic alkyl group having from 1 to 8 carbon atoms, with the proviso that at least one of R^1 and R^2 must be other than H.

13. The compound of claim 12, wherein R^1 and R^2 are independently selected from the group consisting of H and an acyclic alkyl group having from 1 to 4 carbon atoms.

14. The compound of claim 13, wherein R^1 and R^2 are independently selected from the group consisting of methyl, ethyl and isobutyl.

15. The compound of claim 8 or 11, wherein R^3 is a cyclic or acyclic alkyl group having from 1 to 6 carbon atoms.

16. The compound of claim 15, wherein R^3 is a linear or branched acyclic alkyl group having from 1 to 4 carbon atoms.

17. The compound of claim 16, wherein R^3 is selected from the group consisting of methyl and ethyl.

18. The compound of claim 17, wherein R^3 is a methyl group.

19. The compound of claim 8 or 11, wherein R^4, R^5, R^6 and R^7 are independently selected from the group consisting of H and an acyclic alkyl group having from 1 to 4 carbon atoms.
20. The compound of claim 19, wherein R^4, R^5, R^6 and R^7 are independently selected from the group consisting of methyl and ethyl.

21. The compound of claim 5 wherein R^1 and R^2 are independently selected from the group consisting of methyl, ethyl and isobutyl, Y is pyrrolidinyl, and R^3 is selected from the group consisting of methyl and ethyl.

22. A method for forming a metal oxide film by a vapour deposition process, the method comprising the steps of:
    a. Providing at least one substrate having functional O-H groups covering the surface,
    b. delivering to said substrate at least one compound of Formula 1 in the gaseous phase,
    c. purging the substrate with purge gas,
    d. delivering to said substrate an oxygen source in the gaseous phase,
    e. purging the substrate with purge gas,
    f. repeating steps b) through e) until a desired thickness of metal oxide has been deposited.

23. The method of claim 22, wherein M is Si.

24. The method of claim 23, wherein A is selected from the group consisting of $-NR^1R^2$, $-N(R^4)(CH_2)_nN(R^5R^6)$, $-N=C(NR^4R^5)(NR^6R^7)$, $OCOR^1$, halo and Y.

25. The method of claim 24, wherein A is selected from the group consisting of acetate, tetraethylguanidinyl, dimethylethylenediaminyl, bromo, iodo, $-NR^1R^{2.}$ and Y.

26. The method of claim 25, wherein A is $-NR^1R^{2.}$

27. The method of claim 26, wherein R^1 and R^2 are independently selected from the group consisting of H and an acyclic alkyl group having from 1 to 4 carbon atoms.

28. The method of claim 27, wherein R^1 and R^2 are independently selected from the group consisting of methyl, ethyl and isobutyl.

29. The method of claim 25, wherein A is Y.

30. The method of claim 29, wherein Y is selected from the group consisting of aziridinyl, azetidinyl, pyrrolidinyl, pyrrolyl, piperidinyl, pyridinyl, azepanyl, and azepinyl.

31. The method of claim 30, wherein Y is selected from the group consisting of aziridinyl, azetidinyl and pyrrolidinyl.

32. The method of claim 28 or 31, wherein R^1 and R^2 are independently selected from the group consisting of H and a cyclic or acyclic alkyl group having from 1 to 8 carbon atoms, with the proviso that at least one of R^1 and R^2 must be other than H.

33. The method of claim 32, wherein R^1 and R^2 are independently selected from the group consisting of H and an acyclic alkyl group having from 1 to 4 carbon atoms.

34. The method of claim 33, wherein R^1 and R^2 are independently selected from the group consisting of methyl, ethyl and isobutyl.

35. The method of claim 28 or 31, wherein R^3 is a cyclic or acyclic alkyl group having from 1 to 6 carbon atoms.

36. The method of claim 35, wherein R^3 is a linear or branched acyclic alkyl group having from 1 to 4 carbon atoms.

37. The method of claim 36, wherein R^3 is selected from the group consisting of methyl and ethyl.

38. The method of claim 37, wherein R^3 is a methyl group.

39. The method of claim 28 or 31, wherein R^4, R^5, R^6 and R^7 are independently selected from the group consisting of H and an acyclic alkyl group having from 1 to 4 carbon atoms.

40. The method of claim 39, wherein R^4, R^5, R^6 and R^7 are independently selected from the group consisting of methyl and ethyl.

41. The method of claim 25 wherein R^1 and R^2 are independently selected from the group consisting of methyl, ethyl and isobutyl, Y is pyrrolidinyl, and R^3 is selected from the group consisting of methyl and ethyl.

42. The method of claim 41, wherein the oxygen source is selected from H_2O in gaseous phase, H_2O_2 in gaseous phase, O_2, O_3 and hydrazine.
43. The method of claim 41 wherein the vapour deposition process is chemical vapour deposition.

44. The method of claim 41 wherein the vapour deposition process is atomic layer deposition.

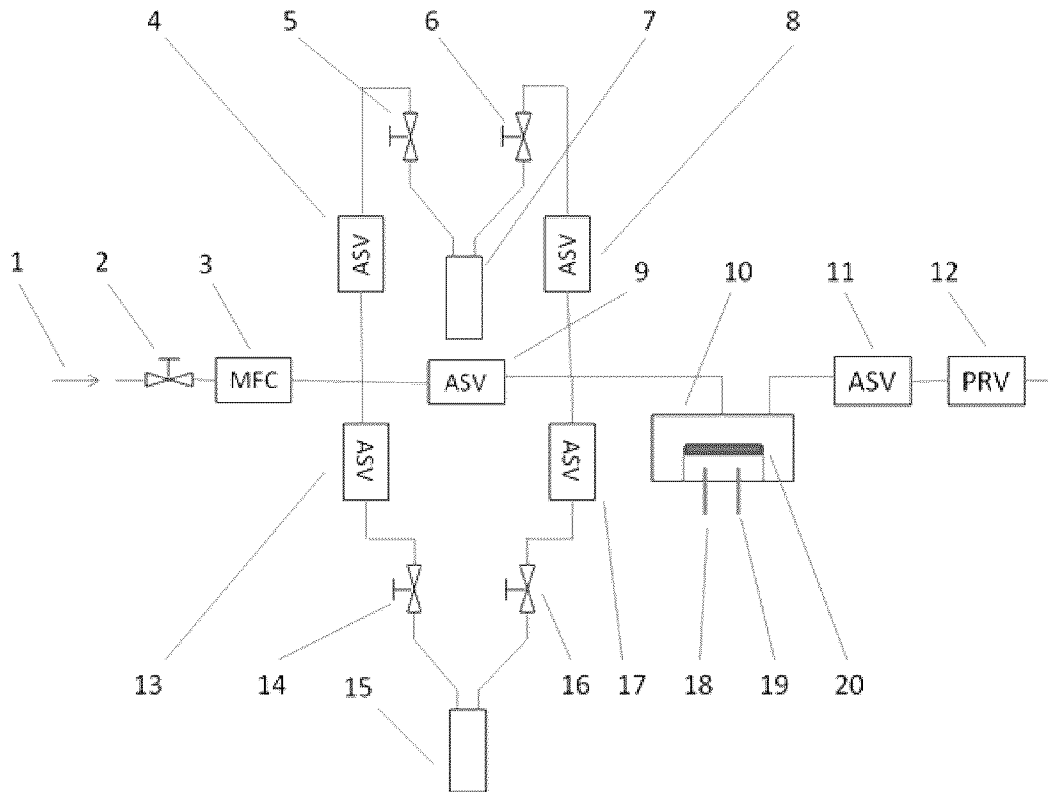


Figure 1 . Sketch of ALD system for thin film deposition.

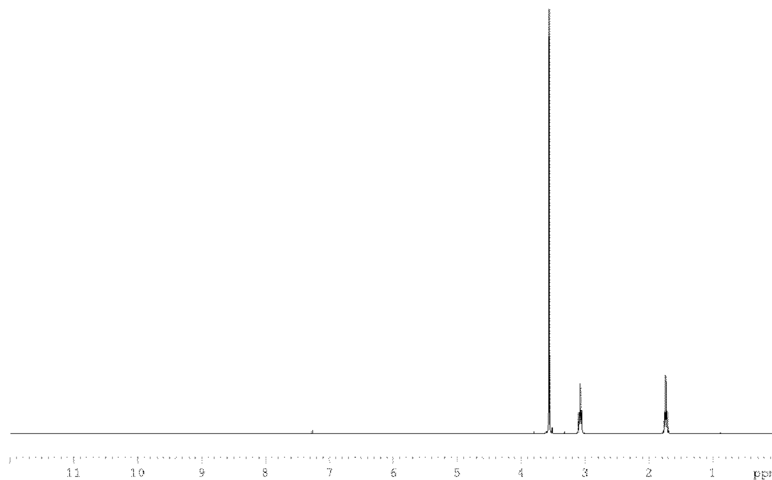


Figure 2 . NMR spectrum of (pyrro)Si(OMe)$_3$

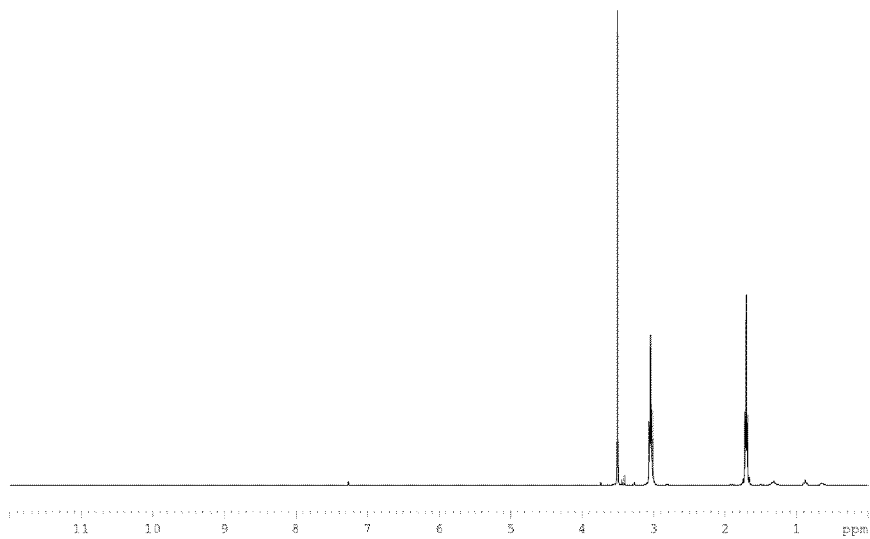


Figure 3. NMR spectrum of $(pyrro)_2Si(OMe)_2$

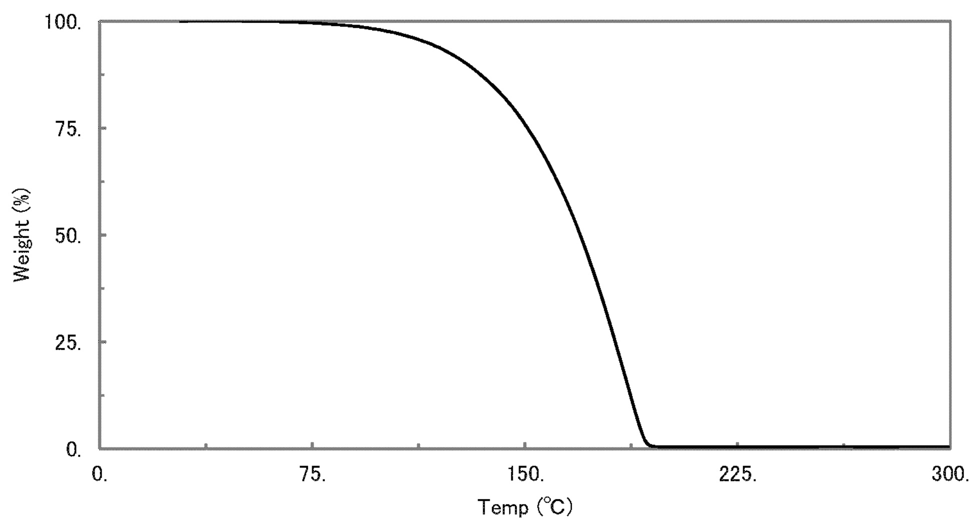


Figure 4. TGA of $(pyrro)_2Si(OMe)_2$

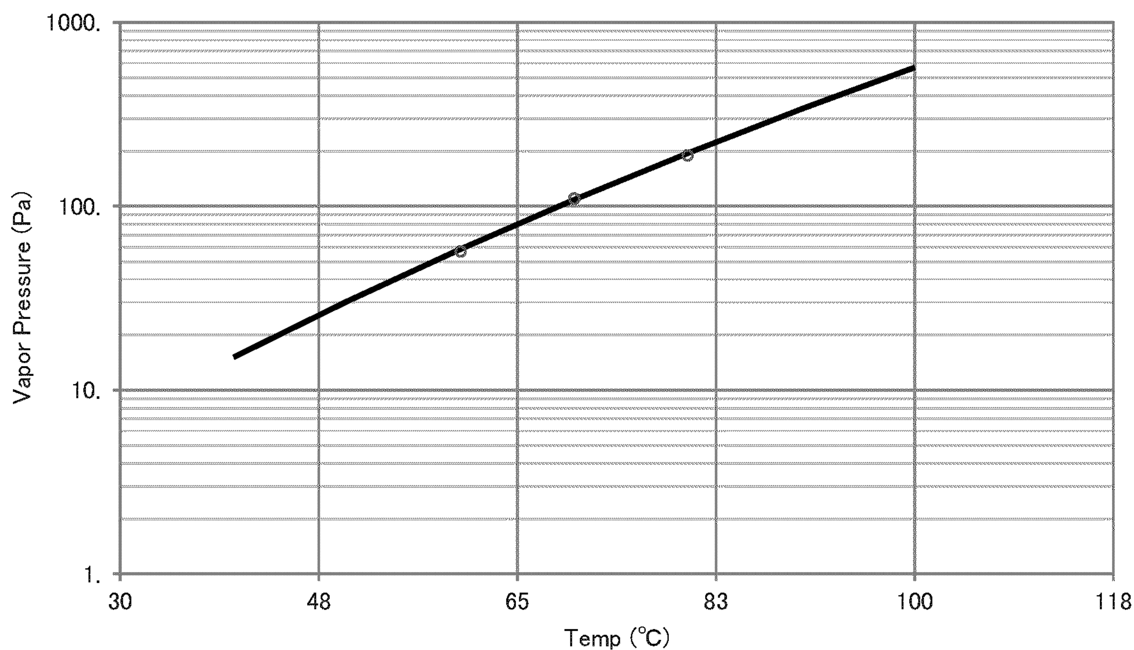


Figure 5. Vapour pressure of $(pyrro)_2Si(OMe)_2$

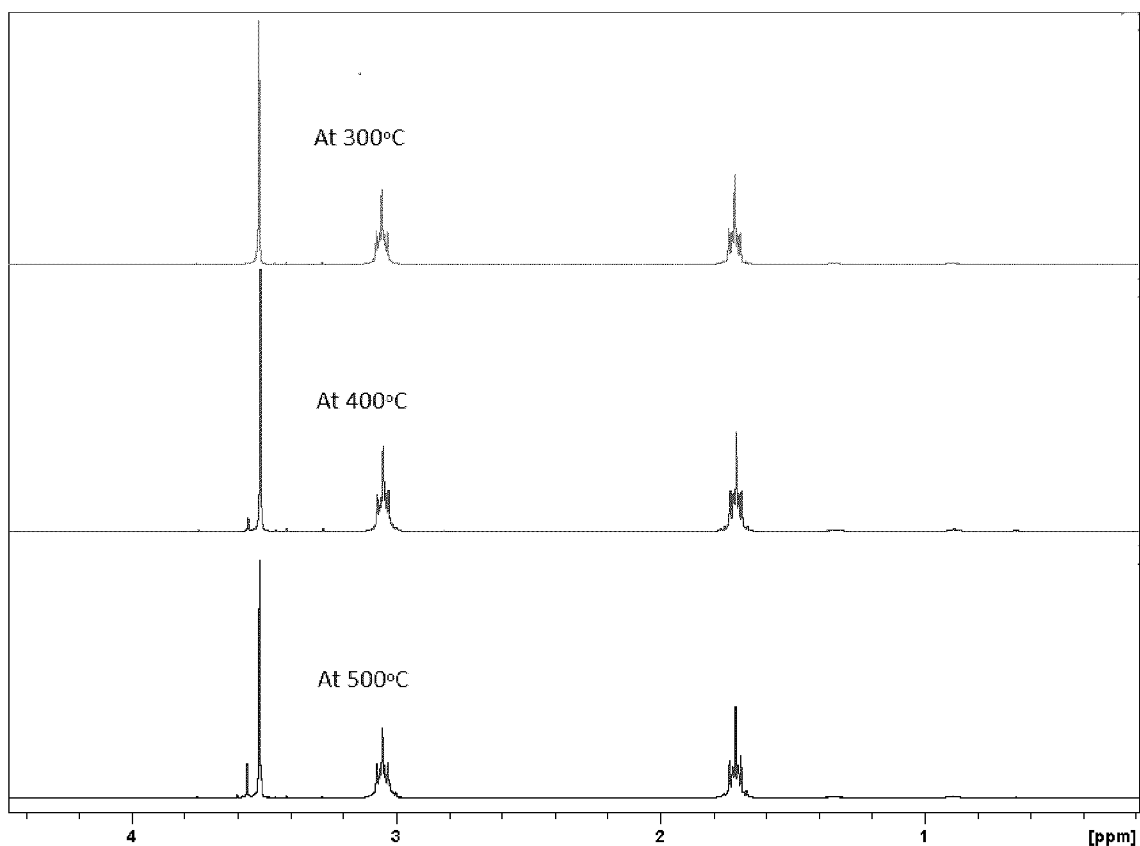


Figure 6. NMR spectra of thermally treated $(pyrro)_2Si(OMe)_2$

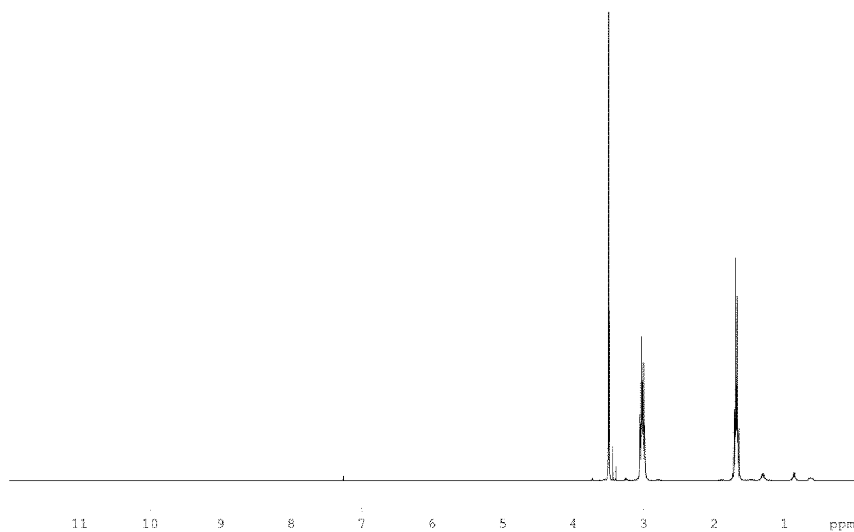


Figure 7. NMR spectrum of $(pyrro)_3Si(OMe)$

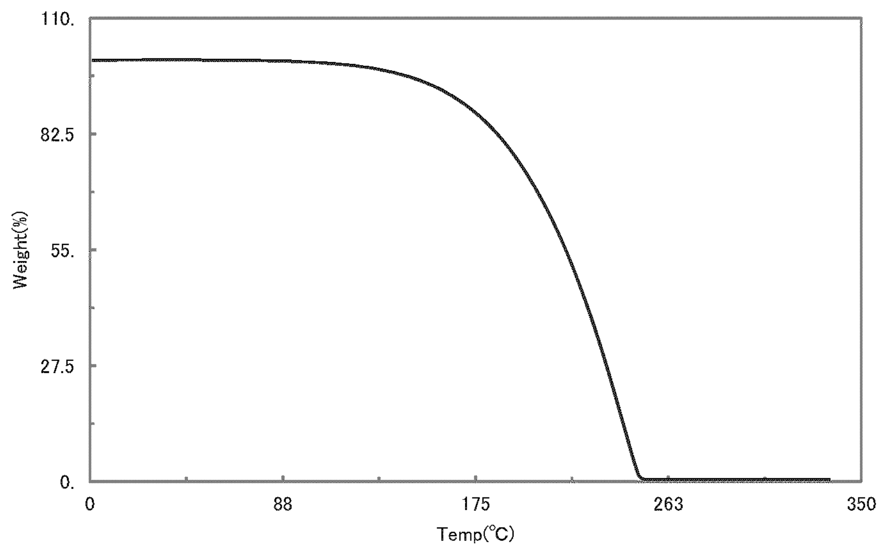


Figure 8. TGA of $(pyrro)_3Si(OMe)$

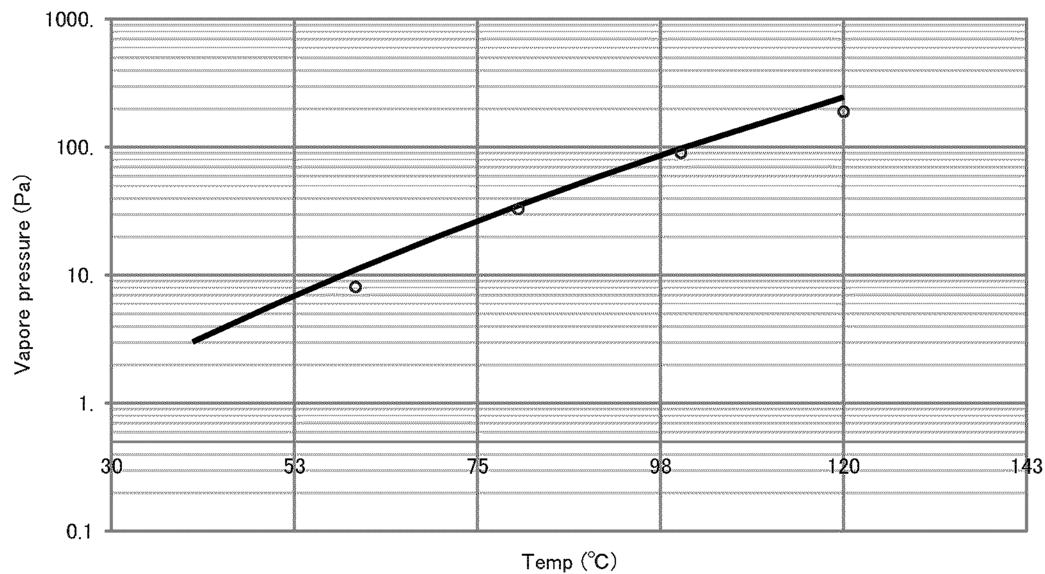


Figure 9. Vapour pressure of (pyrro)$_3$Si(OMe)

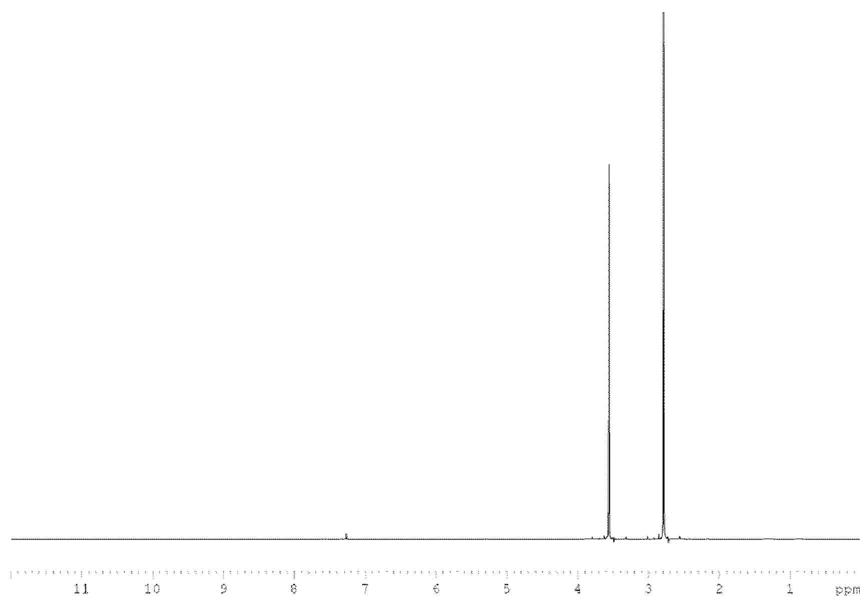


Figure 10. NMR spectrum of (Tetramethylguanidinyl)Si(OMe)$_3$

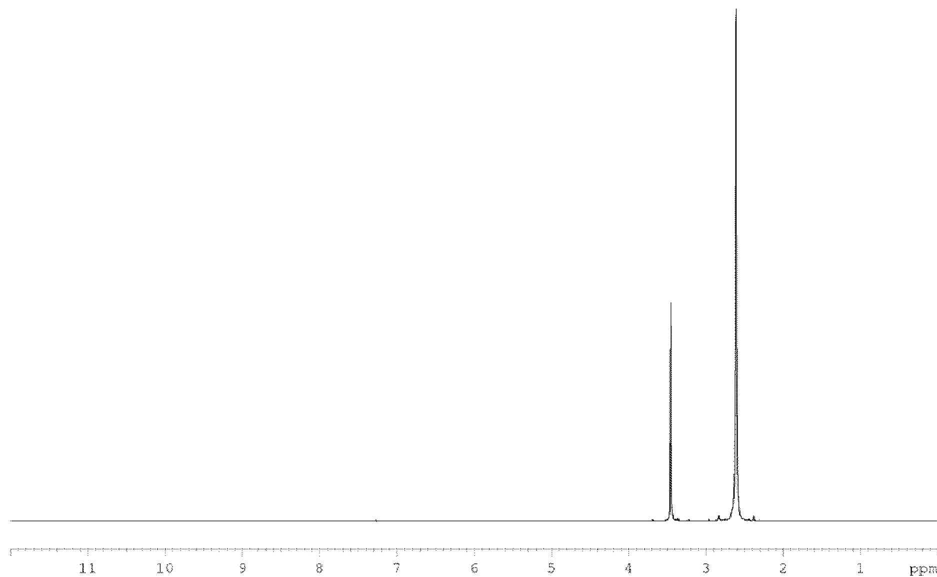


Figure 11. NMR spectrum of (Tetramethylguanidinyl)$_2$Si(OMe)$_2$

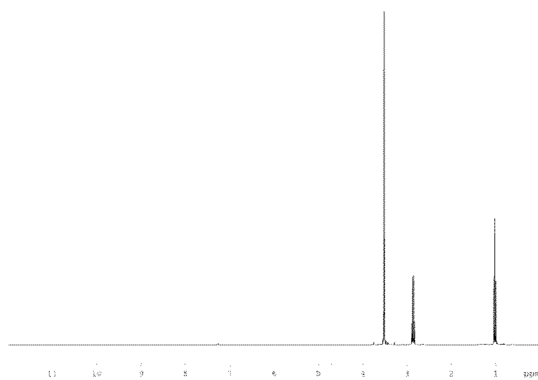


Figure 12. NMR spectrum of (Et_2N)Si(OMe)$_3$

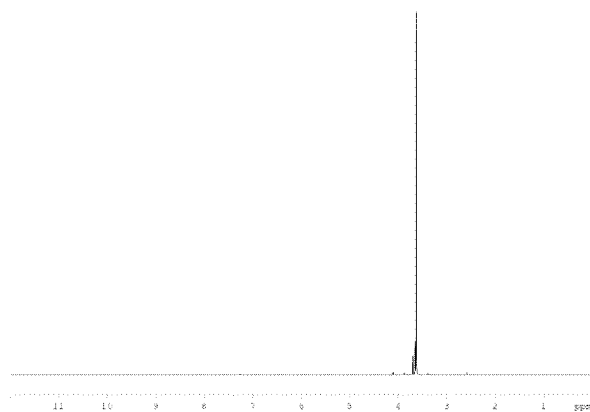


Figure 13. NMR spectrum of $ClSi(OMe)_3$

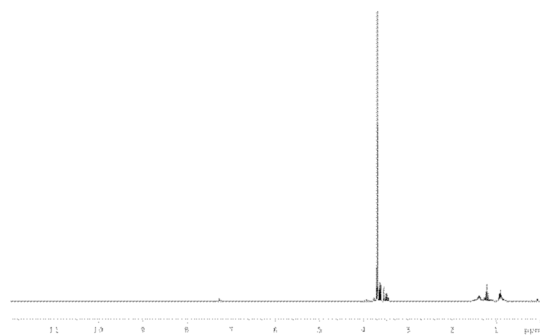


Figure 14. NMR spectrum of $Cl_2Si(OMe)_2$

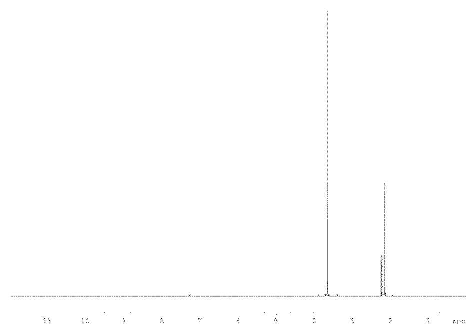


Figure 15. NMR spectrum of $(AcO)Si(OMe)_3$

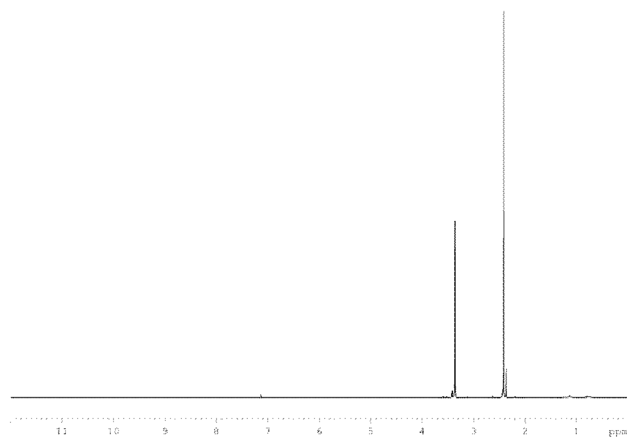


Figure 16. NMR spectrum of $(Me_2N)_2Si(OMe)_2$

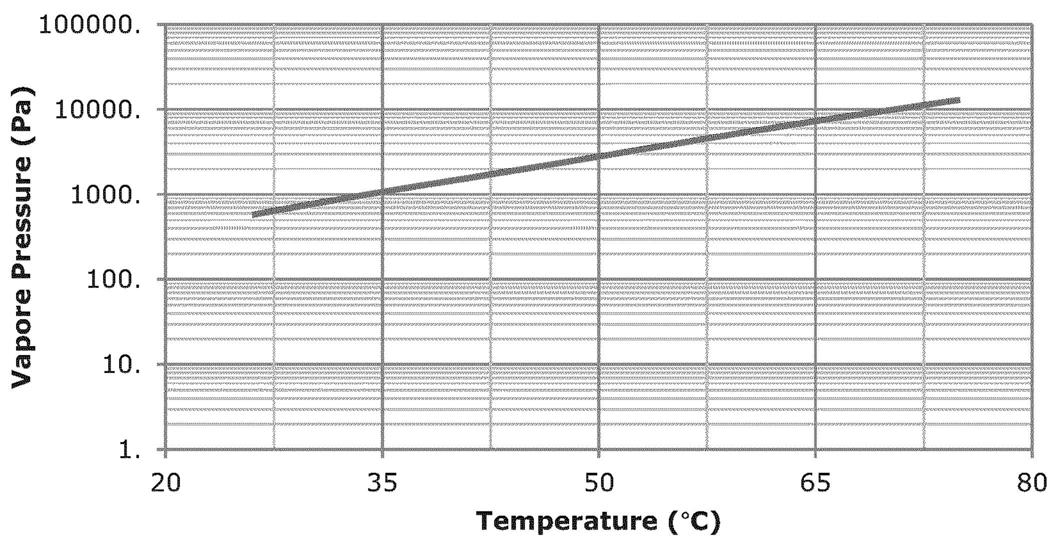


Figure 17. Vapour pressure of $(Me_2N)_2Si(OMe)_2$

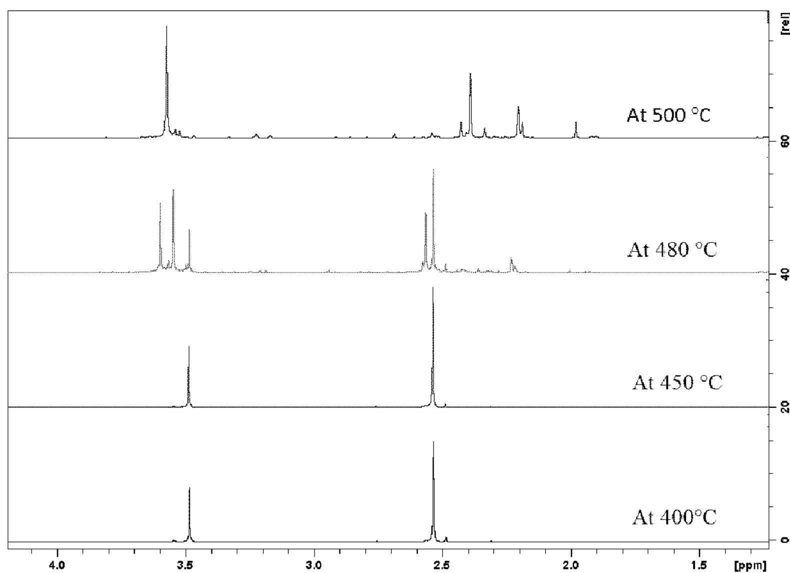


Figure 18. NMR spectra of thermally treated $(Me_2N)_2Si(OMe)_2$

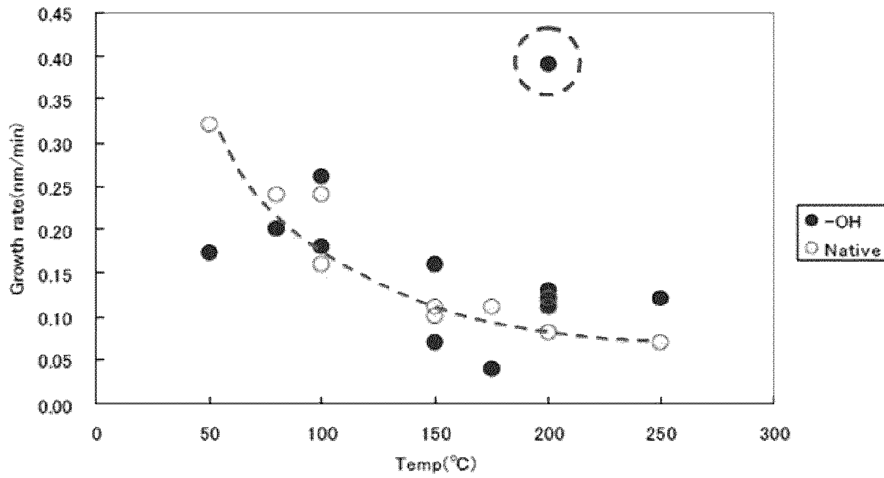


Figure 19. CVD growth rate vs. temperature of of SiO_2 using $(pyrrolidine)_2Si(OMe)_2$ and H_2O at 80 Torr.

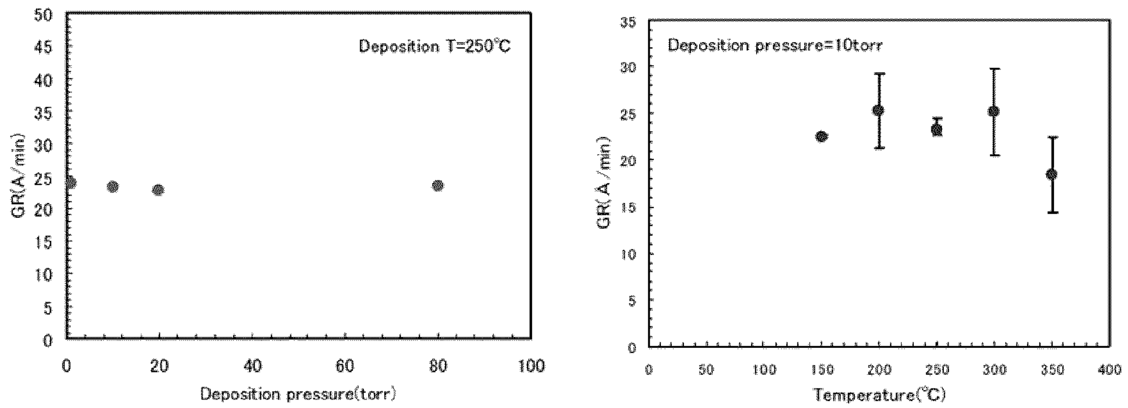


Figure 20. CVD growth rate vs. temperature and pressure of of SiO_2 using $(pyrrolidine)_2Si(OMe)_2$ and O_3

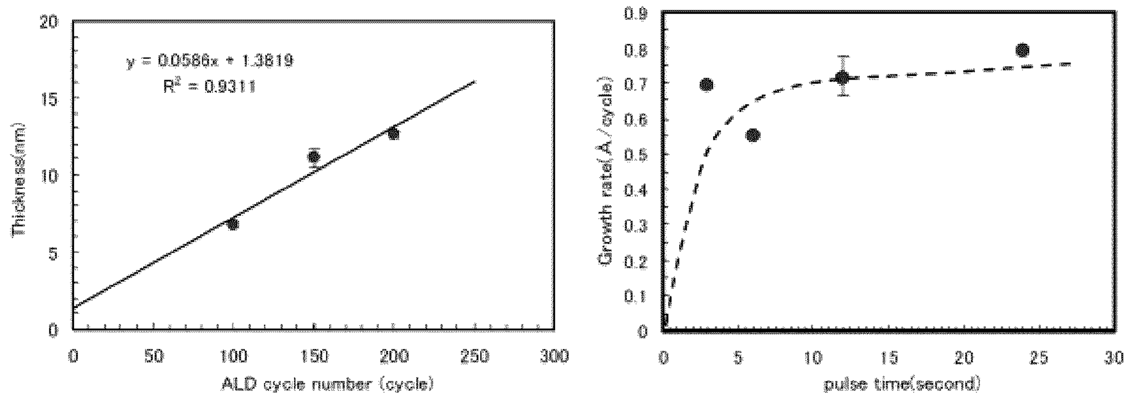


Figure 21. ALD of SiO_2 using $(pyrrolidine)_2Si(OMe)_2$ and O_3 carried out showing linear film thickness with number of ALD cycles and flattening of the growth rate with $(pyrrolidine)_2Si(OMe)_2$ pulse time

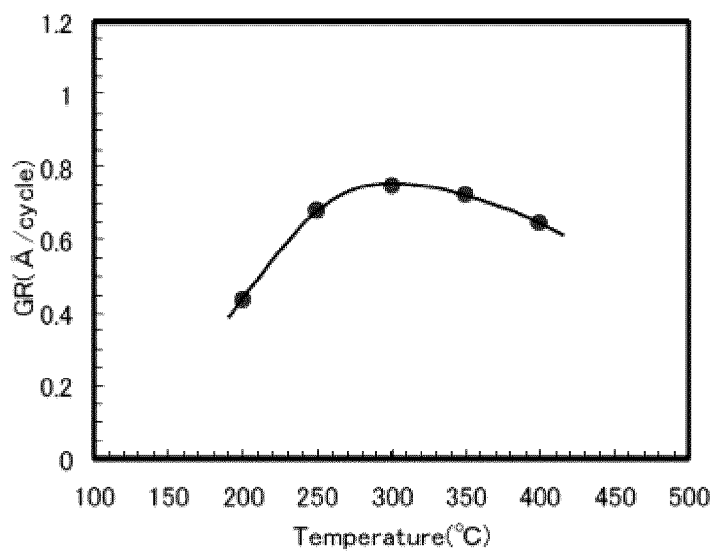


Figure 22. ALD of SiO_2 using $(pyrrolidine)_2Si(OMe)_2$ and O_3 carried out, showing the temperature effect on the growth rate, suggesting best ALD window is 250-400°C

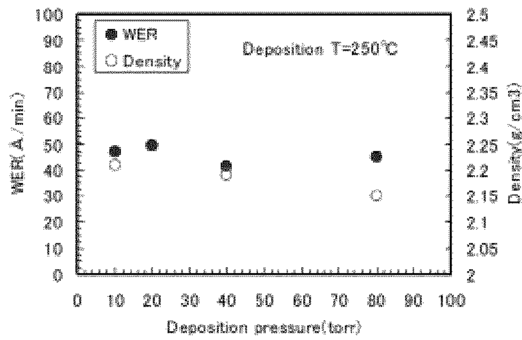


Figure 23. Wet etching rate of SiO_2 films in dilute HF acid (0.1%), films prepared by CVD at 250°C and various pressures using (pyrrolidine)$_2$Si(OMe)$_2$ and O_3

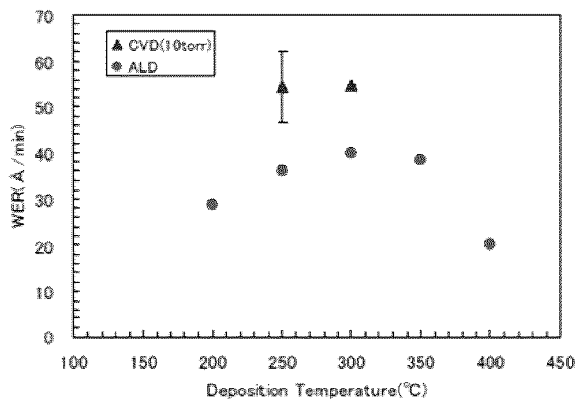


Figure 24. Wet etching rate of SiO_2 films in dilute HF acid (0.1%), films prepared by CVD and ALD at various temperatures using (pyrrolidine)$_2$Si(OMe)$_2$ and O_3

Precursor	Oxidant	Deposition Temperature	Growth Rate (Å/cycle)	Wet Etch Rate (A/minutes in 0.5% HF)
Tris(dimethylamino) silane – 3DMAS	Ozone (O_3)	350 °C	0.9	300
Bis(diethylamino) silane – BDEAS	Ozone (O_3)	350 °C	1.2	300
Amino Silane A	Ozone (O_3)	350 °C	1.8	300
(pyrrolodinyl)$_2$Si(OMe)$_2$ Example 2	Ozone (O_3)	350 °C	0.7	200

Figure 25. Table showing the wet etching rate comparison of the new material with commercially available material used to carry out deposition of silicon oxide films using the same conditions

INTERNATIONAL SEARCH REPORT	International application No. **PCT/CA2017/050158**

A. CLASSIFICATION OF SUBJECT MATTER
IPC: ***C07F 7/04*** (2006.01) , ***C23C 16/40*** (2006.01) , ***C23C 16/44*** (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 7/04*** , ***C23C 16/40*** , ***C23C 16/44***

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 Express (Registry, CAPlus), Canadian Patent Database

Keywords: vapour deposition, atomic layer deposition, organometallic

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US5599387A (NEUMAN, G. A. et al.) 04 February 1997 (04-02-1997) **see column 12, line 3 to column 13, line 14, Table 2 and the claims**	1-5, 21-24, 41-43
X	US5401305A (RUSSO, D. A. et al.) 28 March 1995 (28-03-1995) **see the claims**	1-5, 21-24, 41-43
X	WO9312892A1 (RUSSO, D. A. et al.) 08 July 1993 (08-07-1993) *see claims 1, 14, 15**	1-5, 21-24, 41-43
X	KR101308572B1, (YEUM, H. Y. et al.) 13 September 2013 (13-09-2013) **see the abstract, para. 62 and the claims**	1-8, 12-16, 19-28, 32-36, 39-44
X	JP2011018718A (FUJIMURA, H. et al) 27 January 2011 (27-01-2011) **see the whole document**	1-8, 12-28, 32-44

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

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"E"	earlier application or patent but published on or after the international filing date	"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
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"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		

Date of the actual completion of the international search	Date of mailing of the international search report
05 May 2017 (05-05-2017)	15 May 2017 (15-05-2017)

Name and mailing address of the ISA/CA	Authorized officer
Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 819-953-2476	Guillaume Tessier (819) 639-8671

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