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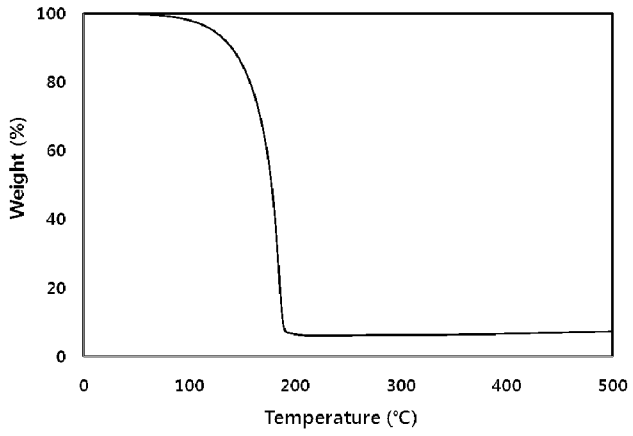
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(54) Title: NOVEL CYCLODISILAZANE DERIVATIVE, METHOD FOR PREPARING THE SAME AND SILICON-CONTAINING THIN FILM USING THE SAME



(57) Abstract: Provided are a novel cyclodisilazane derivative, a method for preparing the same, and a silicon-containing thin film using the same, wherein the cyclodisilazane derivative having thermal stability, high volatility, and high reactivity and being present in a liquid state at room temperature and under a pressure where handling is easy, may form a high purity silicon-containing thin film having excellent physical and electrical properties by various deposition methods.

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Description

Title of Invention: NOVEL CYCLODISILAZANE DERIVATIVE, METHOD FOR PREPARING THE SAME AND SILICON-CONTAINING THIN FILM USING THE SAME

Technical Field

[1] The present invention relates to a novel cyclodisilazane derivative, a method for preparing the same, and a silicon-containing thin film using the same, and more particularly, to a novel cyclodisilazane derivative having thermal stability and high volatility and being present in a liquid state at room temperature and under a pressure where handling is easy, a method for preparing the same, and a silicon-containing thin film using the same.

Background Art

[2] A silicon-containing thin film is manufactured in various shapes, such as a silicon film, a silicon oxide film, a silicon nitride film, a silicon carbonitride film, a silicon oxynitride film, and the like, by various deposition processes in a semiconductor field, and is variously applied to many fields.

[3] In particular, the silicon oxide film and the silicon nitride film may function as an insulating film, a diffusion prevention film, a hard mask, an etching stop layer, a seed layer, a spacer, trench isolation, intermetallic dielectric material and a protective layer in manufacturing a device, due to significantly excellent block property and oxidation resistance.

[4] Recently, polycrystalline silicon thin film has been used for a thin film transistor (TFT), a solar cell, and the like, and therefore, the application field thereof has varied.

[5] As a representative technology known for manufacturing a silicon-containing thin film, there are metal organic chemical vapor deposition (MOCVD) forming a film on a surface of a substrate by reacting a silicon precursor in a mixed gas form and a reactive gas, or forming a film by direct reaction on a surface, and atomic layer deposition (ALD) forming a film by physical or chemical adsorption of a silicon precursor in a gas form on a surface of a substrate, followed by sequential introduction of a reactive gas. In addition, various technologies for manufacturing a thin film such as low pressure chemical vapor deposition (LPCVD), plasma enhanced chemical vapor deposition (PECVD), plasma enhanced atomic layer deposition (PEALD) using plasma capable of being deposited at a low temperature, and the like, are applied to a next-generation semiconductor and a display device manufacturing process, thereby being used to form ultra-fine patterns and deposit ultra-thin film having uniform and excellent properties at a nano-sized thickness.

[6] Representative examples of a precursor used in forming a silicon-containing thin film as described in Korean Patent Laid-Open Publication No. KR 2007-0055898 include silanes, silane chlorides, amino silanes and alkoxysilanes, and more specifically, silane chlorides such as dichlorosilane (SiH_2Cl_2) and hexachlorodisilane ($Cl_3SiSiCl_3$) and trisilylamine ($N(SiH_3)_3$), bis-diethylaminosilane ($H_2Si(N(CH_2CH_3)_2)_2$) and di-isopropylaminosilane ($H_3SiN(i\text{-}C_3H_7)_2$), and the like, and used in a mass production of a semiconductor and a display.

[7] However, a technology of forming an ultra-fine thin film having a uniform and thin thickness and excellent electrical properties at a desired low temperature according to miniaturization of devices caused by ultra-high integration of the devices, an increase in an aspect ratio, and diversification of device material has been demanded, and thus, high temperature process at 600℃ or more, step coverage, etching property, and physical and electrical properties of a thin film at the time of using the existing silicon precursor are emerging as an issue, and accordingly, excellent novel silicon precursor has been demanded to be developed.

[8] [Related Art Document]

[9] (Patent Document 1) Korean Patent Laid-Open Publication No. KR 2007-0055898

[10] (Patent Document 2) U.S. Patent Application Publication No. 2004-0096582A1

Disclosure of Invention

Technical Problem

[11] An object of the present invention is to provide a cyclodisilazane derivative.

[12] In addition, another object of the present invention is to provide a novel cyclo-disilazane derivative which is a precursor compound for thin film deposition.

[13] Further, another object of the present invention is to provide a method for preparing a cyclodisilazane derivative.

[14] In addition, another object of the present invention is to provide a composition for depositing a silicon-containing thin film, which includes the cyclodisilazane derivative of the present invention, a method for manufacturing a silicon-containing thin film by using the cyclodisilazane derivative of the present invention, and the silicon-containing thin film manufactured by including the cyclodisilazane derivative of the present invention.

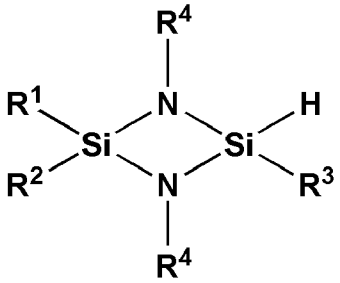
Solution to Problem

[15] In one general aspect, the present invention provides a novel cyclodisilazane derivative capable of forming a silicon thin film having excellent cohesion, high de-position rate, and excellent physical and electrical properties even at a low tem-perature.

[16] The novel cyclodisilazane derivative of the present invention is represented by the

following Chemical Formula 1:

[17] [Chemical Formula 1]

[18] 

[19] in Chemical Formula 1,

[20] R^1 to R^3 are each independently hydrogen, halogen, (C1-C5)alkyl or (C2-C5)alkenyl, and

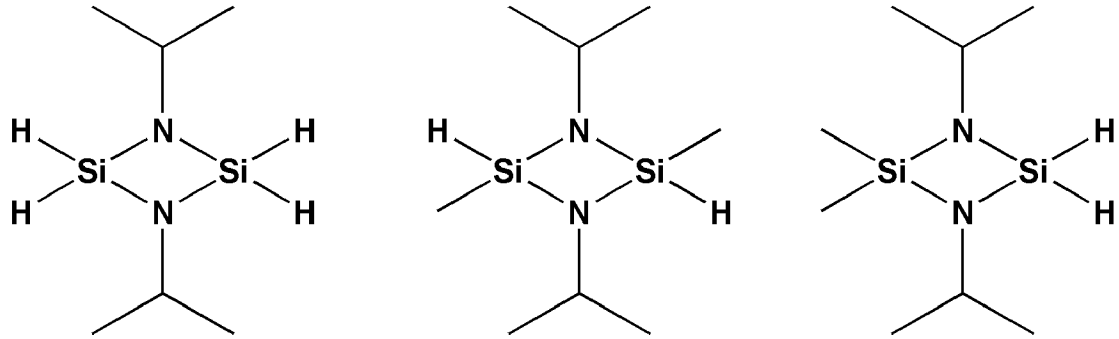
[21] R^4 is hydrogen, (C1-C3)alkyl or (C2-C5)alkenyl.

[22] The cyclodisilazane derivative of the present invention is a liquid-state compound at room temperature and under atmospheric pressure to have superior volatility, thereby allowing a thin film to be easily formed. In addition, the cyclodisilazane derivative, which is a stable square-shaped ring compound having a Si-N bond, has an advantage of controlling symmetry and asymmetry of a compound according to a substituent group to be capable of controlling reactivity. Further, due to the molecular structure having the square-shaped ring, the cyclodisilazane derivative of the present invention has high thermal stability and low activation energy to thereby have excellent re-activity, and does not generate non-volatile by-product to be capable of easily forming a silicon-containing thin film having high purity.

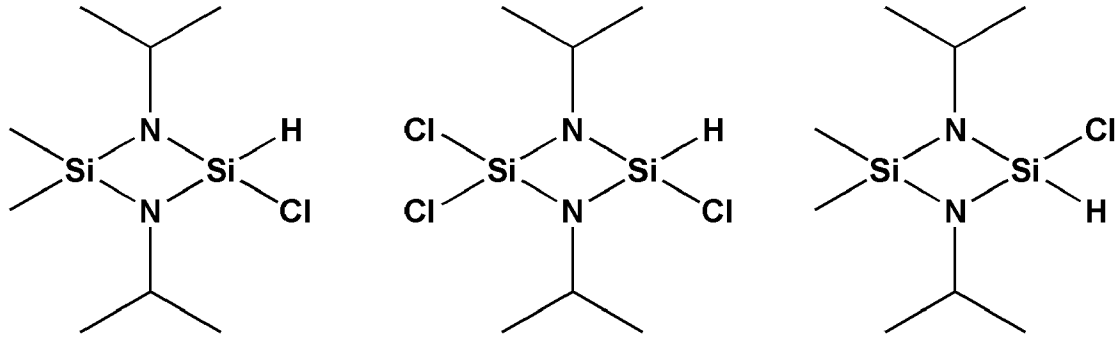
[23] In order for the cyclodisilazane derivative represented by Chemical Formula 1 according to an exemplary embodiment of the present invention to form a thin film having high thermal stability and reactivity, and high purity, it is preferred that in Chemical Formula 1, R^1 to R^3 are each independently hydrogen, halogen, (C1-C3)alkyl or (C2-C3)alkenyl, and R^4 is (C1-C3)alkyl or (C2-C3)alkenyl, and it is more preferred that in Chemical Formula 1, R^1 to R^3 are each independently hydrogen, halogen, methyl or ethenyl, and R^4 is isopropyl or isopropenyl.

[24] The cyclodisilazane derivative represented by Chemical Formula 1 according to an exemplary embodiment of the present invention may be selected from the following compounds, but the present invention is not limited thereto:

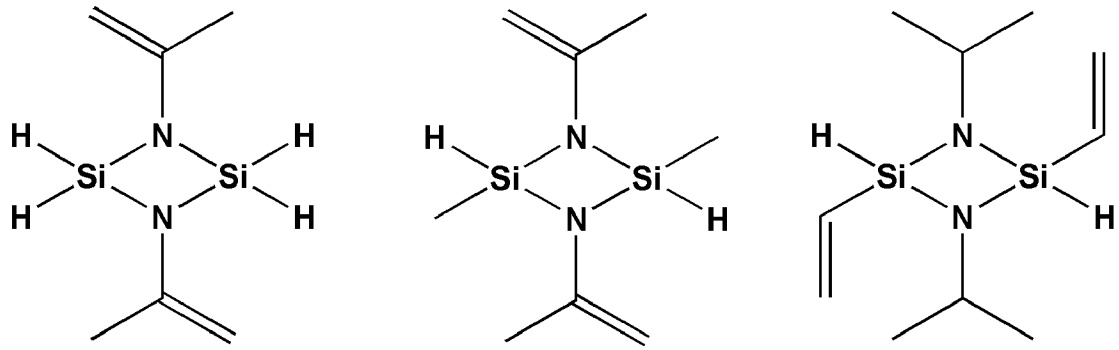
[25]



[26]



[27]



[28] Terms: 「alkyl」 described in the present invention includes both of linear type or branched type.

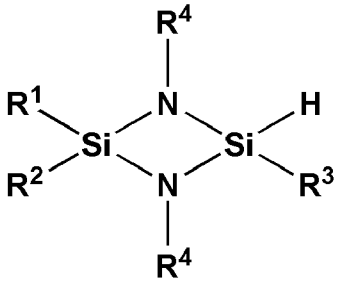
[29] In addition, the cyclodisilazane derivative represented by Chemical Formula 1 of the present invention may be preferably a precursor compound for depositing a silicon-containing thin film.

[30] Further, in another general aspect, the present invention provides a method for preparing a cyclodisilazane derivative represented by the following Chemical Formula 1.

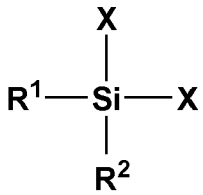
[31] The method for preparing the cyclodisilazane derivative of the present invention includes preparing a diaminosilane derivative represented by the following Chemical Formula 4 by reacting a silane derivative represented by the following Chemical Formula 2 with an amine derivative represented by the following Chemical Formula 3; and preparing the cyclodisilazane derivative represented by the following Chemical Formula 1 by an intramolecular cyclization reaction of the diaminosilane derivative represented by the following Chemical Formula 4 with a silane derivative represented

by the following Chemical Formula 5 in the presence of (C1-C7)alkyllithium:

[32] [Chemical Formula 1]

[33] 

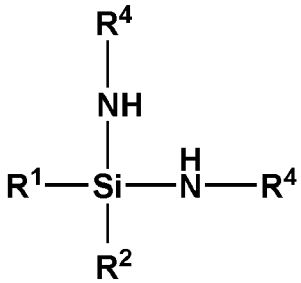
[34] [Chemical Formula 2]

[35] 

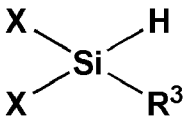
[36] [Chemical Formula 3]

[37] 

[38] [Chemical Formula 4]

[39] 

[40] [Chemical Formula 5]

[41] 

[42] in Chemical Formulas 1 to 5,

[43] R^1 to R^3 are each independently hydrogen, halogen, (C1-C5)alkyl or (C2-C5)alkenyl,

[44] R^4 is hydrogen, (C1-C3)alkyl or (C2-C5)alkenyl, and X is halogen.

[45] In an exemplary embodiment of the present invention, the preparing of the di-aminosilane derivative represented by Chemical Formula 4 may be performed in the presence of a base represented by the following Chemical Formula 10 or (C1-C7)alkyllithium:

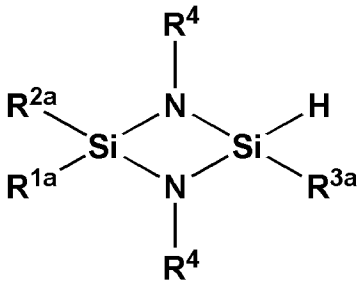
[46] [Chemical Formula 10]

[47] $N(R^6)(R^7)(R^8)$

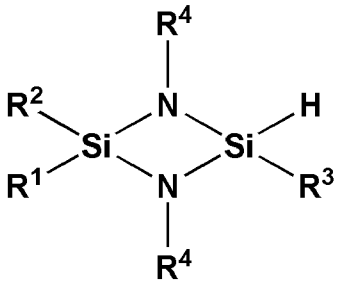
[48] in Chemical Formula 10, R^6 to R^8 are each independently (C1-C7)alkyl.

[49] In another general aspect, the present invention provides a method for preparing a cyclodisilazane derivative represented by the following Chemical Formula 1-2, the method including: preparing the cyclodisilazane derivative represented by the following Chemical Formula 1-2 by reacting a halocyclodisilazane derivative represented by the following Chemical Formula 1-1 with a metal hydride or an alkali metal derivative represented by the following Chemical Formula 8:

[50] [Chemical Formula 1-2]

[51] 

[52] [Chemical Formula 1-1]

[53] 

[54] [Chemical Formula 8]

[55] $M—R^{10}$

[56] in Chemical Formulas 1-1, 1-2, and 8,

[57] M is an alkali metal;

[58] R^{10} is each independently hydrogen or (C1-C5)alkyl;

[59] at least one of R^1 to R^3 is halogen, and the remainder is hydrogen, halogen, (C1-C5)alkyl or (C2-C5)alkenyl;

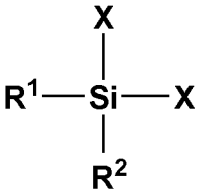
[60] R^4 is hydrogen, (C1-C3)alkyl or (C2-C5)alkenyl; and

[61] at least one of R^{1a} to R^{3a} is hydrogen, and the remainder is hydrogen, (C1-C5)alkyl or (C2-C5)alkenyl, wherein when R^1 is halogen, R^{1a} is hydrogen, and when R^2 is halogen, R^{2a} is hydrogen, and when R^3 is halogen, R^{3a} is hydrogen.

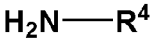
[62] In another general aspect, the present invention provides a method for preparing a cyclodisilazane derivative represented by the following Chemical Formula 9, the method including: preparing an aminosilane derivative represented by the following Chemical Formula 6 by reacting a silane derivative represented by the following Chemical Formula 2 with an amine derivative represented by the following Chemical Formula 3; preparing a halocyclodisilazane derivative represented by the following Chemical

Formula 7 by an intramolecular cyclization reaction of the aminosilane derivative represented by the following Chemical Formula 6 in the presence of (C1-C7)alkyllithium; and preparing the cyclodisilazane derivative represented by the following Chemical Formula 9 by reacting the halocyclodisilazane derivative represented by the following Chemical Formula 7 with a metal hydride or an alkali metal derivative represented by the following Chemical Formula 8:

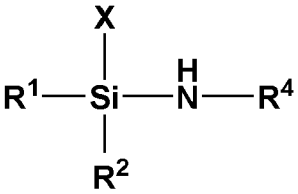
[63] [Chemical Formula 2]

[64] 

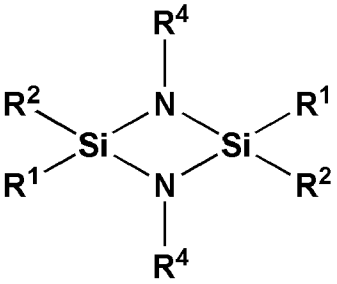
[65] [Chemical Formula 3]

[66] 

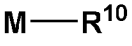
[67] [Chemical Formula 6]

[68] 

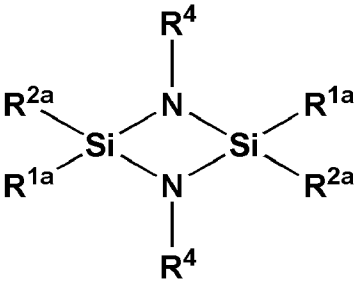
[69] [Chemical Formula 7]

[70] 

[71] [Chemical Formula 8]

[72] 

[73] [Chemical Formula 9]

[74] 

[75] in Chemical Formulas 2, 3 and 6 to 9,

[76] R^1 is halogen;

[77] R^2 is hydrogen, halogen, (C1-C5)alkyl or (C2-C5)alkenyl;

[78] R^4 is hydrogen, (C1-C3)alkyl or (C2-C5)alkenyl;

[79] X is halogen;

[80] M is an alkali metal;

[81] R^{10} is hydrogen or (C1-C5)alkyl;

[82] R^{1a} is hydrogen;

[83] wherein when R^2 is hydrogen or halogen, R^{2a} is hydrogen, and

[84] when R^2 is (C1-C5)alkyl or (C2-C5)alkenyl, R^{2a} is (C1-C5)alkyl or (C2-C5)alkenyl.

[85] In an exemplary embodiment of the present invention, the preparing of the aminosilane derivative represented by Chemical Formula 6 may be performed in the presence of a base represented by the following Chemical Formula 10 or (C1-C7)alkyllithium:

[86] [Chemical Formula 10]

[87] $N(R^6)(R^7)(R^8)$

[88] in Chemical Formula 10, R^6 to R^8 are each independently (C1-C7)alkyl.

[89] (C1-C7)alkyllithium according to an exemplary embodiment of the present invention is a compound where lithium is bonded to (C1-C7)alkyl, for example, methyllithium, n-butyllithium, and the like, and preferably, n-butyllithium.

[90] The metal hydride according to an exemplary embodiment of the present invention may be one or a mixture of two or more, selected from the group consisting of LiH, NaH, KH and $LiAlH_4$.

[91] Solvents used in the preparation method of the present invention are not limited if they are not reacted with the starting material among general organic solvents, for example, may be at least one selected from the group consisting of normalhexane (n-hexane), cyclohexane, normalpentane (n-pentane), diethyl ether, toluene, tetrahydrofuran (THF), dichloromethane (DCM), and trichloromethane (chloroform).

[92] A reaction temperature in the preparation method of the present invention is not limited if a temperature is used for general organic synthesis; however, may be varied depending on an amount of the reaction time, the reaction material, and the starting material, wherein the reaction needs to be finished after confirming that the starting material is completely consumed by NMR, GC, and the like. When the reaction is finished, the solvent may be removed by filtration, followed by simple distillation under reduced pressure, and then a desired material may be separated and refined by general methods such as fractional distillation, distillation under reduced pressure, and the like.

[93] In another general aspect, the present invention provides a composition for depositing a silicon-containing thin film, including the cyclodisilazane derivative as described above.

[94] The composition for depositing the silicon-containing thin film of the present invention may contain the cyclodisilazane derivative of the present invention as a precursor for thin film deposition, and the cyclodisilazane derivative in the composition may have a content within the range which is recognizable by a person skilled in the art in consideration of film forming conditions, or thickness, properties, and the like, of the thin film.

[95] In another general aspect, the present invention provides a method for manufacturing a silicon-containing thin film by using the cyclodisilazane derivative as described above.

[96] In another general aspect, the present invention provides a silicon-containing thin film manufactured by including the cyclodisilazane derivative as described above.

[97] The silicon-containing thin film of the present invention may be manufactured by general methods, for example, metal organic chemical vapor deposition (MOCVD), atomic layer deposition (ALD), low pressure chemical vapor deposition (LPCVD), plasma enhanced chemical vapor deposition (PECVD), plasma enhanced atomic layer deposition (PEALD), and the like.

[98] The cyclodisilazane derivative of the present invention has low activation energy and high reactivity, and minimizes generation of non-volatile by-product, such that the silicon-containing thin film manufactured by using the cyclodisilazane derivative as a precursor may have high purity and excellent physical and electrical properties.

Advantageous Effects of Invention

[99] The cyclodisilazane derivative of the present invention has excellent thermal stability and high reactivity, such that the silicon-containing thin film manufactured by using the cyclodisilazane derivative as a precursor may have high purity and significantly excellent physical and electrical properties.

[100] In addition, the cyclodisilazane derivative of the present invention may have high content of silicon and is present in a liquid state at room temperature and under atmospheric pressure to thereby be easily stored and handled, and may have high volatility and high reactivity to be rapidly and easily deposited, and it is possible to deposit a thin film having excellent cohesion and superior step coverage.

Brief Description of Drawings

[101] The above and other objects, features and advantages of the present invention will become apparent from the following description of preferred embodiments given in conjunction with the accompanying drawings, in which:

[102] FIG. 1 shows a result obtained by thermogravimetric analysis of 1,3-diisopropyl-2,4-dimethylcyclodisilazane prepared by Example 1.

[103] FIG. 2 shows a result obtained by vapor pressure measurement of

1,3-diisopropyl-2,4-dimethylcyclodisilazane prepared by Example 1.

[104] FIG. 3 shows a result obtained by thermogravimetric analysis of 1,3-diisopropyl-4,4-dimethylcyclodisilazane prepared by Example 6.

[105] FIG. 4 shows a result obtained by vapor pressure measurement of 1,3-diisopropyl-4,4-dimethylcyclodisilazane prepared by Example 6.

[106] FIG. 5 shows a method for depositing silicon-containing thin films practiced by Example 7 and Comparative Example 1.

[107] FIG. 6 shows results obtained by a step coverage analysis of the silicon-containing thin films practiced by Example 7, using Transmission Electron Microscopy.

[108] FIG. 7 shows results obtained by an infrared spectroscopic analysis of the silicon-containing thin films practiced by Example 7 and Comparative Example 1.

[109] FIG. 8 shows results obtained by an auger electron spectroscopic analysis of the silicon-containing thin films practiced by Example 7.

[110] FIG. 9 shows results obtained by an etch rate analysis of the silicon-containing thin films practiced by Example 7 and Comparative Example 1, using an Ellipsometer.

[111] FIG. 10 is a diagram showing a method for depositing a silicon-containing thin film practiced by Example 8.

[112] FIG. 11 shows a result obtained by an infrared spectroscopic analysis of the silicon-containing thin film practiced by Example 8.

Mode for the Invention

[113] Hereinafter, the present invention will be described in more detail with reference to the following exemplary embodiments. However, the following exemplary embodiments describe the present invention by way of example only but are not limited thereto.

[114] The following Examples of all compounds were practiced under anhydrous and inert atmosphere using a glovebox or a Schlenk pipe, products were analyzed by ^1H Nuclear Magnetic Resonance (NMR, 400MHz Ultrashield, Buruker), thermogravimetric analysis (TGA, L81-II, LINSEIS) and gas chromatography (GC, 7890A, Agilent Technologies), thickness of deposited thin films were measured by an Ellipsometer (M2000D, Woollam), and components of the films were analyzed by infrared spectroscopy (IFS66V/S & Hyperion 3000, Bruker Optiks)and auger electron spectroscopy (Microlab 350, Thermo Electron).

[115] **[Example 1] Synthesis of 1,**3-diisopropyl-2,4-dimethylcyclodisilazane

[116] 1) Synthesis of 1,3-diisopropyl-2,4-dichlorodimethylcyclodisilazane

[117] 127g (0.86mol) of trichloro(methyl)silane (CH_3SiCl_3) and 1200ml of an organic solvent (n-hexane) were put into a 2000mL flame-dried Schlenk flask and stirred under anhydrous and inert atmosphere, and 101.7g (1.72mol) of isopropylamine ($H_2NCH(CH$

$_3)_2$) was slowly added thereto while maintaining temperature at -10℃. After the addition was completed, a temperature of the reaction solution was slowly raised to room temperature, and the reaction solution was stirred at room temperature for 3 hours. After the stirring was completed, the reaction solution was filtrated, and a white solid obtained by the filtration was removed to obtain a filtrate. 200ml of an organic solvent (n-hexane) was put into dichloro(methyl)(isopropylamino)silane (Cl_2CH_3 SiNHCH$(CH_3)_2$) recovered after the solvent was removed from the filtrate under reduced pressure, and stirred, and then 367.0g (0.90mol) of 1.7M t-butyllithium (t-C_4H_9Li) hexane (C_6H_{14}) solution was slowly added thereto while maintaining temperature at 40℃. After the addition was completed, a temperature of the reaction solution was slowly raised to 65℃, and the reaction solution was stirred for 12 hours. After the stirring was completed, the reaction solution was filtrated, and a white solid obtained by the filtration was removed to obtain a filtrate, and then a solvent was removed from the filtrate under reduced pressure, and 81.4g (0.30mol) of 1,3-diisopropyl-2,4-dichlorodimethylcyclodisilazane ((ClCH$_3$SiNCH$(CH_3)_2)_2$) was obtained by reduced pressure distillation with a yield of 70%.

[118] ^{1}H NMR (in C_6D_6) δ 0.50, 0.53(s, 6H, csi-NSi(C*H*$_3$)Cl, trans-NSi(C*H*$_3$)Cl), 1.07(d, 12H, Si(NCH(C*H*$_3)_2$), 3.27(m, 2H, Si(NC*H*$(CH_3)_2$); Boiling Point 197℃.

[119] 2) Synthesis of 1,3-diisopropyl-2,4-dimethylcyclodisilazane

[120] 100g (0.37mol) of 1,3-diisopropyl-2,4-dichlorodimethyl cyclodisilazane ((ClCH$_3$ SiNCH$(CH_3)_2)_2$) synthesized in the above 1) and 200ml of an organic solvent (THF) were put into a 1000 mL flame-dried Schlenk flask and stirred under anhydrous and inert atmosphere, and 7.33g (0.92mol) of lithium hydride (LiH) was slowly added thereto while maintaining temperature at -15℃. After the addition was completed, a temperature of the reaction solution was slowly raised to 65℃, and the reaction solution was stirred for 12 hours. After the stirring was completed, the reaction solution was filtrated, and a white solid obtained by the filtration was removed to obtain a filtrate, and then a solvent was removed from the filtrate under reduced pressure, and 60g (0.3mol) of 1,3-diisopropyl-2,4-dimethylcyclodisilazane ((HCH$_3$ SiNCH$(CH_3)_2)_2$) was obtained by reduced pressure distillation with a yield of 80%.

[121] ^{1}H NMR (in C_6D_6) δ 0.33(m, 6H, NSiH(C*H*$_3$)), 1.05(m, 12H, Si(NCH(C*H*$_3)_2$), 3.20(m, 2H, Si(NC*H*$(CH_3)_2$), 5.52(m, 2H, NSi*H*(CH_3)); Boiling Point 173~175℃.

[122] **[Example 2] Synthesis of 1,**3-diisopropyl cyclodisilazane

[123] 1) Synthesis of 1,3-diisopropyl-2,2,4,4-tetrachlorocyclodisilazane

[124] 150g (0.89mol) of tetrachlorosilane ($SiCl_4$) and 500ml of an organic solvent (n-hexane) were put into a 2000 mL flame-dried Schlenk flask and stirred under anhydrous and inert atmosphere, and 104.76g (1.77mol) of isopropylamine (H_2 NCH$(CH_3)_2$) was slowly added thereto while maintaining temperature at -10℃. After

the addition was completed, a temperature of the reaction solution was slowly raised to room temperature, and the reaction solution was stirred at room temperature for 3 hours. After the stirring was completed, the reaction solution was filtrated, and a white solid obtained by the filtration was removed to obtain a filtrate. 200ml of an organic solvent (n-hexane) was put into trichloro(isopropylamino)silane ($Cl_3SiNHCH(CH_3)_2$) recovered after the solvent was removed from the filtrate under reduced pressure, and stirred, and then 368.38g (0.90mol) of 1.7M t-butyllithium (t-C_4H_9Li) hexane (C_6H_{14}) solution was slowly added thereto while maintaining temperature at 40℃. After the addition was completed, a temperature of the reaction solution was slowly raised to 65℃, and the reaction solution was stirred for 12 hours. After the stirring was completed, the reaction solution was filtrated, and a white solid obtained by the filtration was removed to obtain a filtrate, and then a solvent was removed from the filtrate under reduced pressure, and 121.7g (0.35mol) of 1,3-diisopropyl-2,2,4,4-tetrachlorocyclodisilazane ($(Cl_2SiNCH(CH_3)_2)_2$) was obtained by reduced pressure distillation with a yield of 88%.

[125] ^1H NMR (in C_6D_6) δ 1.10(d, 12H, Si(NCH(C*H*$_3)_2$), 3.34(m, 2H, Si(NC*H*$(CH_3)_2$); Boiling Point 216~217℃.

[126] 2) Synthesis of 1,3-diisopropyl cyclodisilazane

[127] 80g (0.26mol) of 1,3-diisopropyl-2,2,4,4-tetrachlorocyclodisilazane ($(Cl_2SiNCH(CH_3)_2)_2$) synthesized in the above 1) and 400ml of an organic solvent (diethylether) were put into a 2000 mL flame-dried Schlenk flask and stirred under anhydrous and inert atmosphere, and 12.35g (1.55mol) of lithium aluminum hydride ($LiAlH_4$) was slowly added thereto while maintaining temperature at -15℃. After the addition was completed, a temperature of the reaction solution was slowly raised to 60℃, and the reaction solution was stirred for 12 hours. After the stirring was completed, the reaction solution was filtrated, and a white solid obtained by the filtration was removed to obtain a filtrate, and then a solvent was removed from the filtrate under reduced pressure, and 26.8g (0.16mol) of 1,3-diisopropylcyclodisilazane ($(H_2SiNCH(CH_3)_2)_2$) was obtained by reduced pressure distillation with a yield of 60%.

[128] ^1H NMR (in C_6D_6) δ 1.11(d, 12H, Si(NCH(C*H*$_3)_2$), 3.23(m, 2H, Si(NC*H*$(CH_3)_2$), 4.48(s, 2H, NSi*H*); Boiling Point 155~160℃.

[129] **[Example 3] Synthesis of 1,**3-diisopropyl-2-chloro-4,4-dimethyl cyclodisilazane

[130] 214g (1.66mol) of dichlorodimethylsilane ($Si(CH_3)_2Cl_2$) and 1000ml of an organic solvent (n-hexane) were put into a 2000 mL flame-dried Schlenk flask and stirred under anhydrous and inert atmosphere, and 392.1g (6.63mol) of isopropylamine ($H_2NCH(CH_3)_2$) was slowly added thereto while maintaining temperature at -10℃. After the addition was completed, a temperature of the reaction solution was slowly raised to room temperature, and the reaction solution was stirred at room temperature for 3

hours. After the stirring was completed, the reaction solution was filtrated, and a white solid obtained by the filtration was removed to obtain a filtrate. 300ml of an organic solvent (n-hexane) was put into di(isopropylamino)dimethylsilane ($(CH_3)_2Si(NHCH(CH_3)_2)_2$) recovered after the solvent was removed from the filtrate under reduced pressure, and stirred, and then 1005.3g (3.32mol) of 2.5M n-butyllithium (n-C_4H_9Li) hexane (C_6H_{14}) solution was slowly added thereto while maintaining temperature at -15℃. After the addition was completed, a temperature of the reaction solution was slowly raised to 25℃, and the reaction solution was stirred for 12 hours, and then, 224.6g (1.66mol) of trichlorosilane ($SiHCl_3$) was slowly added thereto. After the addition was completed, a temperature of the reaction solution was slowly raised to 65℃, and the reaction solution was stirred for 12 hours. After the stirring was completed, the reaction solution was filtrated, and a white solid obtained by the filtration was removed to obtain a filtrate, and then a solvent was removed from the filtrate under reduced pressure, and 255.3g (1.08mol) of 1,3-diisopropyl-2-chloro-4,4-dimethylcyclodisilazane ($(((CH_3)_2SiNCH(CH_3)_2)(ClSiHNCH(CH_3)_2)$) was obtained by reduced pressure distillation with a yield of 65%.

[131] ^1H NMR (in C_6D_6) δ 0.19 and 0.21 (s, 6H, $NSi(CH_3)_2$), 1.03(d, 12H, $Si(NCH(CH_3)_2)$, 3.17(m, 2H, $Si(NCH(CH_3)_2)$, 5.99(s, 1H, NSi*H*Cl); Boiling Point 190℃.

[132] **[Example 4] Synthesis of 1,**3-diisopropyl-2-chloro-4,4-dimethyl cyclodisilazane

[133] 107g (0.83mol) of dichlorodimethylsilane ($(CH_3)_2SiCl_2$) and 400ml of an organic solvent (n-hexane) were put into a 1000 mL flame-dried Schlenk flask and stirred under anhydrous and inert atmosphere, and 167.7g (1.66mol) of triethylamine ($(C_2H_5)_3N$) was slowly added thereto while maintaining temperature at -10℃, and then 98.0g (1.65mol) of isopropylamine ($H_2NCH(CH_3)_2$) was slowly added thereto while maintaining temperature at -10℃. After the addition was completed, a temperature of the reaction solution was slowly raised to room temperature, and the reaction solution was stirred at room temperature for 3 hours. After the stirring was completed, the reaction solution was filtrated, and a white solid obtained by the filtration was removed to obtain a filtrate. 200ml of an organic solvent (n-hexane) was put into di(isopropylamino)dimethylsilane ($(CH_3)_2Si(NHCH(CH_3)_2)_2$) recovered after the solvent was removed from the filtrate under reduced pressure, and stirred, and then 351.8g (1.16mol) of 2.5M n-butyllithium (n-C_4H_9Li) hexane (C_6H_{14}) solution was slowly added thereto while maintaining temperature at -10℃. After the addition was completed, a temperature of the reaction solution was slowly raised to room temperature, and the reaction solution was stirred for 12 hours, and then, 224.6g (1.66mol) of trichlorosilane ($SiHCl_3$) was slowly added thereto. After the addition was completed, a temperature of the reaction solution was slowly raised to 65℃, and the

reaction solution was stirred for 12 hours. After the stirring was completed, the reaction solution was filtrated, and a white solid obtained by the filtration was removed to obtain a filtrate, and then a solvent was removed from the filtrate under reduced pressure, and 255.3g (1.08mol) of 1,3-diisopropyl-2-chloro-4,4-dimethylcyclodisilazane (($(CH_3)_2SiNCH(CH_3)_2$)($ClSiHNCH(CH_3)_2$)) was obtained by reduced pressure distillation with a yield of 65%.

[134] ^1H NMR (in C_6D_6) δ 0.19 and 0.21 (s, 6H, $NSi(CH_3)_2$), 1.03(d, 12H, $Si(NCH(CH_3)_2$), 3.17(m, 2H, $Si(NCH(CH_3)_2)$), 5.99(s, 1H, NSi*H*Cl); Boiling Point 190°C.

[135] **[Example 5] Synthesis of 1,**3-diisopropyl-2-chloro-4,4-dimethyl cyclodisilazane

[136] 98.0g (1.65mol) of isopropylamine ($H_2NCH(CH_3)_2$) and 400ml of an organic solvent (n-hexane) were put into a 1000 mL flame-dried Schlenk flask and stirred under anhydrous and inert atmosphere, and 500.4g (1.65mol) of 2.5M n-butyllithium (n-C_4H_9 Li) hexane (C_6H_{14}) solution was slowly added thereto while maintaining temperature at -10°C. After the addition was completed, a temperature of the reaction solution was slowly raised to room temperature, and the reaction solution was stirred at room temperature for 3 hours, and then 107g (0.83mol) of dichlorodimethylsilane ($(CH_3)_2SiCl_2$) was slowly added thereto while maintaining temperature at -10°C. After the addition was completed, a temperature of the reaction solution was slowly raised to room temperature, and the reaction solution was stirred at room temperature for 3 hours. After the stirring was completed, the reaction solution was filtrated, and a white solid obtained by the filtration was removed to obtain a filtrate. 200ml of an organic solvent (n-hexane) was put into di(isopropylamino)dimethylsilane ($(CH_3)_2Si(NHCH(CH_3)_2)_2$) recovered after the solvent was removed from the filtrate under reduced pressure, and stirred, and then 351.8g (1.16mol) of 2.5M n-butyllithium (n-C_4H_9Li) hexane (C_6H_{14}) solution was slowly added thereto while maintaining temperature at -10°C. After the addition was completed, a temperature of the reaction solution was slowly raised to room temperature, and the reaction solution was stirred for 12 hours, and then, 224.6g (1.66mol) of trichlorosilane ($SiHCl_3$) was slowly added thereto. After the addition was completed, a temperature of the reaction solution was slowly raised to 65°C, and the reaction solution was stirred for 12 hours. After the stirring was completed, the reaction solution was filtrated, and a white solid obtained by the filtration was removed to obtain a filtrate, and then a solvent was removed from the filtrate under reduced pressure, and 196.4g (0.83mol) of 1,3-diisopropyl-2-chloro-4,4-dimethylcyclodisilazane (($(CH_3)_2SiNCH(CH_3)_2$)($ClSiHNCH(CH_3)_2$)) was obtained by reduced pressure distillation with a yield of 50%.

[137] ^1H NMR (in C_6D_6) δ 0.19 and 0.21 (s, 6H, $NSi(CH_3)_2$), 1.03(d, 12H, $Si(NCH(CH_3)_2$),

3.17(m, 2H, Si(NC*H*$(CH_3)_2$), 5.99(s, 1H, NSi*H*Cl); Boiling Point 190℃.

[138] **[Example 6] Synthesis of 1,**3-diisopropyl-4,4-dimethylcyclodisilazane

[139] 200g (0.84mol) of 1,3-diisopropyl-2-chloro-4,4-dimethylcyclodisilazane ($(CH_3)_2$ SiNCH$(CH_3)_2$)(ClSiHNCH$(CH_3)_2$)) synthesized in Example 3 above and 600ml of an organic solvent (THF) were put into a 2000 mL flame-dried Schlenk flask and stirred under anhydrous and inert atmosphere, 7.4g (0.93mol) of lithium hydride (LiH) was slowly added thereto while maintaining temperature at -15℃. After the addition was completed, a temperature of the reaction solution was slowly raised to 65℃, and the reaction solution was stirred for 12 hours. After the stirring was completed, the reaction solution was filtrated, and a white solid obtained by the filtration was removed to obtain a filtrate, and then a solvent was removed from the filtrate under reduced pressure, and 85.46g (0.42mol) of 1,3-diisopropyl-4,4-dimethylcyclodisilazane ($(CH_3)_2$SiNCH$(CH_3)_2$)(SiH_2NCH$(CH_3)_2$)) was obtained by reduced pressure distillation with a yield of 50%.

[140] ^{1}H NMR (in C_6D_6) δ 0.26(s, 6H, NSi(C*H*$_3)_2$), 1.06(d, 12H, Si(NCH(C*H*$_3)_2$), 3.18(m, 2H, Si(NC*H*$(CH_3)_2$), 5.51(s, 1H, NSi*H*$_2$); Boiling Point 175℃.

[141] **[Example 7] Deposition of Silicon Oxide Film by Plasma Enhanced Atomic Layer Deposition (PEALD) Using Cyclodisilazane Derivative**

[142] Film forming evaluation was conducted by using 1,3-diisopropyl-2,4-dimethylcyclodisilazane of Example 1 and 1,3-diisopropyl-4,4-dimethylcyclodisilazane of Example 6 according to the present invention as a composition for forming a silicon oxide film in a general plasma enhanced atomic layer deposition (PEALD) apparatus using the known PEALD method. Oxygen together with plasma was used as the reaction gas, and argon which is an inert gas was used for purge. Hereinafter, FIG. 5 and Table 1 specifically show a method for depositing a silicon oxide thin film.

[143] Table 1

[Table 1]

Deposition Condition of Silicon Oxide Thin film

		Precursor			
		1,3-diisopropyl-2,4-dimethylcyclodisilazane (Example 1)		1,3-diisopropyl-4,4-dimethylcyclodisilazane (Example 6)	
Heating Temperature (℃) of Precursor		40	40	40	40
Substrate Temperature (℃)		100	100	100	100
Kind of Substrate		Si wafer	Si Pattern wafer.Hole Size 200nmAspect Ratio: 5	Si wafer	Si Pattern wafer.Hole Size 200nmAspect Ratio: 5
Injection Time (sec) of Precursor		6	18	9	18
Purge	Flow Amount (sccm)	1100	1100	1100	1100
	Time (sec)	20	60	20	60
400W Oxygen Plasma	Flow Amount (sccm) of Oxygen/Argon	300/100	300/100	300/100	300/100
	Time (sec)	10	20	10	20
Purge	Flow Amount (sccm)	1100	1100	1100	1100
	Time (sec)	15	30	15	30
Frequency of Deposition	Cycle	50	273	50	406

[144] A thickness of the deposited thin film was measured by an Ellipsometer, and formation of SiO_2 thin film and components of the thin film were analyzed by infrared spectroscopy and auger electron spectroscopy. In 50 cycles on a Si wafer, a thickness of the thin film of 1,3-diisopropyl-2,4-dimethylcyclodisilazane (Example 1) was

76.98Å and a thickness of the thin film of 1,3-diisopropyl-4,4-dimethylcyclodisilazane (Example 6) was 78.84Å. In addition, in 273 cycles on a Si pattern wafer, a thickness of the thin film manufactured by including 1,3-diisopropyl-2,4-dimethylcyclodisilazane (Example 1) was 317Å and in 406 cycles on a Si pattern wafer, a thickness of the thin film manufactured by including 1,3-diisopropyl-4,4-dimethylcyclodisilazane (Example 6) was 436Å. Further, step coverage was 98.17 to 101.89%. Therefore, it is determined that these thin films are capable of being effectively used throughout all silicon oxide thin film application fields requiring a high deposition rate and excellent step coverage (FIG. 6).

[145] In addition, as shown in FIGS. 7 and 8, all of the deposited thin films were formed as silicon oxide films, and peak of impurities such as C-H, Si-OH was not observed (FIG. 7). A ratio between oxygen and silicon in the thin film formed by using 1,3-diisopropyl-2,4-dimethylcyclodisilazane (Example 1) was 2.07 : 1 and a ratio between oxygen and silicon in the thin film formed by using 1,3-diisopropyl-4,4-dimethylcyclodisilazane (Example 6) was 2.03 : 1, and carbon and nitrogen had a content of 0%, and therefore, it could be confirmed that high purity silicon oxide thin film was formed (FIG. 8).

[146] In addition, an etch rate of the deposited thin film was confirmed by using buffered oxide etchant (BOE) solution (300: 1). The silicon oxide thin film deposited by using 1,3-diisopropyl-2,4-dimethylcyclodisilazane (Example 1) was etched at a rate of 0.58Å/sec, and the silicon oxide thin film deposited by using 1,3-diisopropyl-4,4-dimethylcyclodisilazane (Example 6) was etched at a rate of 0.59Å/sec. As a result obtained by thermal treating each sample at 750℃ for 30 minutes and confirming an etch rate, an etch rate of the oxide thin film of 1,3-diisopropyl-2,4-dimethylcyclodisilazane was 0.47Å/sec and an etch rate of the oxide thin film of 1,3-diisopropyl-4,4-dimethylcyclodisilazane was 0.54Å/sec, which was confirmed that an etch rate was decreased. It was confirmed that an etch rate of a thermal oxide thin film deposited at 1000℃ used as a comparative sample was 0.30Å/sec (FIG. 9).

[147] That is, it was confirmed that the novel cyclodisilazane derivative prepared by the present invention has high utilization value in forming a high purity silicon oxide thin film having a high deposition rate, excellent step coverage, and etch resistance by plasma enhanced atomic layer deposition (PEALD).

[148] [Comparative Example 1] Deposition of Silicon Oxide Film by Plasma Enhanced Atomic Layer Deposition (PEALD) Using Known Aminosilyl Amine Compound

[149] The film forming evaluation of Comparative Example was conducted by the known PEALD under the same deposition conditions as practiced by Example 7 above except for using known aminosilyl amine compound as shown in the following Table 2, then,

the deposited thin film was analyzed by the same analysis method and conditions as practiced by Example 7 above, and the analysis result thereof was obtained. Hereinafter, FIG. 5 and Table 2 specifically show a method for depositing the silicon oxide thin film.

[150] Table 2

[Table 2]

Silicon Oxide Thin film Deposition Condition

		Precursor	
		Bis-diethylamino silane (Precursor A)	Bis-ethylmethylamino silane (Precursor B)
Heating Temperature (℃) of Precursor		40	40
Substrate Temperature (℃)		100	100
Kind of Substrate		Si wafer	Si wafer
Injection Time (sec) of Precursor		0.5	0.2
Purge	Flow Amount (sccm)	1100	1100
	Time (sec)	20	20
400W Oxygen Plasma	Flow Amount (sccm) of Oxygen/Argon	300/100	300/100
	Time (sec)	10	10
Purge	Flow Amount (sccm)	1100	1100
	Time (sec)	15	15
Frequency of De-position	Cycle	50	50

[151] A thickness of each deposited thin film was measured by an Ellipsometer, and formation of SiO_2 thin film was analyzed by infrared spectroscopy. In 50 cycles on a Si wafer, the thickness of the thin films were 72.5Å (precursor A) and 68.5Å (precursor B), which showed low deposition rate as compared to the cyclodisilazane derivatives practiced by Example 7, and all of the thin films were formed as silicon oxide films

(FIG. 7).

[152] In addition, an etch rate of the deposited thin film was confirmed by using buffered oxide etchant (BOE) solution (300: 1). The silicon oxide thin film deposited by using precursor A was etched at a rate of 0.86Å/sec, and the silicon oxide thin film deposited by using precursor B was etched at a rate of 0.94Å/sec. As a result obtained by thermal treating each sample at 750℃ for 30 minutes and confirming an etch rate, an etch rate of the oxide thin film of the precursor A was 0.66Å/sec and an etch rate of the oxide thin film of the precursor B was 0.69Å/sec, which was confirmed that an etch rate was decreased. It was confirmed that an etch rate of a thermal oxide thin film deposited at 1000℃ used as a comparative sample was 0.30Å/sec (FIG. 9).

[153] **[Example 8] Deposition of silicon nitride film by Plasma Enhanced Atomic Layer Deposition (PEALD) using cyclodisilazane derivative**

[154] Film formation evaluation was conducted by using 1,3-diisopropyl-2,4-dimethylcyclodisilazane of Example 1 according to the present invention as a composition for forming a silicon nitride film in a general plasma enhanced atomic layer deposition (PEALD) apparatus using the known PEALD method. Nitrogen together with plasma was used as a reaction gas, and the same nitrogen gas was used for purge. Hereinafter, FIG. 10 and Table 3 specifically show a method for depositing the silicon nitride thin film.

[155] Table 3

[Table 3]

Silicon Nitride Thin-Film Deposition Conditions

		Precursor
		1,3-diisopropyl-2,4-dimethylcyclodisilazane (Example 1)
Heating Temperature (℃) of Precursor		40
Substrate Temperature (℃)		300
Kind of Substrate		Si wafer
Injection Time (sec) of Precursor		5
Purge	Flow Amount (sccm)	2000
	Time (sec)	16
400W Nitrogen Plasma	Flow Amount (sccm) of Nitrogen	400
	Time (sec)	10
Purge	Flow Amount (sccm)	2000
	Time (sec)	12
Frequency of Deposition	Cycle	500

[156] A thickness of the deposited thin film was measured by an Ellipsometer, and formation of SiN thin film and components of the thin film were analyzed by infrared spectroscopy and auger electron spectroscopy. In 500 cycles on a Si wafer, a thickness of the thin film was 150.70Å.

[157] In addition, as shown in FIG. 11, it was observed that all of the deposited thin films were formed as silicon nitride films, and a small number of bonds such as N-H, Si-H were included.

[158] Further, an etch rate of the deposited thin film was confirmed by using buffered oxide etchant (BOE) solution (300: 1). The deposited silicon nitride thin film was etched at a rate of 0.05Å/sec, and a thermal oxide thin film deposited at 1000℃ used as a comparative sample was etched at a rate of 0.34Å/sec, and a silicon nitride thin film deposited by low pressure chemical vapor deposition (LPCVD) at 770℃ using dichlorosilane was etched at a rate of 0.02Å/sec.

[159] That is, it was confirmed that the novel cyclodisilazane derivative prepared by the present invention has high utilization value in forming a high purity silicon nitride thin

film having a high deposition rate and excellent etch resistance by plasma enhanced atomic layer deposition (PEALD).

Industrial Applicability

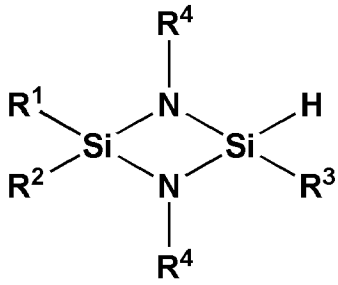
[160] The cyclodisilazane derivative of the present invention has excellent thermal stability and high reactivity, such that the silicon-containing thin film manufactured by using the cyclodisilazane derivative as a precursor may have high purity and significantly excellent physical and electrical properties.

[161] In addition, the cyclodisilazane derivative of the present invention may have high content of silicon and is present in a liquid state at room temperature and under atmospheric pressure to thereby be easily stored and handled, and may have high volatility and high reactivity to be rapidly and easily deposited, and it is possible to deposit a thin film having excellent cohesion and superior step coverage.

Claims

[Claim 1] A cyclodisilazane derivative represented by the following Chemical Formula 1:

[Chemical Formula 1]

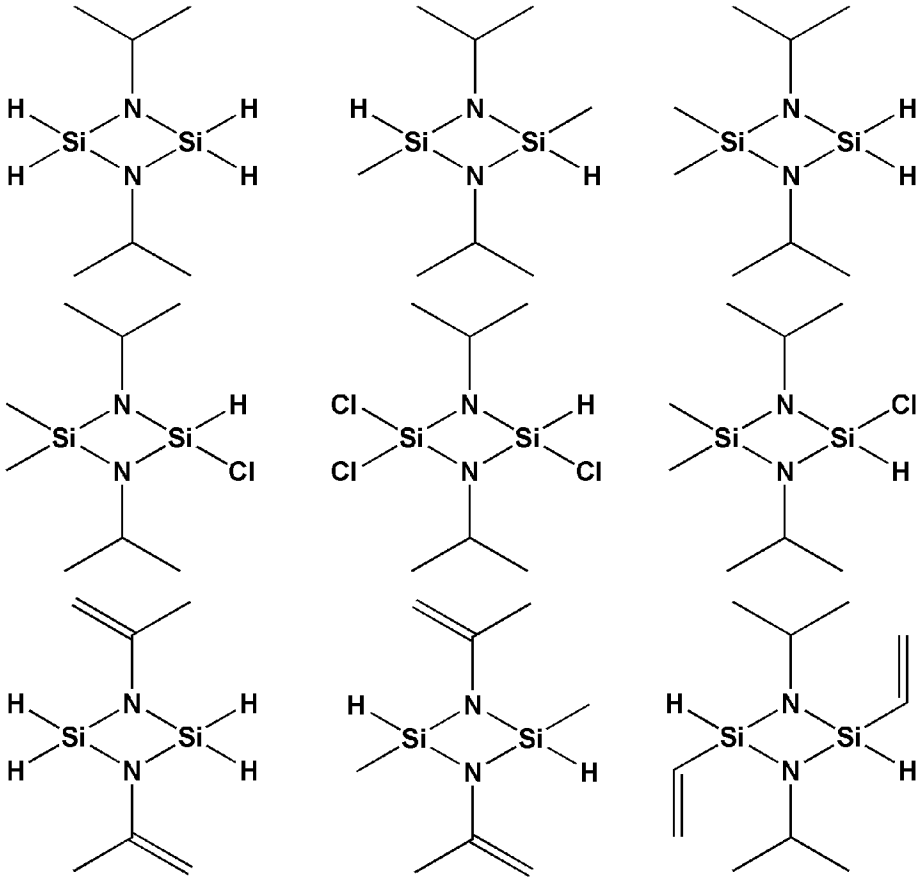


in Chemical Formula 1,

R^1 to R^3 are each independently hydrogen, halogen, (C1-C5)alkyl or (C2-C5)alkenyl, and

R^4 is hydrogen, (C1-C3)alkyl or (C2-C5)alkenyl.

[Claim 2] The cyclodisilazane derivative of claim 1, wherein it is selected from the following compounds:

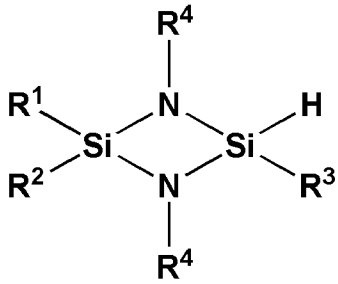


[Claim 3] A method for preparing a cyclodisilazane derivative represented by the following Chemical Formula 1, comprising:

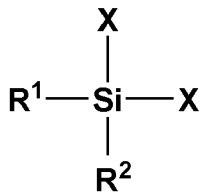
preparing a diaminosilane derivative represented by the following Chemical Formula 4 by reacting a silane derivative represented by the following Chemical Formula 2 with an amine derivative represented by the following Chemical Formula 3; and

preparing the cyclodisilazane derivative represented by the following Chemical Formula 1 by an intramolecular cyclization reaction of the diaminosilane derivative represented by the following Chemical Formula 4 with a silane derivative represented by the following Chemical Formula 5 in the presence of (C1-C7)alkyllithium:

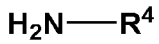
[Chemical Formula 1]



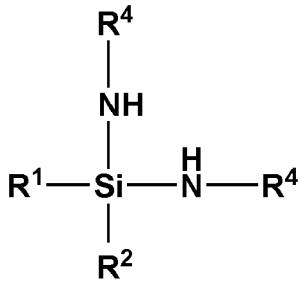
[Chemical Formula 2]



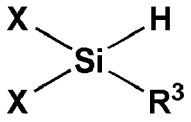
[Chemical Formula 3]



[Chemical Formula 4]



[Chemical Formula 5]



in Chemical Formulas 1 to 5,

R^1 to R^3 are each independently hydrogen, halogen, (C1-C5)alkyl or

(C2-C5)alkenyl,

R^4 is hydrogen, (C1-C3)alkyl or (C2-C5)alkenyl, and X is halogen.

[Claim 4] The method of claim 3, wherein the preparing of the diaminosilane derivative represented by Chemical Formula 4 is performed in the presence of a base represented by the following Chemical Formula 10 or (C1-C7)alkyllithium:

[Chemical Formula 10]

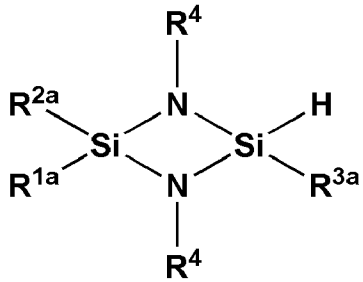
$N(R^6)(R^7)(R^8)$

in Chemical Formula 10, R^6 to R^8 are each independently (C1-C7)alkyl.

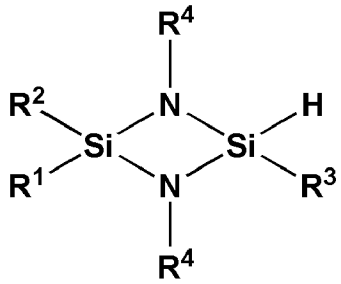
[Claim 5] A method for preparing a cyclodisilazane derivative represented by the following Chemical Formula 1-2, the method comprising:

preparing the cyclodisilazane derivative represented by the following Chemical Formula 1-2 by reacting a halocyclodisilazane derivative represented by the following Chemical Formula 1-1 with a metal hydride or an alkali metal derivative represented by the following Chemical Formula 8:

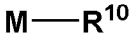
[Chemical Formula 1-2]



[Chemical Formula 1-1]



[Chemical Formula 8]



in Chemical Formulas 1-1, 1-2, and 8,

M is an alkali metal;

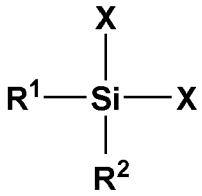
R^{10} is each independently hydrogen or (C1-C5)alkyl;

at least one of R^1 to R^3 is halogen, and the remainder is hydrogen, halogen, (C1-C5)alkyl or (C2-C5)alkenyl;

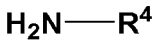
R^4 is hydrogen, (C1-C3)alkyl or (C2-C5)alkenyl; and
at least one of R^{1a} to R^{3a} is hydrogen, and the remainder is hydrogen, (C1-C5)alkyl or (C2-C5)alkenyl, wherein when R^1 is halogen, R^{1a} is hydrogen, and when R^2 is halogen, R^{2a} is hydrogen, and when R^3 is halogen, R^{3a} is hydrogen.

[Claim 6] A method for preparing a cyclodisilazane derivative represented by the following Chemical Formula 9, the method comprising:
preparing an aminosilane derivative represented by the following Chemical Formula 6 by reacting a silane derivative represented by the following Chemical Formula 2 with an amine derivative represented by the following Chemical Formula 3;
preparing a halocyclodisilazane derivative represented by the following Chemical Formula 7 by an intramolecular cyclization reaction of the aminosilane derivative represented by the following Chemical Formula 6 in the presence of (C1-C7)alkyllithium; and
preparing the cyclodisilazane derivative represented by the following Chemical Formula 9 by reacting the halocyclodisilazane derivative represented by the following Chemical Formula 7 with a metal hydride or an alkali metal derivative represented by the following Chemical Formula 8:

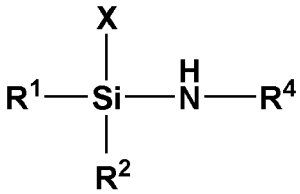
[Chemical Formula 2]



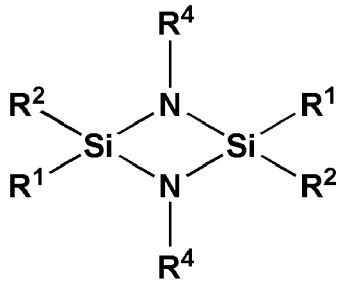
[Chemical Formula 3]



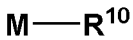
[Chemical Formula 6]



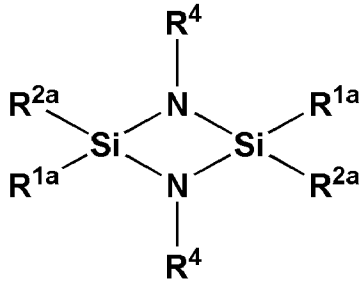
[Chemical Formula 7]



[Chemical Formula 8]



[Chemical Formula 9]



in Chemical Formulas 2, 3 and 6 to 9,

R^1 is halogen;

R^2 is hydrogen, halogen, (C1-C5)alkyl or (C2-C5)alkenyl;

R^4 is hydrogen, (C1-C3)alkyl or (C2-C5)alkenyl;

X is halogen;

M is an alkali metal;

R^{10} is hydrogen or (C1-C5)alkyl;

R^{1a} is hydrogen;

wherein when R^2 is hydrogen or halogen, R^{2a} is hydrogen, and when R^2 is (C1-C5)alkyl or (C2-C5)alkenyl, R^{2a} is (C1-C5)alkyl or (C2-C5)alkenyl.

[Claim 7] The method of claim 6, wherein the preparing of the aminosilane derivative represented by Chemical Formula 6 is performed in the presence of a base represented by the following Chemical Formula 10 or (C1-C7)alkyllithium:

[Chemical Formula 10]

$N(R^6)(R^7)(R^8)$

in Chemical Formula 10, R^6 to R^8 are each independently (C1-C7)alkyl.

[Claim 8] The method of claim 5 or 6, wherein the metal hydride is one or a mixture of two or more, selected from the group consisting of LiH, NaH, KH and $LiAlH_4$.

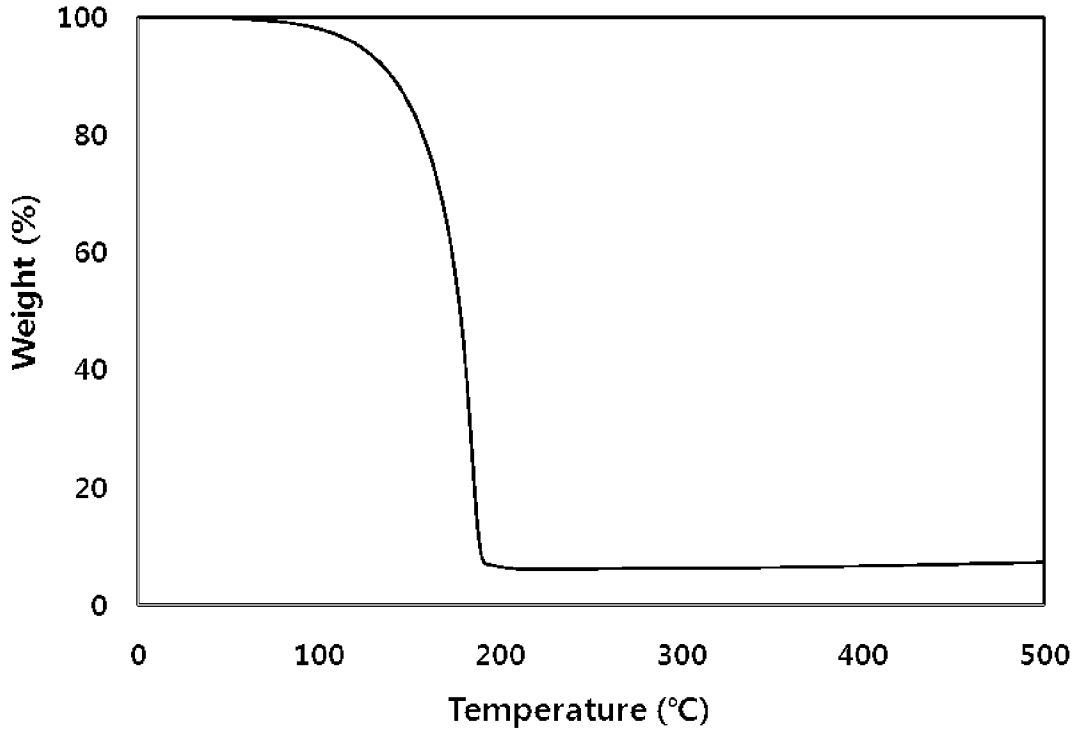
[Claim 9] A composition for depositing a silicon-containing thin film, comprising

the cyclodisilazane derivative of claim 1 or 2.

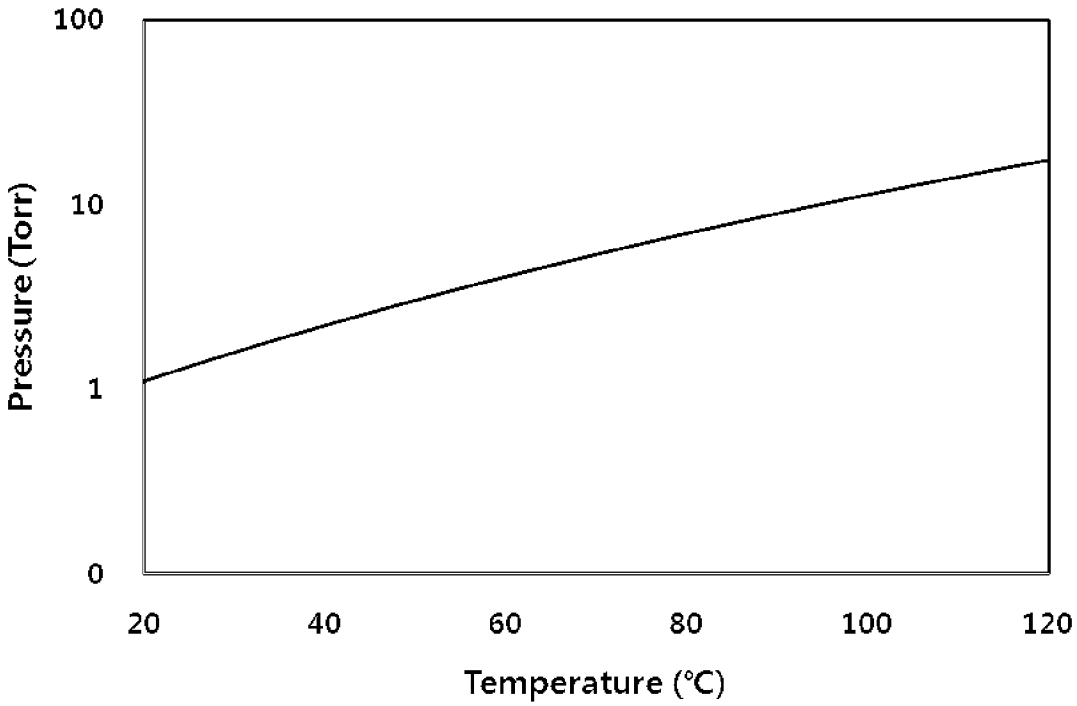
[Claim 10] A method for manufacturing a silicon-containing thin film by using the cyclodisilazane derivative of claim 1 or 2.

[Claim 11] A silicon-containing thin film manufactured by including the cyclo-disilazane derivative of claim 1 or 2.

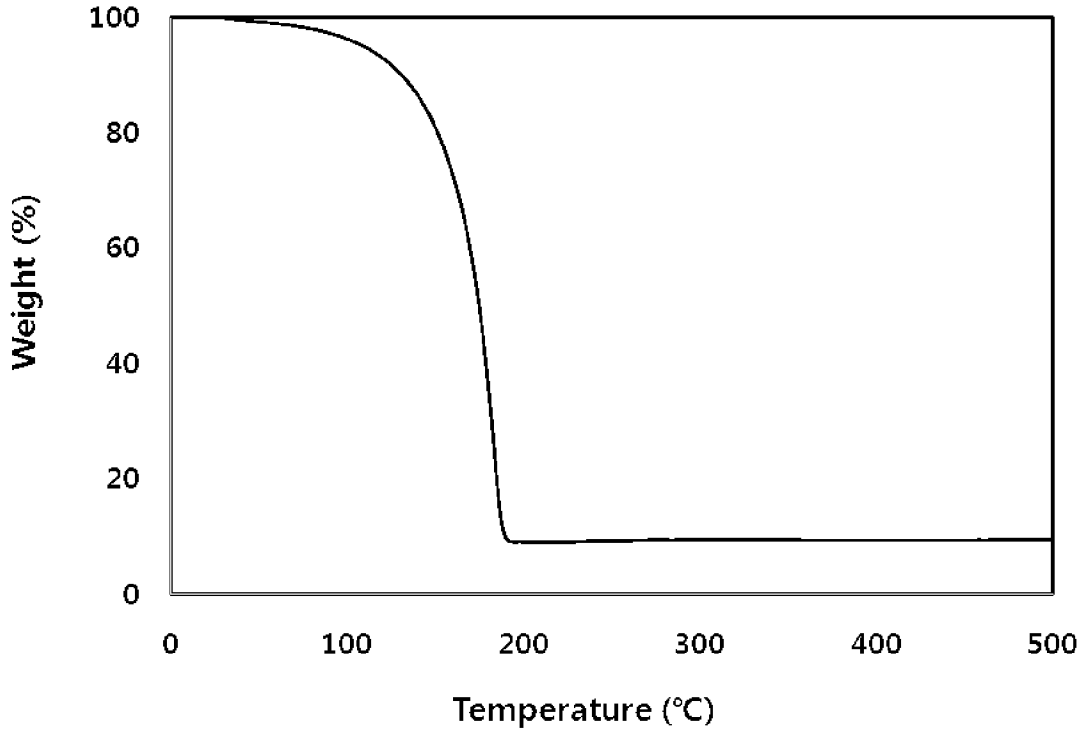
[Fig. 1]


100
80
60
40
20
0
Weight (%)
0
100
200
300
400
500
Temperature (℃)

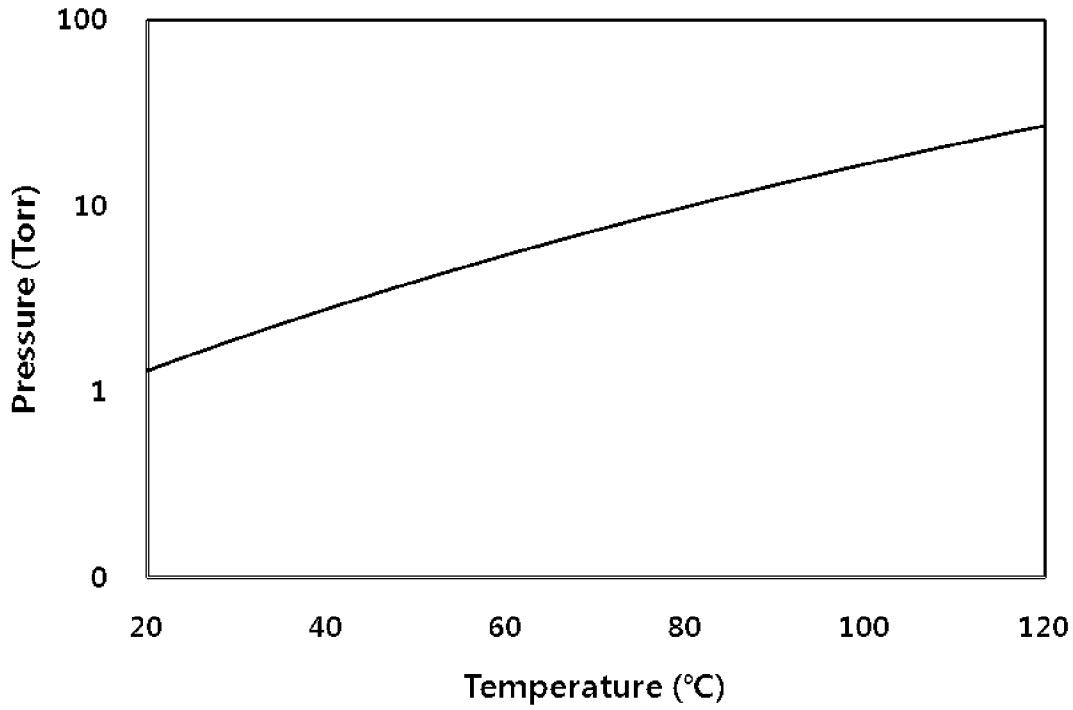
[Fig. 2]


100
10
1
0
Pressure (Torr)
20
40
60
80
100
120
Temperature (℃)

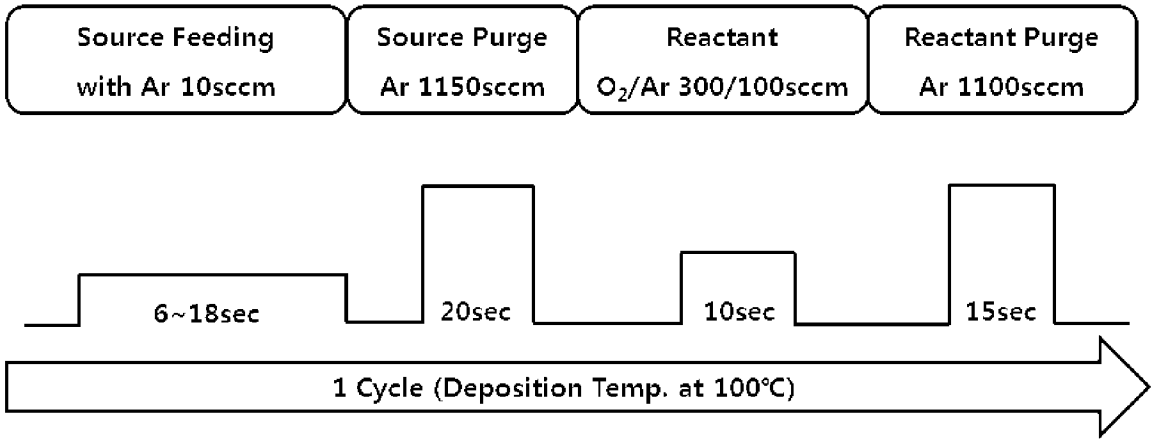
[Fig. 3]


100
80
60
40
20
0
Weight (%)
0
100
200
300
400
500
Temperature (℃)

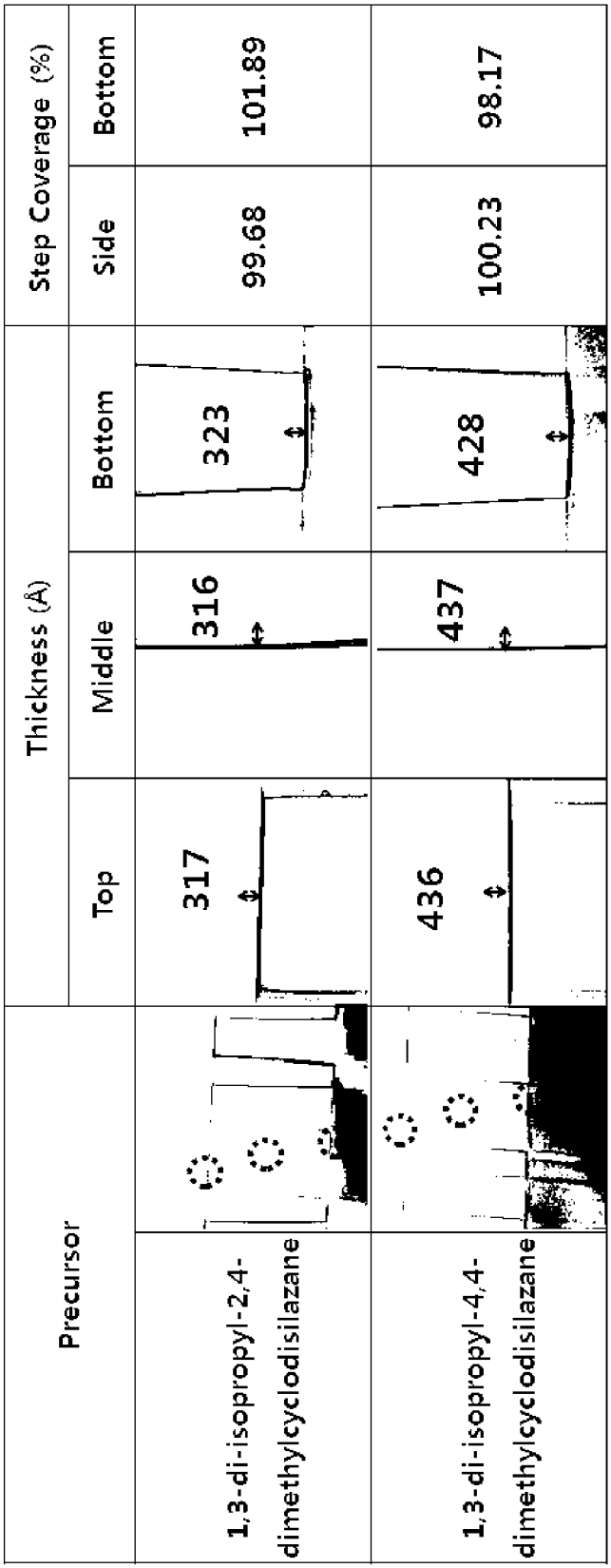
[Fig. 4]


100
10
1
0
Pressure (Torr)
20
40
60
80
100
120
Temperature (℃)

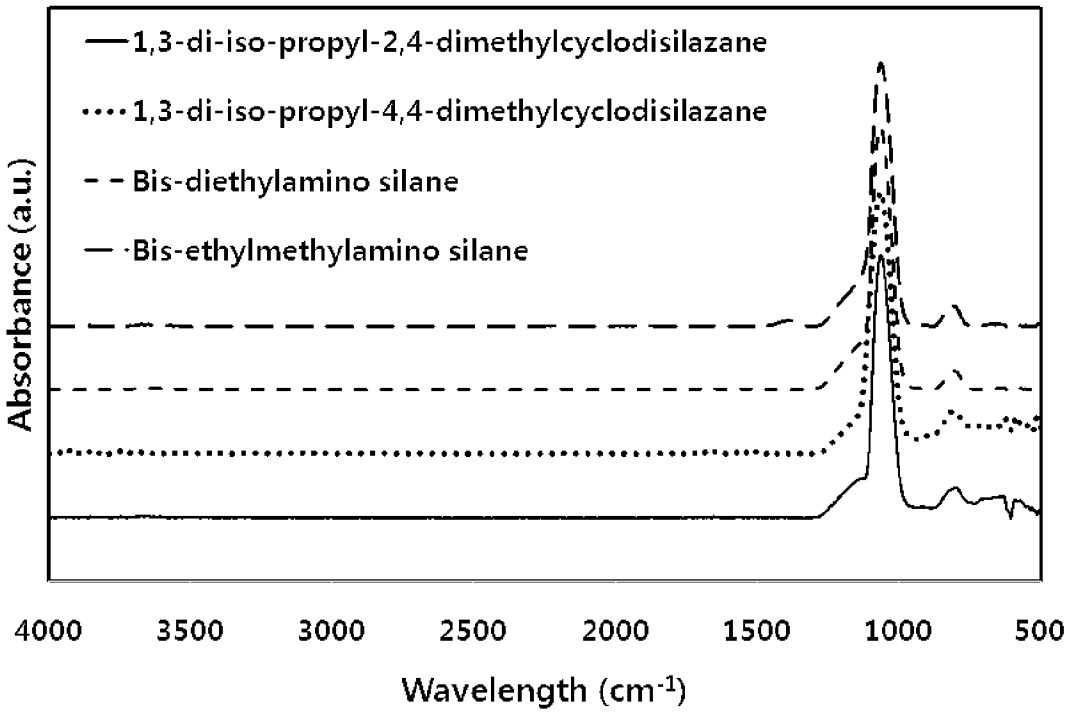
[Fig. 5]


Source Feeding
with Ar 10sccm
Source Purge
Ar 1150sccm
Reactant
O_2/Ar 300/100sccm
Reactant Purge
Ar 1100sccm
6~18sec
20sec
10sec
15sec
1 Cycle (Deposition Temp. at 100℃)

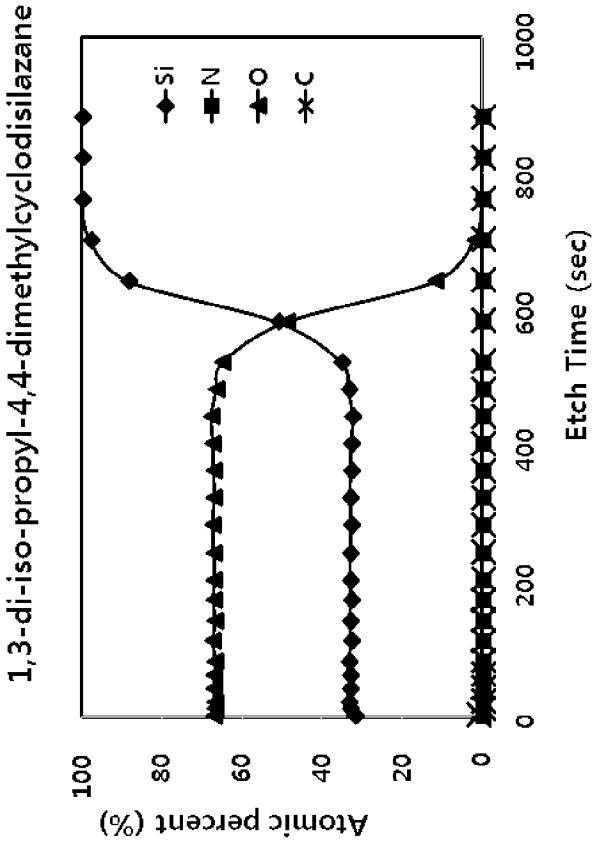
[Fig. 6]

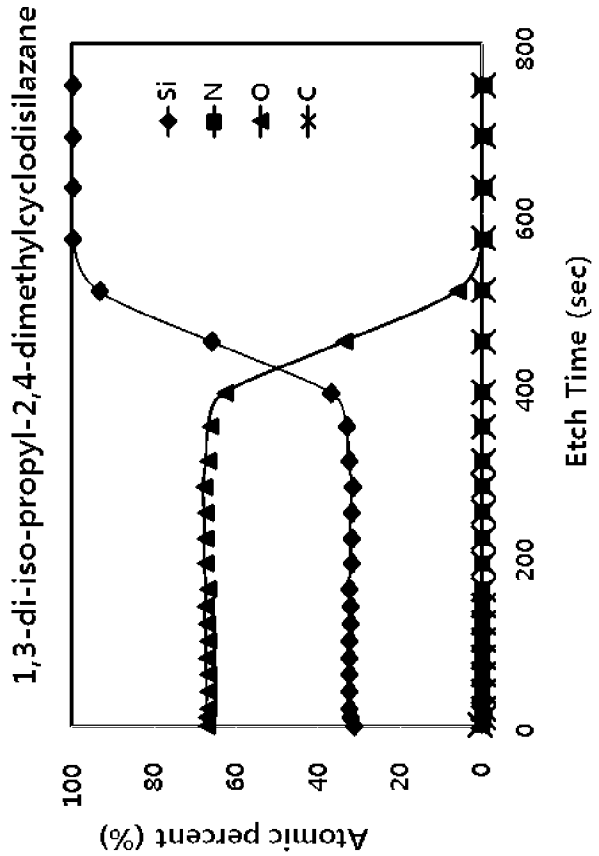

Precursor
Thickness (Å)
Top
Middle
Bottom
Step Coverage (%)
Side
Bottom
1,3-di-isopropyl-2,4-dimethylcyclodisilazane
317
316
323
99.68
101.89
1,3-di-isopropyl-4,4-dimethylcyclodisilazane
436
437
428
100.23
98.17

[Fig. 7]

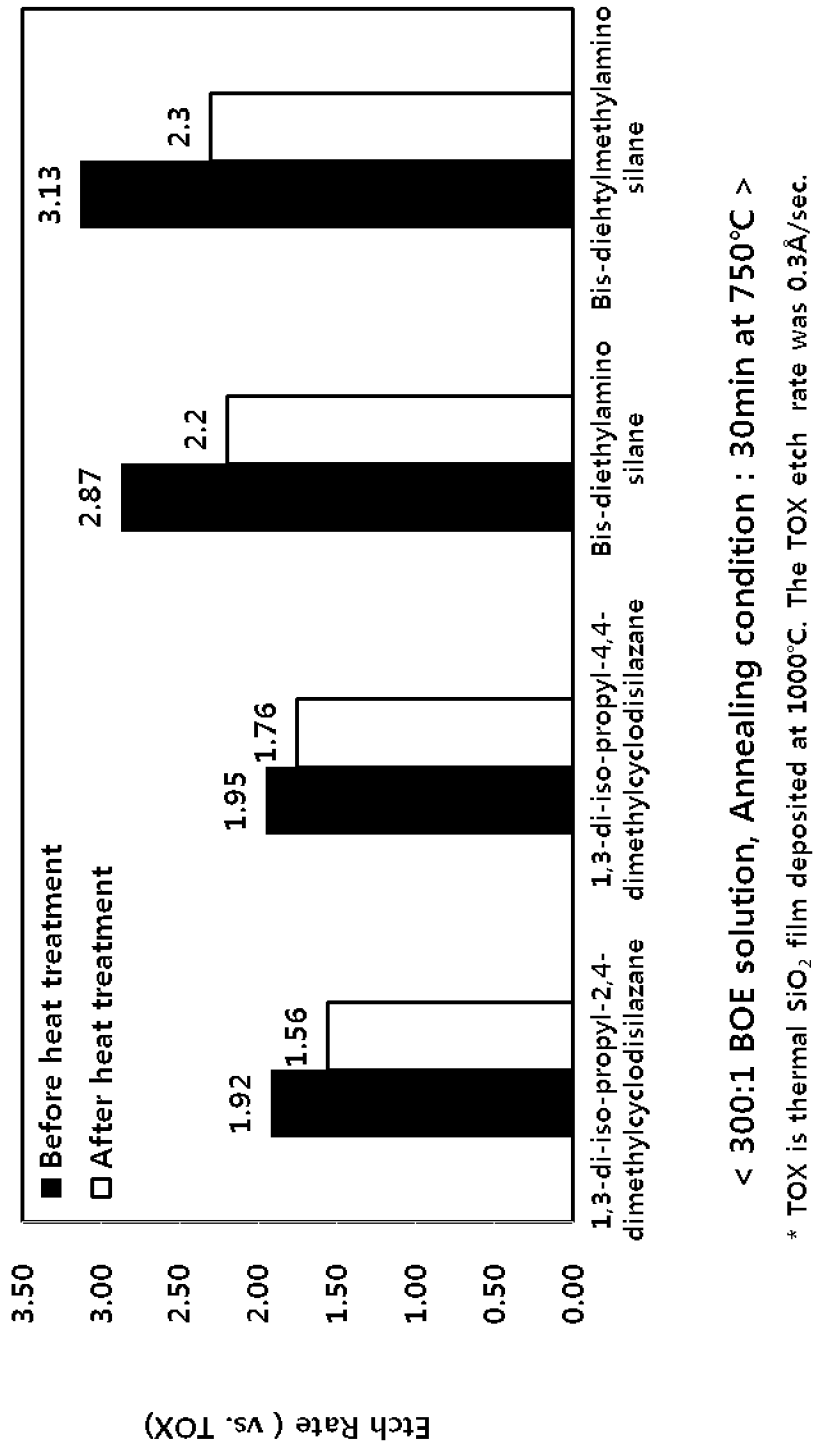

1,3-di-iso-propyl-2,4-dimethylcyclodisilazane
1,3-di-iso-propyl-4,4-dimethylcyclodisilazane
Bis-diethylamino silane
Bis-ethylmethylamino silane
Absorbance (a.u.)
4000
3500
3000
2500
2000
1500
1000
500
Wavelength (cm-1)

[Fig. 8]


1,3-di-iso-propyl-4,4-dimethylcyclodisilazane
Si
N
O
C
Atomic percent (%)
0
20
40
60
80
100
Etch Time (sec)
0
200
400
600
800
1000


1,3-di-iso-propyl-2,4-dimethylcyclodisilazane
Si
N
O
C
Atomic percent (%)
0
20
40
60
80
100
Etch Time (sec)
0
200
400
600
800

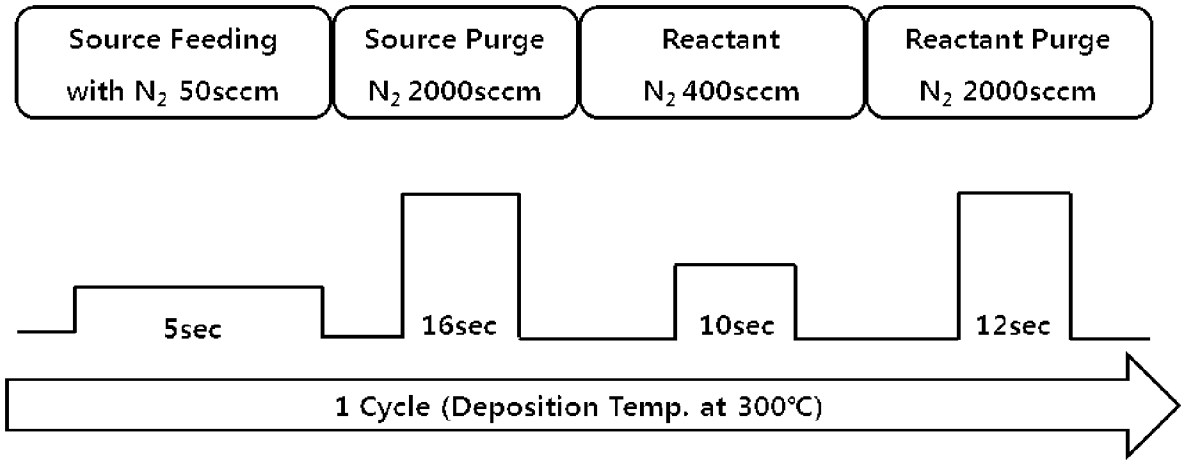
[Fig. 9]



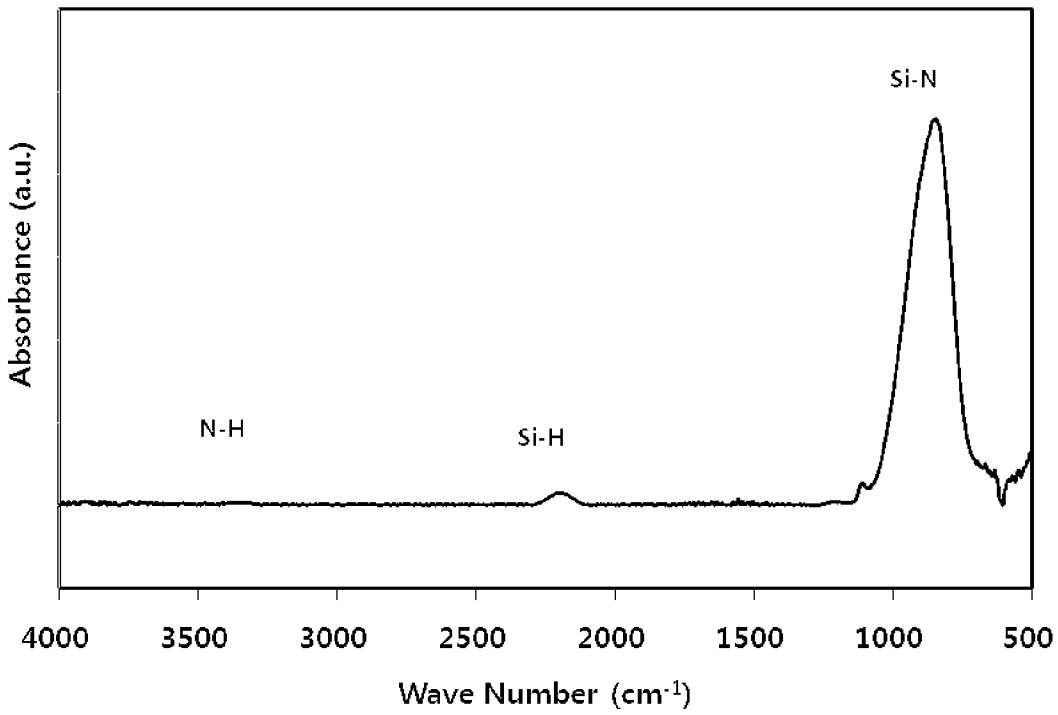
< 300:1 BOE solution, Annealing condition : 30min at 750°C >

* TOX is thermal SiO_2 film deposited at 1000°C. The TOX etch rate was 0.3Å/sec.

[Fig. 10]


Source Feeding
with N_2 50sccm
Source Purge
N_2 2000sccm
Reactant
N_2 400sccm
Reactant Purge
N_2 2000sccm
5sec
16sec
10sec
12sec
1 Cycle (Deposition Temp. at 300℃)

[Fig. 11]


Absorbance (a.u.)
Si-N
N-H
Si-H
4000
3500
3000
2500
2000
1500
1000
500
Wave Number (cm^{-1})

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2015/000189

A. CLASSIFICATION OF SUBJECT MATTER

C07F 7/10(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)
C07F 7/10; H01L 21/469; H01L ; H05B 33/14; C07F 7/21; H01L 21/31; C08G 77/62

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal), Google & Keywords: cyclodisilazane, silicon-containing thin film

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	RAYEZ M.T. et al., `Structures and Si-N bond strengths of some cyclodi- and cyclotrisilazanes`, Journal of Molecular Structure (Theochem), 1999, Vol. 487, pp. 241-250 See Fig. 1, compoumd DH2/2NMe; page 248, right column, lines 5-18.	1
A		2-11
X	IOAN SILAGHI-DUMITRESCU et al., `On the formation of cyclodisdilazanes via the coordination of bis(dialkylaminosilanes) to halogenosilanes: an ab initio and AM1 molecular orbital study of the 4644 R2Si(NR`2)2:SiX4 ring systems`, Journal of Molecular Structure (Theochem), 1997, Vol. 397, pp. 213-222 See page 218, system 4.	1
A		2-11
A	US 04950950 A (PERRY, ROBERT J. et al.) 21 August 1990 See column 10, lines 56-65; column 12, lines 3-32; and claim 18.	1-11
A	WO 2004-044958 A2 (ADVANCED TECHNOLOGY MATERIALS, INC.) 27 May 2004 See paragraph [0015] and claim 53.	1-11
A	US 2006-0228903 A1 (MICHAEL MCSWINEY et al.) 12 October 2006 See claims 4, 6, 14 and 19.	1-11

☒ 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
08 April 2015 (08.04.2015)	**08 April 2015 (08.04.2015)**

Name and mailing address of the ISA/KR
International Application Division
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea
Facsimile No. ++82 42 472 7140

Authorized officer
KIM, Jong Ho
Telephone No. +042 481 8657

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2015/000189

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 92-17527 A1 (ETAT FRANCIS REPRENSENTE PAR LE DELEGUE GENERAL POUR L`ARMEMENT) 15 October 1992 See page 4, line 7 - page 5, line 30.	1-11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2015/000189

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 04950950 A	21/08/1990	WO 90-14744 A1	29/11/1990
WO 2004-044958 A2	27/05/2004	AU 2003-287710 A1	03/06/2004
		AU 2003-287710 A8	03/06/2004
		EP 1567531 A2	31/08/2005
		EP 1567531 A4	20/08/2008
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		US 2004-0138489 A1	15/07/2004
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		US 7446217 B2	04/11/2008
		US 7531679 B2	12/05/2009
		US 7713346 B2	11/05/2010
		US 7786320 B2	31/08/2010
		US 7887883 B2	15/02/2011
		US 7910765 B2	22/03/2011
		US 8236097 B2	07/08/2012
		WO 2004-044958 A3	26/08/2004
US 2006-0228903 A1	12/10/2006	None	
WO 92-17527 A1	15/10/1992	FR 2674859 A1	09/10/1992
		FR 2674859 B1	14/01/1994
		WO 92-17527 A1	15/10/1992