(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
1 December 2016 (01.12.2016)

WIPO | PCT

(10) International Publication Number
WO 2016/191199 A1

(51) International Patent Classification:
C23C 16/455 (2006.01) *C23C 16/32* (2006.01)
C23C 16/40 (2006.01) *C23C 16/24* (2006.01)
C23C 16/34 (2006.01)

(21) International Application Number:
PCT/US2016/033273

(22) International Filing Date:
19 May 2016 (19.05.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/165,312 22 May 2015 (22.05.2015) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

WO 2016/191199 A1

(54) Title: DIISOPROPYLAMINOPENTACHLORODISILANE

(57) Abstract: Disclosed is a Silicon Precursor Compound for deposition, the Silicon Precursor Compound comprising diisopropylamino-pentachlorodisilane, which is of formula (A): $[(CH_3)_2CH]_2NSiCl_2SiCl_3$ (A); a composition for film forming, the composition comprising the Silicon Precursor Compound and at least one of an inert gas, molecular hydrogen, a carbon precursor, nitrogen precursor, and oxygen precursor; a method of forming a silicon- containing film on a substrate using the Silicon Precursor Compound, and the silicon- containing film formed thereby.

DIISOPROPYLAMINOPENTACHLORODISILANE

[0001] The present invention generally relates to a precursor compound and composition for film forming, to a method for forming a film with the precursor compound or composition via a deposition apparatus, and to the film formed by the method.

[0002] Elemental silicon, and other silicon materials such as silicon oxide, silicon carbide, silicon nitride, silicon carbonitride, and silicon oxycarbonitride, have a variety of known uses. For example, silicon film may be used as a semiconductor, an insulating layer or a sacrificial layer in the manufacture of electronic circuitry for electronic or photovoltaic devices.

[0003] Known methods of preparing the silicon material may use one or more silicon precursors. Use of these silicon precursors is not limited to making silicon for electronic or photovoltaic semiconductor applications. For example, silicon precursors may be used to prepare silicon-based lubricants, elastomers, and resins.

[0004] We see a long-felt need in the electronics and photovoltaic industries for improved silicon precursors. We think improved precursors would enable lowering of deposition temperatures and/or making finer semiconductor features for better performing electronic and photovoltaic devices.

SUMMARY OF THE INVENTION

[0005] We have discovered an improved silicon precursor. The present invention provides each of the following embodiments:

[0006] A precursor compound for deposition, the precursor compound comprising diisopropylamino-pentachlorodisilane, which is of formula (A): $[(CH_3)_2CH]_2NSiCl_2SiCl_3$ (A) (hereinafter, "Silicon Precursor Compound").

[0007] A composition for film forming, the composition comprising the Silicon Precursor Compound and at least one of an inert gas, molecular hydrogen, a carbon precursor, nitrogen precursor, and oxygen precursor.

[0008] A method of forming a silicon-containing film on a substrate, the method comprising subjecting a vapor of a silicon precursor comprising the Silicon Precursor Compound to deposition conditions in the presence of the substrate so as to form a silicon-containing film on the substrate.

[0009] A film formed in accordance with the method.

DETAILED DESCRIPTION OF THE INVENTION

[0010] The Brief Summary and Abstract are incorporated here by reference. The invention embodiments, uses and advantages summarized above are further described below.

[0011] Aspects of the invention are described herein using various common conventions. For example, all states of matter are determined at 25° C. and 101.3 kPa unless indicated otherwise. All % are by weight unless otherwise noted or indicated. All % values are, unless otherwise noted, based on total amount of all ingredients used to synthesize or make the composition, which adds up to 100 %. Any Markush group comprising a genus and subgenus therein includes the subgenus in the genus, e.g., in "R is hydrocarbyl or alkenyl," R may be alkenyl, alternatively R may be hydrocarbyl, which includes, among other subgenuses, alkenyl. For U.S. practice, all U.S. patent application publications and patents referenced herein, or a portion thereof if only the portion is referenced, are hereby incorporated herein by reference to the extent that incorporated subject matter does not conflict with the present description, which would control in any such conflict.

[0012] Aspects of the invention are described herein using various patent terms. For example, "alternatively" indicates a different and distinct embodiment. "Comparative example" means a non-invention experiment. "Comprises" and its variants (comprising, comprised of) are open ended. "Consists of" and its variants (consisting of) is closed ended. "Contacting" means bringing into physical contact. "May" confers a choice, not an imperative. "Optionally" means is absent, alternatively is present.

[0013] Aspects of the invention are described herein using various chemical terms. The meanings of said terms correspond to their definitions promulgated by IUPAC unless otherwise defined herein. For convenience, certain chemical terms are defined.

[0014] The term "deposition" is a process of generating, on a specific place, condensed matter. The condensed matter may or may not be restricted in dimension. Examples of deposition are film-forming, rod-forming, and particle-forming depositions.

[0015] The term "film" means a material that is restricted in one dimension. The restricted dimension may be characterized as "thickness" and as the dimension that, all other things being equal, increases with increasing length of time of a process of depositing said material to form the film.

[0016] The term "halogen" means fluorine, chlorine, bromine or iodine, unless otherwise defined.

[0017] The term "IUPAC" refers to the International Union of Pure and Applied Chemistry.

[0018] The term "lack" means free of or a complete absence of.

[0019] "Periodic Table of the Elements" means the version published 2011 by IUPAC.

[0020] The term "precursor" means a substance or molecule containing atoms of the indicated element and being useful as a source of that element in a film formed by a deposition method.

[0021] The term "separate" means to cause to physically move apart, and thus as a result is no longer in direct touching.

[0022] The term "substrate" means a physical support having at least one surface upon which another material may be hosted.

[0023] This invention provides the Silicon Precursor Compound and the composition for film forming. The Silicon Precursor Compound is particularly suitable for deposition process for forming silicon-containing films, although the Silicon Precursor Compound is not limited to such applications. For example, the Silicon Precursor Compound may be utilized in other applications, e.g. as a reactant for preparing siloxane or silazane materials. This invention further provides the method of forming a film and the film formed in accordance with the method.

[0024] The Silicon Precursor Compound has the chemical name, diisopropylamino-pentachlorodisilane, which is of formula (A): $[(CH_3)_2CH]_2NSiCl_2SiCl_3$ (A). When the Silicon Precursor Compound is used in the present composition and method, the Silicon Precursor Compound may have a purity of from 99 area% (GC) to 99.9999999 area% (GC).

[0025] The Silicon Precursor Compound may be provided in any manner. For example, the Silicon Precursor Compound may be synthesized or otherwise obtained for use in the method. In an embodiment the Silicon Precursor Compound is synthesized by the following formal process: $HN(i\text{-}Pr)_2 + SiCl_3SiCl_3 \rightarrow [(CH_3)_2CH]_2NSiCl_2SiCl_3 +$ "HCl," wherein i-Pr is isopropyl and the "HCl" indicates a formal reaction by-product, which in usual practice reacts with an acid scavenger, as described below, to give a salt. An example of the formal process is: $2\ HN(i\text{-}Pr)_2 + SiCl_3SiCl_3 \rightarrow [(CH_3)_2CH]_2NSiCl_2SiCl_3 + H_2N(i\text{-}Pr)_2Cl$. The $H_2N(i\text{-}Pr)_2Cl$ salt may precipitate in the reaction and may be separated therefrom such as via filtration or decantation. The process may comprise contacting, in a hydrocarbon vehicle, hexachlorodisilane ($SiCl_3SiCl_3$) with a source of diisopropylamino group to give the Silicon Precursor Compound; wherein the source of diisopropylamino group is, relative to the hexachlorodisilane, from 0.50 to 1.19 molar equivalents of a metal diisopropylamide, $[(i\text{-}Pr)_2N]_mM^A$, wherein subscript m is 1 or 2, wherein when m is 1, M^A is an element of Group I of the Periodic Table of the Elements and when m is 2, M^A is an element of Group II of the Periodic Table of the Elements, or the source of diisopropylamino group is from 1.0 to 2.39

molar equivalents of diisopropylamine, or the source of diisopropylamino group is a mixture of from 0.50 to 1.19 molar equivalents of diisopropylamine ($(i\text{-}Pr)_2NH$) and from 0.50 to 1.19 molar equivalents of a pyridine compound or a trialkylamine ($Alkyl_3N$), wherein each alkyl independently is a (C_2-C_{10})alkyl. Examples of the pyridine compound are pyridine and 2,6-dimethylpyridine.

[0026] The process of synthesizing the Silicon Precursor Compound may be carried out in a hydrocarbon vehicle or an ether vehicle. The ether vehicle may comprise a disilyl ether, a dihydrocarbyl ether, or an alkylene glycol dialkyl ether, or a mixture of any two or more thereof. The dihydrocarbyl ether may be a straight chain ether, a cyclic ether, or a diaryl ether, or a mixture of any two or more thereof. Examples of the ether vehicle are diethyl ether, dimethyl ether, tetrahydrofuran, 1,2-dimethoxyethane, tetraethylene glycol dimethyl ether. The alkylene glycol dialkyl ether may be a tetramethylene glycol di(C_1-C_4)alkyl ether, a propylene glycol di(C_2-C_4)alkyl ether, an ethylene glycol di(C_3 or C_4)alkyl ether, or a mixture of any two or more thereof. The hydrocarbon vehicle may comprise an alkane having at least 5 carbon atoms, a cycloalkane having at least 5 carbon atoms, an arene having at least 6 carbon atoms, or a mixture of any two or more thereof. The hydrocarbon vehicle may comprise a pentane, hexane, hexanes, cyclohexane, a heptane, benzene, toluene, a xylene, or a mixture of any two or more thereof.

[0027] The composition of the hydrocarbon vehicle may be conceived to optimize the contacting steps (e.g., selecting a hydrocarbon vehicle having a boiling point for achieving a desired reaction temperature or a hydrocarbon vehicle lacking ability to solubilize a reaction by-product). Additionally or alternatively, the composition of the hydrocarbon vehicle may be conceived to optimize the optional separating step (e.g., selecting a hydrocarbon vehicle having a desired boiling point enabling evaporation thereof without evaporating the Silicon Precursor Compound). The hydrocarbon vehicle may consist of carbon and hydrogen atoms or may be a halogenated hydrocarbon vehicle consisting of carbon, hydrogen, and halogen atoms. The hydrocarbon vehicle consisting of C and H atoms may be alkanes, aromatic hydrocarbons, and mixtures of any two or more thereof. The alkanes may be hexanes, cyclohexane, heptanes, isoparaffins, or mixtures of any two or more thereof. The aromatic hydrocarbon may be toluene, xylenes, or mixtures of any two or more thereof. The halogenated hydrocarbon vehicle may be dichloromethane. The process having different compositions for hydrocarbon vehicle may differ from each other in at least one result,

property, function, and/or use. Different compositions of the hydrocarbon vehicle may provide different solubilities for the Silicon Precursor Compound, the source of the diisopropylamino group, a reaction by-product, or a combination of any two or more thereof.

[0028] As mentioned above, the composition for film forming comprises the Silicon Precursor Compound and at least one of an inert gas, molecular hydrogen, a carbon precursor, a nitrogen precursor, and an oxygen precursor, alternatively an inert gas, a nitrogen precursor, and an oxygen precursor. The molecular hydrogen may be used with the Silicon Precursor Compound in the composition for forming an elemental silicon film including amorphous, polycrystalline silicon and moncrystalline films. A vaporous or gaseous state of the molecular hydrogen, carbon precursor, nitrogen precursor or oxygen precursor may be generally referred to herein as an additional reactant gas.

[0029] The carbon precursor may be used with the Silicon Precursor Compound in the composition for forming a silicon carbon film according to an embodiment of the method. The silicon carbon film contains Si and C atoms and may comprise silicon carbide. The carbon precursor may comprise, alternatively consist essentially of, alternatively consist of C, H, and optionally Si atoms. The carbon precursor that comprises C, H, and optionally Si atoms may further comprise N or O atoms when the carbon precursor is used in the method for forming a silicon carbonitride film or silicon oxycarbide film, respectively, or may further comprise N and O atoms when the carbon precursor is used in the method for forming a silicon oxycarbonitride film. The carbon precursor that consists essentially of C, H, and optionally Si atoms lacks N and O atoms, but may optionally have one or more halogen atoms (e.g., Cl). Examples of the carbon precursor consisting of C and H atoms are hydrocarbons such as alkanes. Examples of the carbon precursor consisting of C, H and Si atoms are hydrocarbylsilanes such as butyldisilane or tetramethylsilane.

[0030] The nitrogen precursor may be used with the Silicon Precursor Compound in the composition for forming a silicon nitrogen film according to an embodiment of the method. The silicon nitrogen film contains Si and N atoms and optionally C and/or O atoms and may comprise silicon nitride, silicon oxynitride, or silicon oxycarbonitride. The nitrogen precursor is different than the Silicon Precursor Compound. The silicon nitrogen film contains Si and N atoms and optionally C and/or O atoms and may comprise silicon nitride, silicon oxynitride, or silicon oxycarbonitride. The silicon nitride may be Si_XN_Y wherein subscript x is 1, 2 or 3 and subscript y is an integer from 1 to 5. The nitrogen precursor may comprise N atoms and optionally H atoms, alternatively the nitrogen precursor may consist essentially of N atoms

and optionally H atoms, alternatively the nitrogen precursor may consist of N and optionally H atoms. The nitrogen precursor that comprises N and optionally H atoms may further comprise C or O atoms when the nitrogen precursor is used in the method for forming a silicon carbonitride film or silicon oxynitride film, respectively, or for may further comprise C and O atoms when the nitrogen precursor is used in the method for forming a silicon oxycarbonitride film. The nitrogen precursor that consists essentially of N atoms and optionally H atoms lacks C and O atoms, but optionally may have one or more halogen atoms (e.g., Cl). An example of the nitrogen precursor consisting of N atoms is molecular nitrogen. Examples of the nitrogen precursor consisting of N and H atoms are ammonia and hydrazine. An example of the nitrogen precursor consisting of O and N atoms is nitric oxide (N_2O) and nitrogen dioxide (NO_2).

[0031] The oxygen precursor may be used with the Silicon Precursor Compound in the composition for forming a silicon oxygen film according to an embodiment of the method. The silicon oxygen film contains Si and O atoms and optionally C and/or N atoms and may comprise silicon oxide, silicon oxycarbide, silicon oxynitride, or silicon oxycarbonitride. The silicon oxide may be SiO or SiO_2. The oxygen precursor may comprise O atoms and optionally H atoms, alternatively may consist essentially of O atoms and optionally H atoms, alternatively may consist of O atoms and optionally H atoms. The oxygen precursor that comprises O atoms and optionally H atoms may further comprise C or N atoms when the oxygen precursor is used in the method for forming a silicon oxycarbide or silicon oxynitride film, respectively, or may further comprise C and N atoms when the oxygen precursor is used in the method for forming a silicon oxycarbonitride film. Examples of the oxygen precursor consisting of O atoms are molecular oxygen and ozone. Ozone can be delivered at up to 5% v/v in air or up to 14% v/v in molecular oxygen. Examples of the oxygen precursor consisting of O and H atoms are water and hydrogen peroxide. An example of the oxygen precursor consisting of O and N atoms is nitric oxide and nitrogen dioxide.

[0032] The inert gas may be used in combination with any one of the foregoing precursors and any embodiment of the composition or method. Examples of the inert gas are helium, argon, and a mixture thereof. For example, helium may be used in combination with the Silicon Precursor Compound and molecular hydrogen or HCl in an embodiment of the method wherein the silicon containing film that is formed is an elemental silicon film. Alternatively, helium may be used with the Silicon Precursor Compound and any one of the carbon precursor, nitrogen precursor and oxygen precursor in an embodiment of the method wherein

the silicon containing film that is formed is a silicon carbon film, silicon nitrogen film, or silicon oxygen film respectively.

[0033] The film formed by the method is a material containing Si and is restricted in one dimension, which may be referred to as thickness of the material. The silicon containing film may be an elemental silicon film, a silicon carbon film, a silicon nitrogen film, or a silicon oxygen film. (e.g., silicon nitride, silicon carbonitride, silicon oxynitride, or silicon oxycarbonitride film, alternatively a silicon nitrogen film or a silicon oxygen film (e.g., silicon nitride, silicon oxide). The elemental silicon film formed by the method lacks C, N and O atoms and may be an amorphous or crystalline Si material. The silicon carbon film formed by the method contains Si and C atoms and optionally N and/or O atoms. The silicon nitrogen film formed by the method contains Si and N atoms and optionally C and/or O atoms. The silicon oxygen film formed by the method contains Si and O atoms and optionally C and/or N atoms.

[0034] The film may be useful in electronics and photovoltaic applications. E.g., the silicon nitride film may be formed as an insulator layer, passivation layer, or a dielectric layer between polysilicon layers in capacitors.

[0035] The method of forming a film uses a deposition apparatus. The deposition apparatus utilized in the method is generally selected based upon the desired method of forming the film and may be any deposition apparatus known by those of skill in the art.

[0036] In certain embodiments, the deposition apparatus comprises a physical vapor deposition apparatus. In these embodiments, the deposition apparatus is typically selected from a sputtering apparatus, an atomic layer deposition apparatus (including plasma enhanced and thermal atomic layer deposition apparatuses), and a direct current (DC) magnetron sputtering apparatus, alternatively the deposition apparatus is an atomic layer deposition apparatus. The optimum operating parameters of each of these physical deposition vapor apparatuses are based upon the Silicon Precursor Compound utilized in the method and the desired application in which the film formed via the deposition apparatus is utilized. In certain embodiments, the deposition apparatus comprises a sputtering apparatus. The sputtering apparatus may be, for example, an ion-beam sputtering apparatus, a reactive sputtering apparatus, or an ion-assisted sputtering apparatus.

[0037] More typically, however, the deposition apparatus comprises an atomic layer deposition apparatus or a chemical vapor deposition apparatus. In embodiments using the atomic layer deposition apparatus, the method of forming the film may be referred to as an atomic layer deposition method and includes plasma enhanced atomic layer deposition

methods (PEALD), spatial atomic layer deposition (SALD) and thermal atomic layer deposition (TALD) methods. Likewise in embodiments using the chemical vapor deposition apparatus, the method of forming the film may be referred to as a chemical vapor deposition method. Atomic layer deposition and chemical vapor deposition apparatuses and methods are generally well known in the art. The present method is exemplified below by reference to use of a chemical vapor deposition apparatus, although the present method may be readily adapted for use with the atomic layer apparatus.

[0038] In embodiments of the method using the chemical vapor deposition apparatus, the chemical vapor deposition apparatus may be selected from, for example, a flowable chemical vapor apparatus, a thermal chemical vapor deposition apparatus, a plasma enhanced chemical vapor deposition apparatus, a photochemical vapor deposition apparatus, an electron cyclotron resonance apparatus, an inductively coupled plasma apparatus, a magnetically confined plasma apparatus, a low pressure chemical vapor deposition apparatus and a jet vapor deposition apparatus. The optimum operating parameters of each of these chemical deposition vapor apparatuses are based upon the Silicon Precursor Compound utilized in the method and the desired application in which film formed via the deposition apparatus is utilized. In certain embodiments, the deposition apparatus comprises a plasma enhanced chemical vapor deposition apparatus. In other embodiments, the deposition apparatus comprises a low pressure chemical vapor deposition apparatus.

[0039] In chemical vapor deposition, gases for forming the film are typically mixed and reacted in a deposition chamber. The reaction forms the proper film elements or molecules in a vapor state. The elements or molecules then deposit on a substrate (or wafer) and build up to form the film. Chemical vapor deposition generally requires the addition of energy to the system, such as heating of the deposition chamber and substrate.

[0040] Reaction of gaseous species is generally well known in the art and any conventional chemical vapor deposition (CVD) technique can be carried out via the present method. For example, methods such as simple thermal vapor deposition, plasma enhanced chemical vapor deposition (PECVD), electron cyclotron resonance (ECRCVD), atmospheric pressure chemical vapor deposition (APCVD), low pressure chemical vapor deposition (LPCVD), ultrahigh vacuum chemical vapor deposition (UHVCVD), aerosol-assisted chemical vapor deposition (AACVD), direct liquid injection chemical vapor deposition (DLICVD), microwave plasma-assisted chemical vapor deposition (MPCVD), remote plasma-enhanced chemical vapor deposition (RPECVD), atomic layer chemical vapor deposition (ALCVD), hot wire

chemical vapor deposition (HWCVD), hybrid physical-chemical vapor deposition (HPCVD), rapid thermal chemical vapor deposition (RTCVD), and vapor-phase epitaxy chemical vapor deposition (VPECVD), photo-assisted chemical vapor disposition (PACVD), flame assisted chemical vapor deposition (FACVD), or any similar technique may be used.

[0041] When plasma enhanced atomic layer deposition methods are employed, the plasma comprises forming gas, nitrogen plasma, or ammonia plasma in either nitrogen or argon gas as a carrier or oxygen plasma. Forming gas comprises nitrogen and hydrogen. One skilled in the art would understand the composition of forming gas.

[0042] Chemical vapor deposition may be utilized to form films having a wide variety of thicknesses contingent on a desired end use of the film. For instance, the film may have a thickness of a few nanometers or a thickness of a few microns, or a greater or lesser thickness (or a thickness falling between these values). These films may optionally be covered by coatings, such as SiO_2 coatings, SiO_2/modifying ceramic oxide layers, silicon-containing coatings, silicon carbon-containing coatings, silicon carbide-containing coatings, silicon nitrogen-containing coatings, silicon nitride-containing coatings, silicon nitrogen carbon-containing coatings, silicon oxygen nitrogen containing coatings, and/or diamond like carbon coatings. Such coatings and their methods of deposition are generally known in the art.

[0043] The substrate utilized in the method is not limited. In certain embodiments, the substrate is limited only by the need for thermal and chemical stability at the temperature and in the environment of the deposition chamber. Thus, the substrate can be, for example, glass, metal, plastic, ceramic, semiconductor including, but not limited to, silicon (e.g. monocrystalline silicon, polycrystalline silicon, amorphous silicon, etc). The substrate can have a flat or a patterned surface. A patterned surface has features with an aspect ratio ranging from 1 to 500, alternatively from 1 to 50, alternatively from 10 to 50. The CVD or ALD films can be conformal on both the flat or patterned substrate surface.

[0044] Embodiments of the present method may include a reactive environment comprising nitrous oxide (N_2O). Such reactive environments are generally known in the art. In these embodiments, the method generally involves decomposing the Silicon Precursor Compound in the presence of nitrous oxide. An example of such a method is described in U.S. Pat. No. US 5,310,583. Utilizing nitrous oxide may modify the composition of the resulting film formed in the chemical vapor deposition method.

[0045] The chemical vapor deposition apparatus and, thus, the chemical vapor deposition method utilized is generally selected by balancing a number of factors, including, but not

limited to, the Silicon Precursor Compound, desired purity of the film, geometric configuration of the substrate, and economic considerations.

[0046] The main operating variables manipulated in chemical vapor deposition and atomic layer deposition include, but are not limited to, reactor temperature, substrate temperature, pressure, concentration in the gas phase of the Silicon Precursor Compound, any additional reactant gas concentration (e.g., concentration of gas of any carbon precursor, nitrogen precursor, and/or oxygen precursor), total gas flow, and substrate. Chemical vapor deposition and atomic layer deposition are generated from chemical reactions which include, but are limited to, pyrolysis, oxidation, reduction, hydrolysis, and combinations thereof. Selecting the optimal temperature for chemical vapor deposition and atomic layer deposition requires an understanding of both the kinetics and thermodynamics of the Silicon Precursor Compound and the chosen chemical reaction.

[0047] Conventional chemical vapor and atomic layer deposition methods generally require significantly high temperatures, such as greater than 600° C., e.g. 600° to 1000° C. However, it is believed that the Silicon Precursor Compound may be utilized in chemical vapor or atomic layer deposition at much lower temperatures. For example, the method may be carried out at a temperature of from 100° to 700°, alternatively from 200° to 700°, alternatively from 200° to 600°, alternatively from 200° to 500°, alternatively from 200° to 400° C, alternatively from 100° to 300° C. The temperature at which the method is carried out may be isothermal or dynamic.

[0048] Chemical vapor and atomic layer deposition processes generally conducted at a pressure from 0.01 torr to 100 torr, alternatively 0.01 torr to 10 torr, alternatively from 0.1 to 10 torr, alternatively from 1 to 10 torr.

[0049] Chemical vapor and atomic layer deposition processes generally involve generating a precursor, transporting the precursor into a reaction chamber, and either absorption of precursors onto a heated substrate or chemical reaction of the precursor and subsequent absorption onto the substrate. The following sets forth a cursory survey of chemical vapor deposition methods to illustrate some of the vast options available.

[0050] Chemical vapor and atomic layer deposition processes deposit films of thickness from 0.01 nanometers to 1 micrometer, alternatively from 0.1 to 100 nanometers, alternatively from 1 to 100 nanometers.

[0051] In thermal CVD, the film is deposited by passing a stream of a vaporized form of the Silicon Precursor Compound over a heated substrate. When the vaporized form of the Silicon

Precursor Compound contacts the heated substrate, the Silicon Precursor Compound generally reacts and/or decomposes to form the film.

[0052] In PECVD, a vaporized form of the Silicon Precursor Compound is reacted by passing it through a plasma field to form a reactive species. The reactive species is then focused and deposited on the substrate the form the film. Generally, an advantage of PECVD over thermal CVD is that lower substrate temperature can be used. The plasmas utilized in PECVD comprise energy derived from a variety of sources such as electric discharges, electromagnetic fields in the radio-frequency or microwave range, lasers or particle beams. Generally, PECVD utilizes radio frequency (10 kilohertz (kHz)-102 megahertz (MHz)) or microwave energy (0.1-10 gigahertz (GHz)) at moderate power densities (0.1-5 watts per square centimeter (W/cm^2)), although any of these variables may be modified. The specific frequency, power, and pressure, however, are generally tailored to the deposition apparatus.

[0053] In AACVD, the Silicon Precursor Compound is dissolved in a chemical medium to form a mixture. The mixture comprising the Silicon Precursor Compound and the chemical medium is packaged in a traditional aerosol. The aerosol atomizes and introduces the Silicon Precursor Compound into a heated chamber where the Silicon Precursor Compound undergoes decomposition and/or chemical reaction. One advantage of AACVD is the ability to form the film without necessitating a vacuum.

[0054] The chosen deposition process and operating parameters will have impact the structure and properties of the film. Generally, it is possible to control the orientation of film structure, the manner in which the film coalesces, the uniformity of the film, and crystalline/non-crystalline structure of the film.

[0055] It is to be noted that environments which facilitate the desired deposition can also be used in the deposition chamber. For instance, reactive environments such as air, oxygen, oxygen plasma, ammonia, amines, hydrazine, etc. or inert environments may all be used herein.

[0056] Additionally, the present invention provides a film formed in accordance with the method. The composition and structure of the film is a function of not only the deposition apparatus and its parameters, but also the Silicon Precursor Compound utilized and the presence or absence of any reactive environment during the method. The Silicon Precursor Compound may be utilized in combination with any other known precursor compounds or may be utilized in the method free from any other precursor compounds.

[0057] Because the Silicon Precursor Compound contains a Si-N bond, the Silicon Precursor Compound may be utilized to form silicon nitride films without use of a nitrogen precursor, although a nitrogen precursor may be also used if desired. That is, the addition of a nitrogen precursor (e.g., second vapor) may not be necessary to form a silicon nitride film. One may be able to optimize the deposition conditions to control whether the present method forms an elemental Si film or a SiN film. If desired the nitrogen precursor may be used in the second vapor to enrich the nitrogen content of the SiN film.

[0058] Alternatively, the Silicon Precursor Compound may be utilized with other silicon-based precursor compounds traditionally utilized to form silicon films comprising crystalline silicon or silicon nitride. In such embodiments, the films may be, for example, crystalline or epitaxial. Contingent on the presence of reactive environments during the method, the film may further comprise oxygen and/or carbon in addition to silicon and nitrogen.

[0059] Purity of the Silicon Precursor Compound may be determined by ^{29}Si-NMR, reverse phase liquid chromatography or, more likely, by gas chromatography (GC) as described later. For example, the purity determined by GC may be from 60 area% to ≤ 100 area% (GC), alternatively from 70 area% to ≤ 100 area% (GC), alternatively from 80 area% to ≤ 100 area% (GC), alternatively from 90 area% to ≤ 100 area% (GC), alternatively from 93 area% to ≤ 100 area% (GC), alternatively from 95 area% to ≤ 100 area% (GC), alternatively from 97 area% to ≤ 100 area% (GC), alternatively from 99.0 area% to ≤ 100 area% (GC). Each ≤ 100 area% (GC) independently may be as defined previously.

[0060] The invention is further illustrated by, and an invention embodiment may include any combinations of features and limitations of, the non-limiting examples thereof that follow. Ambient temperature is about 23° C. unless indicated otherwise.

[0061] Gas Chromatography-Flame Ionization Detector (GC-FID) conditions: a capillary column with 30 meters length, 0.32 mm inner diameter, and containing a 0.25 μm thick stationary phase in the form of a coating on the inner surface of the capillary column, wherein the stationary phase was composed of phenyl methyl siloxane. Carrier gas is helium gas used at a flow rate of 105 mL per minute. GC instrument is an Agilent model 7890A gas chromatograph. Inlet temperature is 150° C. GC experiment temperature profile consist of soaking (holding) at 50° C. for 2 minutes, ramping temperature up at a rate of 15° C./minute to 250° C., and then soaking (holding) at 250° C. for 10 minutes.

[0062] GC-MS instrument and conditions: Sample is analyzed by electron impact ionization and chemical ionization gas chromatography-mass spectrometry (EI GC-MS and CI GC-MS).

Agilent 6890 GC conditions include a DB-1 column with 30 meters (m) x 0.25 millimeter (mm) x 0.50 micrometer (μm) film configuration. An oven program of soaking at 50° C. for 2 minutes, ramping at 15° C./minute to 250° C., and soaking at 250° C. for 10 minutes. Helium carrier gas flowing at constant flow of at 70 mL/minute and a 50:1 split injection. Agilent 5973 MSD conditions include a MS scan range from 15 to 800 Daltons, an EI ionization and CI ionization using a custom CI gas mix of 5% NH_3 and 95% CH_4.

[0063] ^{29}Si-NMR instrument and solvent: a Varian 400 MHz Mercury spectrometer is used. C_6D_6 is used as the solvent.

[0064] ^{1}H-NMR instrument and solvent: a Varian 400 MHz Mercury spectrometer is used. C_6D_6 is used as the solvent.

[0065] Example (Ex.) A: synthesis of diisopropylamino-pentachlorodisilane using 2.21 mol equiv. of diisopropylamine: mixed hexachlorodisilane (HCDS; 20.0 milliliters (mL), 0.116 mol) and anhydrous hexanes (200 mL) in a 1 liter (L) round-bottom flask. Cooled the mixture to -20° C. with dry ice. Under agitation of a mechanical stirrer, added a solution of diisopropylamine (DiPA; 35.8 mL, 0.256 mol) in hexanes (100 mL) in 35 minutes near -20° C. After the addition, warmed the slurry to 23° C., and stirred (bodied) for one night. Added another 100 mL hexanes to dilute the slurry, and filtered the diluted slurry through a Type D glass frit covered with 1 inch of thick diatomaceous earth (CELITE). Rinsed the resulting filtercake with 100 mL hexanes. Collected a clear filtrate (about 400 mL). Distilled the filtrate under vacuum (< 1 Torr) to remove volatile organics. Recovered 28.43 g (73.5% yield) of crude diisopropylamino-pentachlorodisilane as a clear yellowish liquid.

[0066] Ex. B: synthesis of diisopropylamino-pentachlorodisilane using 1.10 mol equiv. of diisopropylamine and 1.10 mol equiv. triethylamine: replicate the procedure of Ex. A except instead of the 35.8 mL of DiPA in hexanes (100 mL) use a solution of DiPA (17.9 mL, 0.128 mol) and triethylamine (17.8 mL, 0.128 mol) in hexanes (100 mL). The amount of clear filtrate was about 450 mL. After distillation to remove volatile organics, recovered 29.2 g (75.5% yield) of crude diisopropylamino-pentachlorodisilane as a clear yellowish liquid.

[0067] Ex. C: synthesis of diisopropylamino-pentachlorodisilane using 1.10 mol equiv. of lithium diisopropylamide: mixed 10.0 M n-BuLi solution in hexanes (92.0 mL; 0.920 mol) and anhydrous hexanes (828 mL) in a 2 L round-bottom flask. Under agitation of a magnetic stirrer, added DiPA (129.0 mL, 0.920 mol) in 15 minutes at up to 40° C. Stirred the resultant lithium diisopropylamide solution for 1 hour at 23° C. To another 2 L round-bottom flask added HCDS

(144.0 mL, 0.836 mol) and 93.1 mL hexanes. Cooled the 2nd flask with some dry ice near 0° C. Under agitation of a mechanical stirrer, pressure fed at a feed rate the lithium diisopropylamide solution through a ¼ inch (0.635 centimeter (cm)) inner diameter poly(tetrafluoroethylene) tubing into the 2nd flask. A white precipitate formed immediately. Controlled the feed rate to maintain the reaction temperature below 40° C. The addition took 1 hour 15 minutes. After the addition, stirred (bodied) the slurry for one night. Then filtered the slurry and removed volatile organics using the procedures analogous to those as in Ex. 1 to give 199.8 g (71.6% yield) of crude diisopropylamino-pentachlorodisilane as a clear yellow liquid.

[0068] Ex. D: distilled diisopropylamino-pentachlorodisilane from the crude diisopropylamino-pentachlorodisilane of Ex. A to give a distillate comprising purified diisopropylamino-pentachlorodisilane.

[0069] Ex. E: Differential Scanning Calorimetry (DSC) instrument and standard conditions: a known weight of a sample material was loaded into a 20 microliter (µL) high pressure DSC crucible, and the crucible was sealed using a press and loaded into a furnace of a Mettler Toledo TGA/DSC 1 instrument. The furnace was thermally equilibrated at 35 °C for 20 minutes then ramped from 35 °C to a specific temperature (400 °C for example) at a rate of 10 °C per minute. When the specific temperature was reached (400 °C for example), the furnace was held at that temperature for 20 minutes followed by cooled to ambient temperature (23° C ± 1 C) at a cooling rate of 10 ° C per minute[FF]. The sample was then reheated to the temperature (for example 400 °C) at a heating rate of 10 °C per minute. The crucible was next removed from the furnace, allowed to cool, and the sample was reweighed to determine if the sample lost mass during the test method. This method was used with diisopropylaminopentachlorodisilane to determine that the thermal decomposition onset temperature of diisopropylaminopentachlorodisilane was 352 °C.

[0070] Example (Ex) 1 (prophetic): forming a silicon nitride film using the Silicon Precursor Compound with atomic layer deposition (ALD): using an ALD reactor and a bubbler containing the Silicon Precursor Compound and in fluid communication with the ALD reactor, heat the bubbler containing Silicon Precursor Compound to 100° C. to increase vapor pressure thereof. Purge the ALD reactor with nitrogen, wherein the ALD reactor contains a plurality of horizontally oriented and spaced apart silicon wafers heated to 500° C. Then flow the nitrogent carrier gas through the bubbler to carry vapor of Silicon Precursor Compound into the ALD reactor for 10 seconds. Purge the ALD reactor again with nitrogen to remove any residual

vapor of the Silicon Precursor Compound. Then flow ammonia into the ALD reactor for 10 seconds. Repeat the foregoing sequence of steps until a conformal silicon nitride film with a desired thickness is formed on the wafers. One cycle is equal to one sequence of ten second precursor dose, followed by a ten second nitrogen purge, followed by a ten second ammonia dose, and followed by a ten second nitrogen purge.

[0071] Ex. 2 (prophetic): forming a silicon nitride film using the Silicon Precursor Compound and ammonia (NH_3) with LPCVD: using a LPCVD reactor and a bubbler containing the Silicon Precursor Compound and in fluid communication with the LPCVD reactor, heat the bubbler containing the Silicon Precursor Compound to 100° C. to increase vapor pressure thereof. Then flow nitrogen carrier gas through the bubbler to carry vapor of the Silicon Precursor Compound into the LPCVD reactor, wherein the LPCVD reactor contains vaporous ammonia and a plurality of vertically oriented and spaced apart silicon wafers heated to 500° C. so a conformal silicon nitride film is formed on the wafers.

[0072] Ex. 3 (prophetic): form a silicon nitride film using the Silicon Precursor Compound with ammonia and PEALD using a PEALD reactor and a bubbler containing the Silicon Precursor Compound and in fluid communication with the PEALD reactor. Heat the bubbler containing the Silicon Precursor Compound to 100 °C to increase the vapor pressure thereof. Purge the PEALD reactor with nitrogen. (The PEALD reactor contains a plurality of horizontally oriented and spaced apart silicon wafers heated to 500 °C.) Then flow nitrogen carrier gas through the bubbler to carry vapor of the Silicon Precursor Compound into the ALD reactor. Purge the ALD reactor again with nitrogen to remove any residual vapor of the Silicon Precursor Compound. Then flow ammonia into the ALD reactor with plasma power on. The ALD reactor was then purged again with nitrogen to remove any residual reactive species generated by plasma. Repeat the foregoing sequence of steps until a conformal silicon nitride film with a desired thickness is formed on the wafers. One cycle is equal to one sequence of a one second precursor dose, followed by a 30 second nitrogen purge, followed by a fifteen second plasma treatment, and followed by a 30 second nitrogen purge.

[0073] Ex. 4 (prophetic): forming a silicon nitride film using the Silicon Precursor Compound with ammonia and PECVD: using a PECVD reactor and a bubbler in fluid communication with the PECVD reactor, heat the bubbler containing the Silicon Precursor Compound to 70° C. to increase vapor pressure thereof. Then flow He carrier gas through the bubbler to carry vapor of the Silicon Precursor Compound into the PECVD reactor, wherein the PECVD reactor has an ammonia-derived plasma and contains a plurality of horizontally oriented and spaced apart

silicon wafers heated to 500° C. such that a conformal silicon nitride film is formed on the wafers.

[0074] Ex. 5 (prophetic: form a silicon oxide film using the Silicon Precursor Compound with ozone and ALD using an ALD reactor and a bubbler containing the Silicon Precursor Compound and in fluid communication with the ALD reactor. Heat the bubbler containing Silicon Precursor Compound to 100 °C to increase the vapor pressure thereof. Purge the ALD reactor with argon, wherein the ALD reactor contains a plurality of horizontally oriented and spaced part silicon wafers heated to 500 °C. Then flow argon carrier gas through the bubbler to carry vapor of Silicon Precursor Compound into the ALD reactor. Purge the ALD reactor again with argon to remove any residual vapor of the Silicon Precursor Compound. Next flow ozone in oxygen into the ALD reactor. Repeat the foregoing sequence of steps until a conformal silicon oxide film with a desired thickness is formed on the wafers. One cycle is equal to one sequence of a three second precursor dose, followed by a 10 second argon purge, followed by a 10 second ozone treatment, and followed by a 10 second argon purge.

[0075] Ex. 6 (prophetic): forming a silicon oxide film using the Silicon Precursor Compound with LPCVD: using a LPCVD reactor and a bubbler in fluid communication with the LPCVD reactor, heat the bubbler containing the Silicon Precursor Compound to 100° C. to increase vapor pressure thereof. Then flow Argon carrier gas through the bubbler to carry vapor of the Silicon Precursor Compound into the LPCVD reactor, wherein the LPCVD reactor has an ozone in oxygen atmosphere and contains a plurality of vertically oriented and spaced apart silicon wafers heated to 500° C. such that a conformal silicon oxide film is formed on the wafers.

[0076] Ex. 7 (prophetic): forming a silicon carbide film using the Silicon Precursor Compound with methane and PECVD: using a PECVD reactor and a bubbler in fluid communication with the PECVD reactor, heat the bubbler containing the Silicon Precursor Compound to 100° C. to increase vapor pressure thereof. Then flow He carrier gas through the bubbler to carry vapor of the Silicon Precursor Compound into the PECVD reactor, wherein the PECVD reactor has a methane-derived plasma and contains a plurality of horizontally oriented and spaced apart silicon wafers heated to 500° C. such that a conformal silicon carbide film is formed on the wafers.

[0077] The below claims are incorporated by reference here, and the terms “claim” and “claims” are replaced by the term “aspect” or “aspects,” respectively. Embodiments of the invention also include these resulting numbered aspects.

What is claimed is:

1. A method of forming a silicon-containing film on a substrate, the method comprising subjecting a vapor of a silicon precursor comprising diisopropylamino-pentachlorodisilane, which is of formula (A): $[(CH_3)_2CH]_2NSiCl_2SiCl_3$ (A), to deposition conditions in the presence of the substrate so as to form a silicon-containing film on the substrate.
2. The method of claim 1 wherein the silicon-containing film is an elemental silicon film, a silicon carbon film, a silicon nitrogen film, or a silicon oxygen film.
3. The method of claim 1 comprising subjecting a first vapor of a silicon precursor comprising diisopropylamino-pentachlorodisilane and a second vapor comprising helium, hydrogen, or HCl to deposition conditions in the presence of the substrate so as to form a silicon-containing film on the substrate, wherein the silicon-containing film is an elemental silicon film.
4. The method of claim 1 comprising subjecting a first vapor of a silicon precursor comprising diisopropylamino-pentachlorodisilane and a second vapor of a carbon precursor comprising a hydrocarbon, hydrocarbylsilane or a combination of any two thereof to deposition conditions in the presence of the substrate so as to form a silicon-containing film on the substrate, wherein the silicon-containing film is a silicon carbon film.
5. The method of claim 1 comprising subjecting a first vapor of a silicon precursor comprising diisopropylamino-pentachlorodisilane and a second vapor of a nitrogen precursor comprising molecular nitrogen, ammonia, amine, hydrazine, or a combination of any two or three thereof to deposition conditions in the presence of the substrate so as to form a silicon-containing film on the substrate, wherein the silicon-containing film is a silicon nitrogen film.
6. The method of claim 1 comprising subjecting a first vapor of a silicon precursor comprising diisopropylamino-pentachlorodisilane and a second vapor of an oxygen precursor comprising molecular oxygen, ozone, nitric oxide, nitrogen dioxide, water, hydrogen peroxide, or a combination of any two or three thereof to deposition conditions in the presence of the substrate so as to form a silicon-containing film on the substrate, wherein the silicon-containing film is a silicon oxygen film.
7. The method of any one of claims 3-6 wherein the substrate is heated and disposed in a deposition reactor that is configured for atomic layer deposition, the method

comprising repeatedly feeding the first vapor of a silicon precursor comprising diisopropylamino-pentachlorodisilane, purging with an inert gas, feeding the second vapor into the deposition reactor, and purging with an inert gas so as to form the silicon-containing film on the heated substrate using atomic layer deposition, wherein the atomic layer deposition comprises plasma enhanced atomic layer deposition or thermal atomic layer deposition and wherein the feeds may be the same or different.

8. The method of claim 7, wherein the atomic layer deposition is plasma enhanced atomic layer deposition and wherein the plasma is ammonia plasma in nitrogen or argon or wherein the plasma is forming gas, nitrogen, or oxygen plasma.
9. The method of any one of claims 3-6 wherein the substrate is heated and disposed in a deposition reactor that is configured for chemical vapor deposition, the method comprising feeding the first vapor of a silicon precursor comprising diisopropylamino-pentachlorodisilane and feeding the second vapor into the deposition reactor so as to form the silicon-containing film on the heated substrate using chemical vapor deposition, wherein the feeds may be the same or different.
10. The method of claim 5, wherein the vapor deposition conditions lack carbon and oxygen and the silicon nitrogen film comprises a silicon nitride film.
11. The method of any one of the preceding claims wherein the substrate is a semiconductor material.
12. A composition for forming a silicon nitrogen film, the composition comprising a silicon precursor comprising diisopropylamino-pentachlorodisilane and a nitrogen precursor.
13. Use of the composition of claim 11 in a method of forming of a silicon nitrogen film.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/033273

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23C16/455 C23C16/40 C23C16/34 C23C16/32 C23C16/24
ADD.

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)
C23C

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, COMPENDEX, INSPEC, IBM-TDB, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HEINZ SCHUH ET AL: "Disilanyl-amines - compounds comprising the structural unit SiSiN, as single-source precursors for plasma-enhanced chemical vapour deposition (PE-CVD) of silicon nitride", ZEITSCHRIFT FUR ANORGANISCHE UND ALLGEMEINE CHEMIE, WILEY - V C H VERLAG GMBH & CO. KGAA, DE, vol. 619, no. 8, 1 January 1993 (1993-01-01), pages 1347-1352, XP002486454, ISSN: 0044-2313, DOI: 10.1002/ZAAC.19936190805	1,2,5, 9-13
Y	page 1348, left-hand column, line 4 - page 1349, right-hand column, line 12	3,4,6-8

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[X] Further documents are listed in the continuation of Box C.

[X] 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

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 June 2016	07/07/2016

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/033273

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	US 2015/024608 A1 (MAYORGA STEVEN GERARD [US] ET AL) 22 January 2015 (2015-01-22) paragraphs [0015], [0080]	3,4,6-8
A	US 2014/187025 A1 (OBU TOMOYUKI [JP] ET AL) 3 July 2014 (2014-07-03) paragraphs [0024] - [0079]	1-13

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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