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(54) Title: DEPOSITION OF FILMS USING DISILOXANE PRECURSORS

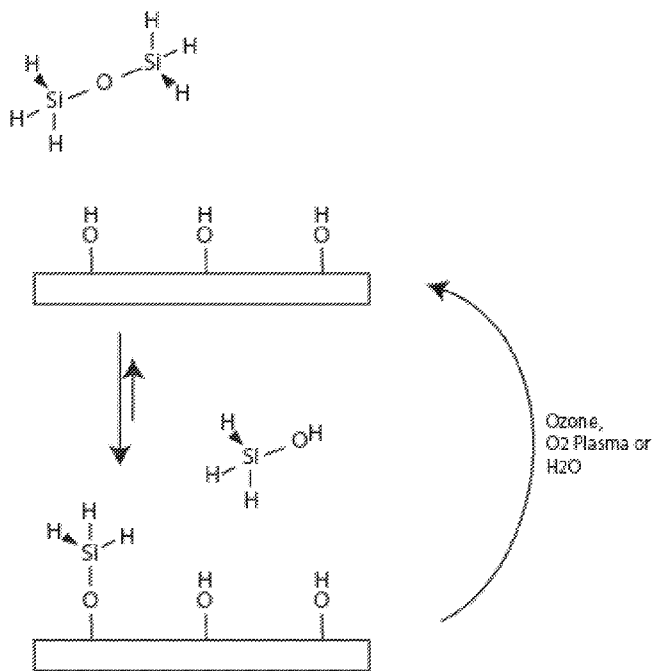


FIGURE 1

(57) Abstract: Provided are methods of for deposition of various silicon-containing films using disiloxane or disiloxane derivative. Certain methods relate to deposition of Si_xO_y using an oxygen-containing compound, plasma or halosilane. Certain other methods relate to deposition of metal oxides using a metal halide and disiloxane. Yet other methods pertain to deposition of SiOC films using disiloxane or carbon-containing disiloxane derivatives, possibly with organic hydroxides.



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DEPOSITION OF FILMS USING DISILOXANE PRECURSORS

TECHNICAL FIELD

[0001] The present invention relates generally to methods of depositing thin films. In particular, the invention relates to atomic layer deposition processes for the deposition of Si-containing films.

BACKGROUND

[0002] Deposition of thin films on a substrate surface is an important process in a variety of industries including semiconductor processing, diffusion barrier coatings and dielectrics for magnetic read/write heads. In the semiconductor industry, in particular, miniaturization requires atomic level control of thin film deposition to produce conformal coatings on high aspect structures. One method for deposition of thin films with control and conformal deposition is chemical vapor deposition (CVD). CVD involves exposing a substrate (*e.g.*, a wafer) to one or more precursors, which react to deposit a film onto the substrate.

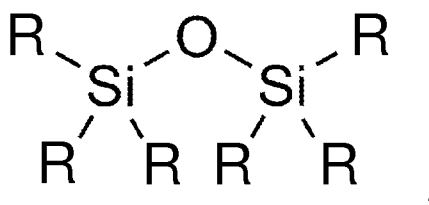
[0003] There is a need for new deposition chemistries that are commercially viable. The present invention addresses this problem by providing novel chemistries which are specifically designed and optimized to take advantage of the deposition process. There is especially a need for new chemistries for the deposition of silicon-containing films and metal oxide films. Films, such as SiO_2 , SiOC , etc. are ubiquitous in the field of semiconductors, so new methods for their deposition are always sought after.

SUMMARY

[0004] One aspect of the invention pertains to a method of depositing a film. In one or more embodiments, the method comprises exposing a substrate surface to a first precursor and a co-reactant, the first precursor comprising disiloxane to provide a film comprising Si_xO_y . In some embodiments, the co-reactant comprises an oxygen source, and the deposited film comprises Si_xO_y . In one or more embodiments, x has a value of 1 to 2 and y has a value of 1 to 2. In some embodiments, the substrate surface is exposed to the first precursor and the co-reactant simultaneously. In one or more embodiments, the co-reactant comprises a plasma. In

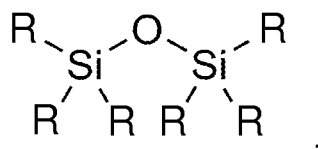
some embodiments, the co-reactant comprises $\text{SiX}_m\text{H}_{4-m}$, wherein X is a halogen selected from Cl, Br and I, and m has a value between 2 and 4, and the deposited film comprises Si_xO_y . In one or more embodiments, the co-reactant comprises $\text{X}_z\text{H}_{3-z}\text{Si-SiX}_z\text{H}_{3-z}$, wherein X is a halogen selected from Cl, Br and I, and z has a value between 1 and 3, and the deposited film comprises Si_xO_y . In some embodiments, the co-reactant comprises a metal precursor, and the deposited film comprises a metal oxide. In one or more embodiments, the metal comprises a transition metal and the metal precursor comprises a metal halide.

[0005] Another aspect of the invention pertains to a method of depositing a film comprising SiOC, the method comprising exposing a substrate surface to a first precursor and a co-reactant, the first precursor comprising a compound having a structure represented by:



wherein each R is independently hydrogen, $\text{C}_n\text{H}_{2n+2}$ or OR' , wherein R' is $\text{C}_n\text{H}_{2n+2}$ and n has a value of 1 to 5, to provide a film comprising SiOC. In some embodiments, each R group is hydrogen. In one or more embodiments, the co-reactant comprises carbon. In some embodiments, the co-reactant comprises acetylene, ethylene or a carbosilane. In one or more embodiments, the co-reactant comprises $\text{SiX}_m\text{H}_{4-m}$, wherein X is a halogen selected from Cl, Br and I, and m has a value between 2 and 4. In some embodiments, the co-reactant comprises $\text{X}_z\text{H}_{3-z}\text{Si-SiX}_z\text{H}_{3-z}$, wherein X is a halogen selected from Cl, Br and I, and z has a value between 1 and 3. In one or more embodiments, the co-reactant comprises an organic hydroxide containing at least two hydroxide groups. In some embodiments, at least one of the R groups is not hydrogen, and the co-reactant is selected from the group consisting of H_2O , H_2O_2 , O_2 , or O_3 .

[0006] Another aspect of the invention pertains to a method of depositing a film comprising silicon and oxygen. In some embodiments, the method comprises exposing a substrate surface to a first precursor comprising a compound having a structure represented by formula (I):



wherein each R is independently hydrogen, C1-C6 alkyl, or OR', wherein R' is C1-C6 alkyl or (CH₂)_pNH₂, wherein p has a value ranging from 1 to 6, with the proviso that at least one R group is O(CH₂)_pNH₂, to provide a film comprising silicon and oxygen. In one or more
 5 embodiments, SiO₂ is deposited. In some embodiments, the method further comprises contacting the substrate surface with a co-reagent comprising one or more of H₂O, H₂O₂, O₂, and O₃.

BRIEF DESCRIPTION OF THE DRAWINGS

10 [0007] So that the manner in which the above recited features of the present invention can be understood in detail, a more particular description of the invention, briefly summarized above, may be had by reference to embodiments, some of which are illustrated in the appended drawings. It is to be noted, however, that the appended drawings illustrate only typical
 15 embodiments of this invention and are therefore not to be considered limiting of its scope, for the invention may admit to other equally effective embodiments.

[0008] FIGURE 1 is a proposed chemical schematic of a process in accordance with one or more embodiments of the invention;

[0009] FIGURE 2 is a graph of the growth per cycle and refractive indices as a function of temperature of films according to one or more embodiments of the invention; and

20 [0010] FIGURE 3 is a graph of the growth per cycle and refractive indices as a function of temperature of films according to one or more embodiments of the invention.

DETAILED DESCRIPTION

[0011] Before describing several exemplary embodiments of the invention, it is to be understood that the invention is not limited to the details of construction or process steps set
 25 forth in the following description. The invention is capable of other embodiments and of being practiced or being carried out in various ways. It is also to be understood that the chemical

compounds of the present invention may be illustrated herein using structural formulas which have a particular stereochemistry. These illustrations are intended as examples only and are not to be construed as limiting the disclosed structure to any particular stereochemistry. Rather, the illustrated structures are intended to encompass all such complexes and ligands having the indicated chemical formula.

[0012] Disiloxane ($\text{H}_3\text{Si-O-SiH}_3$) may be an effective compound during various deposition processes. Specifically, disiloxane may be useful as a precursor for the deposition of silicon oxides (Si_xO_y) or silicon oxycarbides (SiOC), and as a co-reagent for the deposition of metal oxides.

[0013] Accordingly, one aspect of the invention pertains to method of depositing a film comprising silicon oxide. The method comprises exposing a substrate surface to a first precursor and a co-reactant, the first precursor comprising disiloxane to provide a film comprising Si_xO_y . It is thought that films deposited by this process will be non-oxidizing Si_xO_y . That is, when this Si_xO_y is deposited over another substrate, it will not oxidize. This can be advantageous, especially for channel regions because of better thickness control. The Si_xO_y deposited by one or more embodiments of the invention will not thicken due to oxidation, and the resulting thickness will be known precisely as what is deposited (*i.e.*, the oxidized thickness will not have to be estimated). In one or more embodiments, Si_xO_y comprises SiO_2 .

[0014] The deposited silicon oxide film may be represented as having an empirical formula Si_xO_y . In some embodiments, x ranges from 1 to 2 and y ranges from 1 to 2. In one or more embodiments, the deposited film comprises SiO_2 . In some embodiments, the resulting silicon oxide film is silicon-rich. In one or more embodiments, "silicon-rich" means that the ratio of silicon to oxygen is about 2 to about 1 (*i.e.*, Si_2O_1). While not wishing to be bound to any particular theory, SiO_2 is generally considered to be thermally stable, and would therefore be the predicted ratio of silicon and oxygen in a deposited film. However, one or more embodiments of the invention provides films which can maintain the ratio of silicon to carbon of the precursors in the deposited film.

[0015] A "substrate" as used throughout this specification, refers to any substrate or material surface formed on a substrate upon which film processing is performed during a fabrication process. For example, a substrate surface on which processing can be performed

include materials such as silicon, silicon oxide, strained silicon, silicon on insulator (SOI), carbon doped silicon oxides, silicon nitride, doped silicon, germanium, gallium arsenide, glass, sapphire, and any other materials such as metals, metal nitrides, metal alloys, and other conductive materials, depending on the application. Substrates include, without limitation, semiconductor wafers. Substrates may be exposed to a pretreatment process to polish, etch, reduce, oxidize, hydroxylate, anneal and/or bake the substrate surface. In addition to film processing directly on the surface of the substrate itself, in the present invention any of the film processing steps disclosed may also be performed on an underlayer formed on the substrate as disclosed in more detail below, and the term "substrate surface" is intended to include such underlayer as the context indicates.

[0016] A substrate can be any type of substrate described above. An optional process step involves preparation of a substrate by treating the substrate with a plasma or other suitable surface treatment to provide active sites on the surface of the substrate. Examples of suitable active sites include, but are not limited to O-H, N-H, or S-H terminated surfaces.

[0017] In some embodiments, the disiloxane may be used with an oxygenating plasma to achieve films comprising Si_xO_y . In one or more embodiments, Si_xO_y comprises SiO_2 . In one or more embodiments, the co-reactant comprises an oxygen source (*i.e.*, is an oxygen precursor). In some embodiments, the oxygen source comprises H_2O , H_2O_2 , O_2 , O_3 , or an oxygen plasma.

[0018] In some embodiments pertaining to an oxygenating plasma, the substrate surface may be exposed to the disiloxane and plasma sequentially or substantially sequentially. As used herein throughout the specification, "substantially sequentially" means that the majority of the duration of the disiloxane exposure does not overlap with the exposure of the co-reagent, although there may be some overlap. In other embodiments, the substrate surface may be exposed to the disiloxane and plasma simultaneously or substantially simultaneously. As used herein throughout the specification, "substantially simultaneously" means that the majority of the duration of the disiloxane exposure overlaps with the exposure of the co-reagent, although they may not be co-extensive.

[0019] The FIGURE shows a possible chemical schematic for an exemplary process. A substrate surface containing $-\text{OH}$ surface functionality is exposed to disiloxane. The disiloxane reacts with the surface, and a SiH_3 group becomes bonded to the surface. Silanol is

released as a byproduct. The substrate surface may then be exposed to ozone, an O₂ plasma or water to provide more –OH groups for the next reaction. As a result, a layer of is deposited, and the film comprises silicon and oxygen.

[0020] In one or more embodiments, one or more of the reactants may be purged.

5 Thus, in some embodiments, the method further comprises purging the first precursor after the substrate is exposed to the first precursor, and purging the co-reactant after the substrate surface is exposed to the co-reactant.

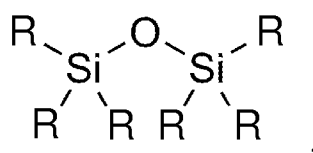
[0021] Carbon doping also be incorporated into the films in one or more embodiments.

10 One way of achieving this is through reaction with a disiloxane derivative, wherein one or more of the hydrogen atoms is replaced with a carbon containing group. Such examples include C1-C6 alkyl, and in further embodiments, ethyl or methyl. Another way of achieving carbon doping is to further use a carbon precursor. Examples of such precursors include, but are not limited to compounds having the formulae (X_mH_{3-m}Si)_zCH_{4-z}, or (X_mH_{3-m}Si)(CH₂)_n(SiX_mH_{3-m}), wherein X is a halogen, m has a value of between 1 and 3, and z has a value of between 1 and 3, and n has a value between 2 and 5.

[0022] Another aspect of the invention pertains to method of depositing a film comprising Si_xO_y, the method comprising exposing a substrate surface to a first precursor and a co-reactant, the first precursor comprising disiloxane to provide a film comprising Si_xO_y, wherein the co-reactant comprises an oxygen-containing compound. In further embodiments, 20 the co-reactant comprises H₂O, H₂O₂, O₂ or O₃. In some embodiments, the film contains substantially no nitrogen. In one or more embodiments, Si_xO_y comprises SiO₂.

[0023] The deposition may take place at a substrate temperature in the range of about 50 to about 600 °C. In further embodiments, the temperature ranges from about 65 to about 250 °C. In some embodiments the substrate temperature may be from about 50, 60, 70, 80, 90, 25 or 100 to about 200, 225, 250, 275, 300, 325, 350, 375 or 400 °C.

[0024] Another aspect of the invention is a method of depositing a film comprising silicon and oxygen. The method comprises exposing a substrate surface to a first precursor comprising a compound having a structure represented by formula (I):



wherein each R is independently hydrogen, C1-C6 alkyl, or OR', wherein R' is C1-C6 alkyl or $(\text{CH}_2)_p\text{NH}_2$, wherein p has a value ranging from 1 to 6, with the proviso that at least one R group is $\text{O}(\text{CH}_2)_p\text{NH}_2$, to provide a film comprising silicon and oxygen. While not wishing to be bound to any particular theory, it is thought that the $-\text{NH}_2$ group may act as a catalyst during deposition. Accordingly, the compound is able to self-catalyze reaction. In some embodiments, it may be used with a co-reagent. That is, in some embodiments, the method further comprises contacting the substrate surface with a co-reagent comprising one or more of H_2O , H_2O_2 , O_2 , and O_3 . In further embodiments, the co-reagent comprises H_2O , and/or O_2 , and particularly O_2 . In one or more embodiments, the deposited film comprises SiO_2 .

[0025] The deposition may take place at a substrate temperature in the range of about 50 to about 600 °C. In further embodiments, the temperature ranges from about 65 to about 250 °C. In some embodiments the substrate temperature may be from about 50, 60, 70, 80, 90, or 100 to about 200, 225, 250, 275, 300, 325, 350, 375 or 400 °C. In a further embodiment, the temperature ranges from about 120 to about 200 °C.

[0026] Carbon doping also be incorporated into the films in one or more embodiments. One way of achieving this is through reaction with a disiloxane derivative, wherein one or more of the hydrogen atoms is replaced with a carbon containing group. Such examples include C1-C6 alkyl, and in further embodiments, ethyl or methyl. Another way of achieving carbon doping is to further use a carbon precursor. Examples of such precursors include, but are not limited to compounds having the formulae $(\text{X}_m\text{H}_{3-m}\text{Si})_z\text{CH}_{4-z}$, or $(\text{X}_m\text{H}_{3-m}\text{Si})(\text{CH}_2)_n(\text{SiX}_m\text{H}_{3-m})$, wherein X is a halogen, m has a value of between 1 and 3, and z has a value of between 1 and 3, and n has a value between 2 and 5.

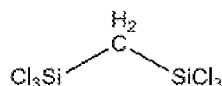
[0027] An exemplary embodiment of the invention pertains to method of depositing a film comprising Si_xO_y , the method comprising exposing a substrate surface to a first precursor and a co-reactant, the first precursor comprising disiloxane to provide a film comprising Si_xO_y , wherein the co-reactant contains a silicon-halide bond. In one or more embodiments, Si_xO_y comprises SiO_2 .

[0028] In one or more embodiments, the co-reactant comprises $\text{SiX}_m\text{H}_{4-m}$, wherein X is a halogen, and m has a value between 2 and 4. In further embodiments, X is selected from Cl, Br and I. In even further embodiments, X is Cl. Specific examples of suitable co-reactants include, but are not limited to, dichlorosilane, tetrachlorosilane, and diiodosilane. While not

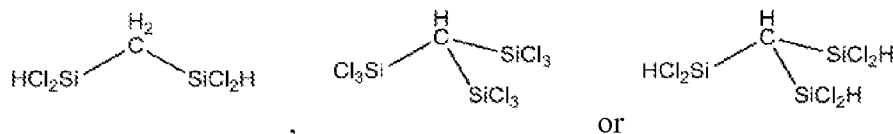
wishing to be bound by any particular theory, it is thought that at least two halides are required for continued film deposition. That is, upon reaction of the co-reactant with the film surface, one halide will be reacted. The other halide will allow for subsequent reactions. In some embodiments, the co-reactant comprises $X_zH_{3-z}Si-SiX_zH_{3-z}$, wherein X is a halogen, and z has a value between 1 and 3. In further embodiments, X is selected from Cl, Br and I. In even further embodiments, X is Cl. Specific examples of suitable co-reactants include, but are not limited to, hexachlorodisilane.

[0029] Additional compounds which can be used as a carbon source include those with formula $(X_mH_{3-m}Si)_zCH_{4-z}$, or $(X_mH_{3-m}Si)(CH_2)_n(SiX_mH_{3-m})$, wherein X is a halogen, m has a value of between 1 and 3, and z has a value of between 1 and 3, and n has a value between 2 and 5. In one or more embodiments, a film comprising SiOC is provided.

[0030] In some embodiments, the first precursor has a formula $(X_yH_{3-y}Si)_zCH_{4-z}$. In one or more embodiments, each X is independently selected from Cl, Br and I. In further embodiments, at least one of the X groups is Cl. In even further embodiments, all X groups are Cl. Such a compound is known as bis(trichlorosilyl)methane, hexachlorodisilylmethylene, 1,1'-methylenebis(1,1,1-trichlorosilane), or methylenebis(trichlorosilane), and has a structure represented by:



Other examples of suitable precursors include, but are not limited to those having a structure represented by:



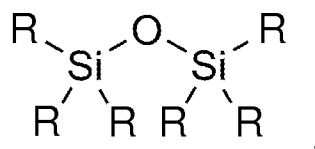
[0031] In other embodiments, the compound has a formula $(X_yH_{3-y}Si)(CH_2)_n(SiX_yH_{3-y})$. In further embodiments, n has a value of 2 or 3, or in even further embodiments, 2. Compounds of this formula may be used to further increase the carbon content, as the starting C:Si ratio will be higher. In one or more embodiments, each X is independently selected from

Cl, Br and I. In further embodiments, at least one of the X groups is Cl. In even further embodiments, all X groups are Cl.

[0032] In some embodiments, a catalyst may be utilized to facilitate the deposition process. The catalyst comprises a neutral two electron donor base. In one or more
5 embodiments, the catalyst comprises an amine. In further embodiments, the catalyst comprises a tertiary amine. In further embodiments, the catalyst comprises pyridine. In other embodiments, the catalyst comprises NH₃. In embodiments relating to SiOC depositions at a temperature greater than 100 °C, a tertiary amine with a vapor pressure lower than pyridine (which is less than about 20 torr at 20 °C) can be used.

[0033] The deposition may take place at a substrate temperature in the range of about 50 to about 600 °C. In further embodiments, the temperature ranges from about 65 to about 250 °C. In some embodiments the substrate temperature may be from about 50, 60, 70, 80, 90,
10 or 100 to about 200, 225, 250, 275, 300, 325, 350, 375 or 400 °C.

[0034] Yet another aspect of the invention pertains to a method of depositing a film
15 comprising SiOC, the method comprising exposing a substrate surface to a first precursor and a co-reactant, the first precursor comprising a compound having a structure represented by formula (I):



wherein each R is independently hydrogen, C_nH_{2n+2} or OR', wherein R' is C_nH_{2n+2} and n has a
20 value of 1 to 5, to provide a film comprising SiOC. OR' is an alkoxy group, which in some embodiments can comprise methoxy or ethoxy. In such examples, the precursor may contribute more oxygen into the film.

[0035] In some embodiments, all of the R groups are hydrogen, which provides disiloxane. In such embodiments, the co-reactant is a carbon source, so that the resulting film
25 may comprise SiOC. In one or more embodiments, the carbon precursor is any precursor known in the art to contribute carbon. Examples of suitable co-reactants comprising carbon include, but are not limited to ethylene, acetylene, carbosilanes, etc. The carbon precursor may be plasma or non-plasma.

[0036] In some embodiments, the co-reagent comprises a compound containing carbon and at least two hydroxyl groups. Such co-reactants can act as a source of carbon and oxygen. In further embodiments, the co-reagent comprises a diol. In even further embodiments, diols may be used which contain carbon. In such embodiments, carbon incorporated into the film may come from both the first and co-reagents. Suitable co-reagents, include, but are not limited to, ethylene glycol, propylene glycol and butane-1,4-diol. In further embodiments, the diol comprises ethylene glycol. While not wishing to be bound to any particular theory, it is thought that at least two hydroxyl groups are necessary in order to allow for subsequent deposition cycles. That is, one OH group is used to deposit the co-reagent, and then the second may be used for the next cycle to react with the Si-Cl in the first precursor.

[0037] In embodiments where the compound of formula (I) contains carbon (*i.e.*, at least one of the R groups contains a carbon atom), it can act as both a carbon source and a silicon source. In some embodiments, the R group is C1-C6 alkyl. In further embodiments, the R group is methyl. Where the compound of formula (I) contains carbon the co-reagent may be an oxygen source. In some embodiments, the co-reagent may comprise water. In embodiments where the co-reagent comprises water, the resulting film will still contain carbon from the first precursor.

[0038] Again, the co-reagent may comprise a compound containing carbon and at least two hydroxyl groups. In further embodiments, the co-reagent comprises a diol. In even further embodiments, diols may be used which contain carbon. In such embodiments, carbon incorporated into the film may come from both the first and co-reagents. Suitable co-reagents, include, but are not limited to, ethylene glycol, propylene glycol and butane-1,4-diol. In further embodiments, the diol comprises ethylene glycol. In some embodiments, the co-reactant comprises a triol. While not wishing to be bound to any particular theory, it is thought that at least two hydroxyl groups are necessary in order to allow for subsequent deposition cycles. That is, one OH group is used to deposit the co-reagent, and then the second may be used for the next cycle to react with the Si-Cl in the first precursor.

[0039] In embodiments, where the compound of formula (I) comprises carbon, the co-reagent may not comprise carbon. That is, in some embodiments, at least one of the R groups is not hydrogen, and the co-reagent comprising one or more of H₂O, H₂O₂, O₂, and O₃. In further embodiments, the co-reagent comprises H₂O, and/or O₂, and particularly O₂.

[0040] Various disiloxane/disiloxane derivatives and co-reagents can be selected to tune the amount of carbon in the deposited film. The higher the carbon:silicon ratio of the precursors, the higher the ratio will be in the resulting SiOC film. Thus, for example, longer carbon chains may be selected where a higher amount of carbon is desired.

5 [0041] The deposition may take place at a substrate temperature in the range of about 50 to about 600 °C. In further embodiments, the temperature ranges from about 65 to about 250 °C. In some embodiments the substrate temperature may be from about 50, 60, 70, 80, 90, or 100 to about 200, 225, 250, 275, 300, 325, 350, 375 or 400 °C.

[0042] One or more embodiments of the invention may have a nucleation delay.
10 Accordingly, one aspect of the invention pertains to activation of the substrate surface to a plasma. That is, in some embodiments, the methods described further comprise exposing the substrate surface to a plasma. It is also thought that this activation procedure will help to increase growth rate at higher temperatures. While not wishing to be bound to any particular theories, it is thought that at higher temperatures, the disiloxane or disiloxane-based molecules
15 will not adhere to the substrate surface as easily. As such, the plasma is thought to help the compound adhere to the surface. In one or more embodiments, the plasma comprises an oxygen plasma. In some embodiments, the substrate has a temperature of above 200, 250 or 300 °C while being exposed to the plasma.

[0043] Conventionally, metal oxides may be deposited using water as a co-reactant.
20 Problems can occur using water, as water has a high "sticking coefficient," due to its hydrogen bonding, sticking to the chamber lines, wall, etc. Thus, as water is flowed through a chamber, it can It is thought that disiloxane will have a much lower sticking coefficient, as it is a linear molecule with no hydrogen bonding.

[0044] Accordingly, another aspect of the invention pertains to a method of depositing
25 a film comprising a metal oxide. The method comprises exposing a substrate surface to a metal precursor and disiloxane to provide a film comprising a metal oxide. It is thought that the disiloxane will react with metal halides as water does. The byproduct produced from such a reaction would be could be a mono halo silane precursor. Such a byproduct is expected to be volatile, allowing for easy removal.

30 [0045] In one or more embodiments, the metal comprises a transition metal. In some embodiments, the metal precursor comprises a metal halide. Any currently used transition

metal halides that are used with water are suitable for use with disiloxane. Examples include, but are not limited to halides of W, Zr, Hf and Ti.

[0046] In some embodiments, the film comprises tungsten oxide. A suitable metal precursor for this film comprises WCl_5 . In other embodiments, the film comprises zirconium oxide. A suitable metal precursor for this film comprises $ZrCl_5$. In one or more embodiments, the film comprises hafnium oxide. A suitable metal precursor for this film comprises $HfCl_2$. In some embodiments, the film comprises titanium oxide. A suitable metal precursor for this film comprises $TiCl_4$.

[0047] The deposition may take place at a substrate temperature in the range of about 50 to about 600 °C. In further embodiments, the temperature ranges from about 65 to about 250 °C. In some embodiments the substrate temperature may be from about 50, 60, 70, 80, 90, or 100 to about 200, 225, 250, 275, 300, 325, 350, 375 or 400 °C.

[0048] In one or more embodiments of any of the above-described reactions, the reaction conditions for the ALD reaction will be selected based on the properties of the film precursors and substrate surface. The deposition may be carried out at atmospheric pressure, but may also be carried out at reduced pressure. The vapor pressure of the reagents should be low enough to be practical in such applications. The substrate temperature should be low enough to keep the bonds of the substrate surface intact and to prevent thermal decomposition of gaseous reactants. However, the substrate temperature should also be high enough to keep the film precursors in the gaseous phase and to provide sufficient energy for surface reactions. The specific temperature depends on the specific substrate, film precursors, and pressure. The properties of the specific substrate, film precursors, etc. may be evaluated using methods known in the art, allowing selection of appropriate temperature and pressure for the reaction. In one or more embodiments, the deposition is carried out at a temperature less than about 600, 550, 500, 450, 400, 350, 300, 250, 200, 150, 125, or 100 °C, and greater than 23 °C, 50 or 75 °C.

[0049] In one or more embodiments, the films are deposited using an ALD or CVD process. In embodiments relating to a CVD process, the substrate may be exposed to more than one precursor continuously simultaneously, or substantially simultaneously, as appropriate. As used herein, the term "substantially simultaneously" means that a majority of the flow of one component overlaps with the flow of another, although there may be some time

where they are not co-flowed. In other embodiments, films are deposited using an atomic layer deposition (ALD) process. Therefore, in one embodiment, contacting the substrate surface with two or more precursors occurs sequentially or substantially sequentially. As used herein, "substantially sequentially" means that a majority of the flow of one component does not
5 coincide with the flow of another, although there may be some overlap.

[0050] In some embodiments of the processes described herein, one or more layers may be formed during a plasma enhanced atomic layer deposition (PEALD) process. In some processes, the use of plasma provides sufficient energy to promote a species into the excited state where surface reactions become favorable and likely. Introducing the plasma into the
10 process can be continuous or pulsed. In some embodiments, sequential pulses of precursors (or reactive gases) and plasma are used to process a layer. In some embodiments, the reagents may be ionized either locally (i.e., within the processing area) or remotely (i.e., outside the processing area). In some embodiments, remote ionization can occur upstream of the deposition chamber such that ions or other energetic or light emitting species are not in direct
15 contact with the depositing film. In some PEALD processes, the plasma is generated external from the processing chamber, such as by a remote plasma generator system. The plasma may be generated via any suitable plasma generation process or technique known to those skilled in the art. For example, plasma may be generated by one or more of a microwave (MW) frequency generator or a radio frequency (RF) generator. The frequency of the plasma may be
20 tuned depending on the specific reactive species being used. Suitable frequencies include, but are not limited to, 2 MHz, 13.56 MHz, 40 MHz, 60 MHz and 100 MHz. Although plasmas may be used during the deposition processes disclosed herein, it should be noted that plasmas are not necessarily required.

[0051] According to one or more embodiments, the substrate is subjected to processing
25 prior to and/or after forming the layer. This processing can be performed in the same chamber or in one or more separate processing chambers. In some embodiments, the substrate is moved from the first chamber to a separate, second chamber for further processing. The substrate can be moved directly from the first chamber to the separate processing chamber, or it can be moved from the first chamber to one or more transfer chambers, and then moved to the desired
30 separate processing chamber. Accordingly, the processing apparatus may comprise multiple chambers in communication with a transfer station. An apparatus of this sort may be referred to as a "cluster tool" or "clustered system", and the like.

[0052] Generally, a cluster tool is a modular system comprising multiple chambers which perform various functions including substrate center-finding and orientation, degassing, annealing, deposition and/or etching. According to one or more embodiments, a cluster tool includes at least a first chamber and a central transfer chamber. The central transfer chamber may house a robot that can shuttle substrates between and among processing chambers and load lock chambers. The transfer chamber is typically maintained at a vacuum condition and provides an intermediate stage for shuttling substrates from one chamber to another and/or to a load lock chamber positioned at a front end of the cluster tool. Two well-known cluster tools which may be adapted for the present invention are the Centura® and the Endura®, both available from Applied Materials, Inc., of Santa Clara, Calif. The details of one such staged-vacuum substrate processing apparatus is disclosed in U.S. Pat. No. 5,186,718, entitled "Staged-Vacuum Wafer Processing Apparatus and Method," Tepman et al., issued on Feb. 16, 1993. However, the exact arrangement and combination of chambers may be altered for purposes of performing specific steps of a process as described herein. Other processing chambers which may be used include, but are not limited to, cyclical layer deposition (CLD), atomic layer deposition (ALD), chemical vapor deposition (CVD), physical vapor deposition (PVD), etch, pre-clean, chemical clean, thermal treatment such as RTP, plasma nitridation, degas, orientation, hydroxylation and other substrate processes. By carrying out processes in a chamber on a cluster tool, surface contamination of the substrate with atmospheric impurities can be avoided without oxidation prior to depositing a subsequent film.

[0053] According to one or more embodiments, the substrate is continuously under vacuum or "load lock" conditions, and is not exposed to ambient air when being moved from one chamber to the next. The transfer chambers are thus under vacuum and are "pumped down" under vacuum pressure. Inert gases may be present in the processing chambers or the transfer chambers. In some embodiments, an inert gas is used as a purge gas to remove some or all of the reactants after forming the layer on the surface of the substrate. According to one or more embodiments, a purge gas is injected at the exit of the deposition chamber to prevent reactants from moving from the deposition chamber to the transfer chamber and/or additional processing chamber. Thus, the flow of inert gas forms a curtain at the exit of the chamber.

[0054] The substrate can be processed in single substrate deposition chambers, where a single substrate is loaded, processed and unloaded before another substrate is processed. The substrate can also be processed in a continuous manner, like a conveyer system, in which

multiple substrate are individually loaded into a first part of the chamber, move through the chamber and are unloaded from a second part of the chamber. The shape of the chamber and associated conveyer system can form a straight path or curved path. Additionally, the processing chamber may be a carousel in which multiple substrates are moved about a central axis and are exposed to deposition, etch, annealing, cleaning, etc. processes throughout the carousel path.

[0055] During processing, the substrate can be heated or cooled. Such heating or cooling can be accomplished by any suitable means including, but not limited to, changing the temperature of the substrate support and flowing heated or cooled gases to the substrate surface. In some embodiments, the substrate support includes a heater/cooler which can be controlled to change the substrate temperature conductively. In one or more embodiments, the gases (either reactive gases or inert gases) being employed are heated or cooled to locally change the substrate temperature. In some embodiments, a heater/cooler is positioned within the chamber adjacent the substrate surface to convectively change the substrate temperature.

[0056] The substrate can also be stationary or rotated during processing. A rotating substrate can be rotated continuously or in discrete steps. For example, a substrate may be rotated throughout the entire process, or the substrate can be rotated by a small amount between exposures to different reactive or purge gases. Rotating the substrate during processing (either continuously or in steps) may help produce a more uniform deposition or etch by minimizing the effect of, for example, local variability in gas flow geometries.

[0057] In atomic layer deposition type chambers, the substrate can be exposed to the first and co-reagents either spatially or temporally separated processes. Temporal ALD is a traditional process in which the first precursor flows into the chamber to react with the surface. The first precursor is purged from the chamber before flowing the co-reagent. In spatial ALD, both the first and co-reagents are simultaneously flowed to the chamber but are separated spatially so that there is a region between the flows that prevents mixing of the precursors. In spatial ALD, the substrate must be moved relative to the gas distribution plate, or vice-versa.

[0058] The substrate and chamber may be exposed to a purge step after stopping the flow of the disiloxane, precursor, co-reagent, etc. In one or more embodiments of any of the aspects described herein, a purge gas may be flowed after any of the precursors is flowed/exposed to a substrate surface. A purge gas may be administered into the processing

chamber with a flow rate within a range from about 10 sccm to about 2,000 sccm, for example, from about 50 sccm to about 1,000 sccm, and in a specific example, from about 100 sccm to about 500 sccm, for example, about 200 sccm. The purge step removes any excess precursor, byproducts and other contaminants within the processing chamber. The purge step may be conducted for a time period within a range from about 0.1 seconds to about 8 seconds, for example, from about 1 second to about 5 seconds, and in a specific example, from about 4 seconds. The carrier gas, the purge gas, the deposition gas, or other process gas may contain nitrogen, hydrogen, argon, neon, helium, or combinations thereof. In one example, the carrier gas comprises nitrogen.

[0059] Reference throughout this specification to "one embodiment," "certain embodiments," "one or more embodiments" or "an embodiment" means that a particular feature, structure, material, or characteristic described in connection with the embodiment is included in at least one embodiment of the invention. Thus, the appearances of the phrases such as "in one or more embodiments," "in certain embodiments," "in one embodiment" or "in an embodiment" in various places throughout this specification are not necessarily referring to the same embodiment of the invention. Furthermore, the particular features, structures, materials, or characteristics may be combined in any suitable manner in one or more embodiments.

[0060] Although the invention herein has been described with reference to particular embodiments, it is to be understood that these embodiments are merely illustrative of the principles and applications of the present invention. It will be apparent to those skilled in the art that various modifications and variations can be made to the method and apparatus of the present invention without departing from the spirit and scope of the invention. Thus, it is intended that the present invention include modifications and variations that are within the scope of the appended claims and their equivalents.

EXAMPLES

Prophetic Example 1 – Silicon Oxide Deposition Using Disiloxane and Oxygen Plasma

[0061] A substrate surface comprising –OH functional groups is provided in a deposition chamber. Disiloxane is then flowed into the chamber, and the substrate surface is

exposed to the disiloxane. The disiloxane reacts with the –OH functionality so that SiH_3 is deposited onto the surface, with silanol as a byproduct. The substrate is then exposed to an O_2 plasma, thereby providing a layer of Si-O, as well as –OH functionality at the substrate surface again.

- 5 [0062] Next, disiloxane is again flowed into the chamber, which again reacts with the –OH functionality so that another layer of SiH_3 is deposited onto the surface, with silanol as a byproduct. The substrate is then exposed to an O_2 plasma, thereby providing a layer of Si-O, as well as –OH functionality at the substrate surface again. The process is repeated until the desired film thickness is achieved.

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Example 2 - Thermal Stability of Disiloxane

[0063] The thermal Stability of disiloxane was tested on $1000\text{\AA}$ of silicon dioxide (SiO_2 1K), silicon(100) with the native oxide (Si(100)-native), and silicon hydrogen terminated (Si(H-term)). The parameters for testing were as follows in Table 1:

15

Table 1:

<u>Parameter</u>	<u>Value</u>
Disiloxane flow rate	200 sccm
Line 1 nitrogen flow rate	200 sccm
Line 2 nitrogen flow rate	200 sccm
Substrate temperatures	150, 200, 250, 300, 350, 400 °C
Total flow time	60 s
Chamber Pressure	1.5 Torr

- [0064] To assess the thermal stability of disiloxane on various surfaces, disiloxane was flowed over SiO_2 1K, Si(100)-native, and Si(H-term) substrates at the flow rates and surface temperatures specified above. According to visual observation and ellipsometry measurements, no self-decomposition occurred on any of the surfaces up to 400 °C. These results indicate that disiloxane possesses sufficient thermal stability to function as an ALD precursor.

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Example 3 – SiO_2 Deposition Using Disiloxane and Oxygen Gas

[0065] Thin films of SiO₂ were deposited by ALD using disiloxane and oxygen gas at substrate temperatures of 100, 150, and 200 °C. The parameters for deposition were as follows in Table 2:

Table 2:

Parameter	Value
Disiloxane flow rate	200 sccm
Disiloxane pulse length	0.3 s
Nitrogen Purge Line 1 flow rate	200 sccm
Nitrogen Purge Line 2 flow rate	200 sccm
Nitrogen purge length between precursors	4.0 s
Oxygen flow rate	200 sccm
Oxygen pulse length	0.5 s
Substrates	SiO ₂ 1K and Si(100)-native
Substrate temperatures	100, 150, 200 °C
Number of cycles	300
Chamber Pressure	1.5 Torr

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[0066] The growth rates and refractive indices were determined using ellipsometry. In order of increasing deposition temperature (100, 150, 200 °C), the growth rates observed on Si(100)-native and SiO₂ 1K were 1.09, 0.95, and 0.72 Å/cycle and 0.81, 0.73, and 0.42 Å/cycle. The calculated refractive indices for films deposited on Si(100)-native and SiO₂ 1K at 100 °C were 1.35 and 1.46, respectively. Both values are similar to what is expected for SiO₂ (refractive index ~1.46).

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Example 4 – Growth Per Cycle and Refractive Indices

[0067] SiO₂ films were deposited using disiloxane and O₂. The pulse length of disiloxane was 0.3 seconds, and it was flowed at a rate of 200 sccm. This was followed by a purge of N₂ for 4.0 seconds at 200 sccm. Next, O₂ was flowed for 0.5 seconds at a rate of 200 sccm. The chamber was again purged with N₂ for 4.0 seconds at 200 sccm. The chamber had a pressure of 1.5 Torr. The film was deposited on SiO₂ 1K at temperatures ranging from about 75 to 130 °C, and on Si(native) at temperatures ranging from about 75 to 100 °C. A graph of the growth per cycle (GPC) and refractive indices (RI) versus temperature is shown in FIGURE 2. The plot was generated with sub-saturative conditions. As seen in the figure, the

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RI for the film on SiO₂ 1K was ~1.46 and on Si(native) was 1.33-1.35. A process window exists from ~75-130 °C on SiO₂ 1K and ~75-100 °C on Si(native). The figure also shows that for at least some of the films, growth rate decreases with an increase in temperature. It is thought that this is due to precursor thermal desorption.

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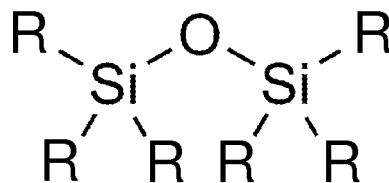
Example 5 - Saturation

[0068] SiO₂ films were deposited using disiloxane and O₂. The pulse length of disiloxane was varied, and it was flowed at a rate of 200 sccm. This was followed by a purge of N₂ for 4.0 seconds at 200 sccm. Next, O₂ was flowed for 0.5 seconds at a rate of 200 sccm.

- 10 The chamber was again purged with N₂ for 4.0 seconds at 200 sccm. The chamber had a pressure of 1.5 Torr. The film was deposited on SiO₂ 1K and on Si(native). A graph of the growth per cycle (GPC) and refractive indices (RI) versus disiloxane pulse length is shown in FIGURE 3. As shown in the figure, saturation starts to occur when the disiloxane pulse lengths is greater than 2 seconds. With saturative doses of disiloxane, the refractive indices for
- 15 SiO₂ 1K and Si(native) are 1.43 and 1.40, respectively. From the data, it appears that disiloxane saturation occurs at ~2s on SiO₂ 1K and Si(native) with growth rates of 2.09 Å/cycle (RI=1.43) and 2.19 Å/cycle (RI=1.40)

What is claimed is:

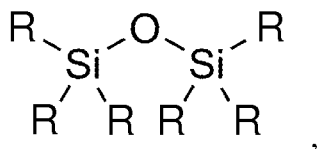
1. A method of depositing a film, the method comprising exposing a substrate surface to a first precursor and a co-reactant, the first precursor comprising disiloxane to provide a film comprising Si_xO_y .
- 5 2. The method of claim 1, wherein the co-reactant comprises an oxygen source, and the deposited film comprises Si_xO_y .
3. The method of claim 1 or 2, wherein x has a value of 1 to 2 and y has a value of 1 to 2.
4. The method of any of claims 1-3, wherein the substrate surface is exposed to the first precursor and the co-reactant simultaneously.
- 10 5. The method of any of claims 1-4, wherein the co-reactant comprises $\text{SiX}_m\text{H}_{4-m}$, wherein X is a halogen selected from Cl, Br and I, and m has a value between 2 and 4, and the deposited film comprises Si_xO_y .
6. The method of any of claims 1-5, wherein the co-reactant comprises $\text{X}_z\text{H}_{3-z}\text{-Si-SiX}_z\text{H}_{3-z}$, wherein X is a halogen selected from Cl, Br and I, and z has a value between 1 and 3, and the deposited film comprises Si_xO_y .
- 15 7. The method of any of claims 1-6, wherein the co-reactant comprises a metal precursor, and the deposited film comprises a metal oxide.
8. A method of depositing a film comprising SiOC , the method comprising exposing a substrate surface to a first precursor and a co-reactant, the first precursor comprising a compound having a structure represented by:
- 20



wherein each R is independently hydrogen, $\text{C}_n\text{H}_{2n+2}$ or OR' , wherein R' is $\text{C}_n\text{H}_{2n+2}$ and n has a value of 1 to 5, to provide a film comprising SiOC .

9. The method of claim 8, wherein each R group is hydrogen.
- 25 10. The method of claim 8 or 9, wherein the co-reactant comprises acetylene, ethylene or a carbosilane.
11. The method of any of claims 8-10, wherein the co-reactant comprises $\text{SiX}_m\text{H}_{4-m}$, wherein X is a halogen selected from Cl, Br and I, and m has a value between 2 and 4.

12. The method of any of claims 8-11, wherein the co-reactant comprises $X_zH_{3-z}Si-SiX_zH_{3-z}$, wherein X is a halogen selected from Cl, Br and I, and z has a value between 1 and 3.
13. The method of any of claims 8-12, wherein the co-reactant comprises an organic hydroxide containing at least two hydroxide groups.
14. The method of any of claims 8-13, wherein at least one of the R groups is not hydrogen, and the co-reactant is selected from the group consisting of H_2O , H_2O_2 , O_2 , or O_3 .
15. A method of depositing a film comprising silicon and oxygen, the method comprising exposing a substrate surface to a first precursor comprising a compound having a structure represented by formula (I):



wherein each R is independently hydrogen, C1-C6 alkyl, or OR' , wherein R' is C1-C6 alkyl or $(CH_2)_pNH_2$, wherein p has a value ranging from 1 to 6, with the proviso that at least one R group is $O(CH_2)_pNH_2$, to provide a film comprising silicon and oxygen.

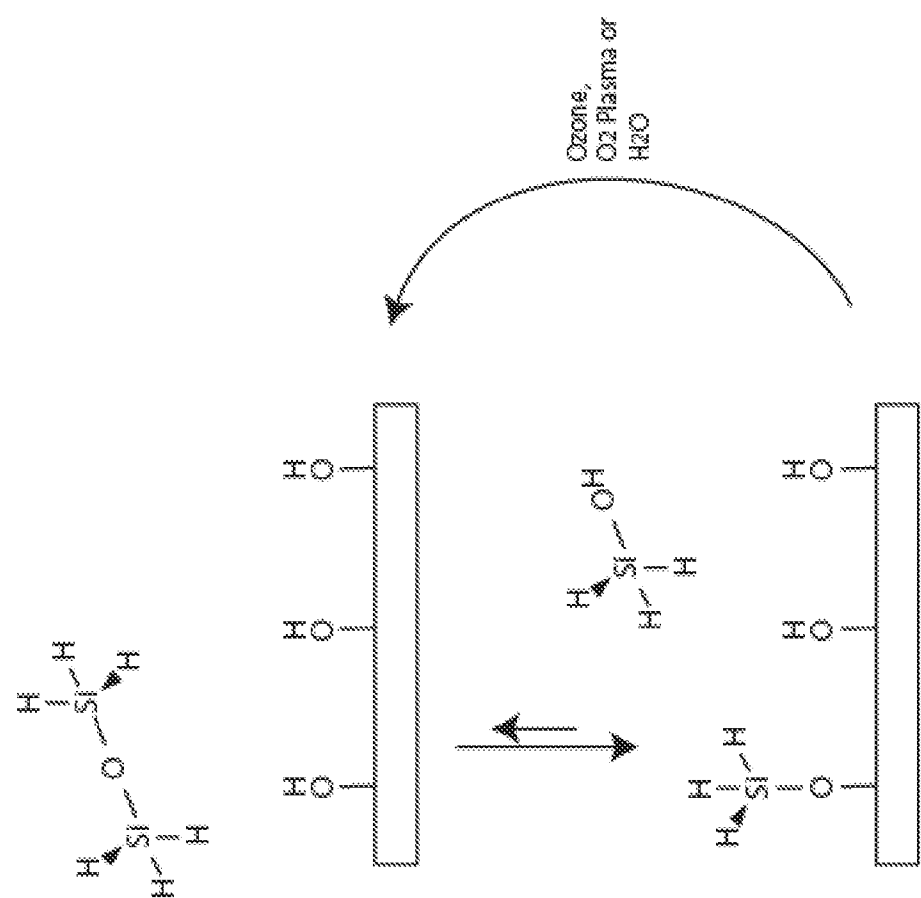


FIGURE 1

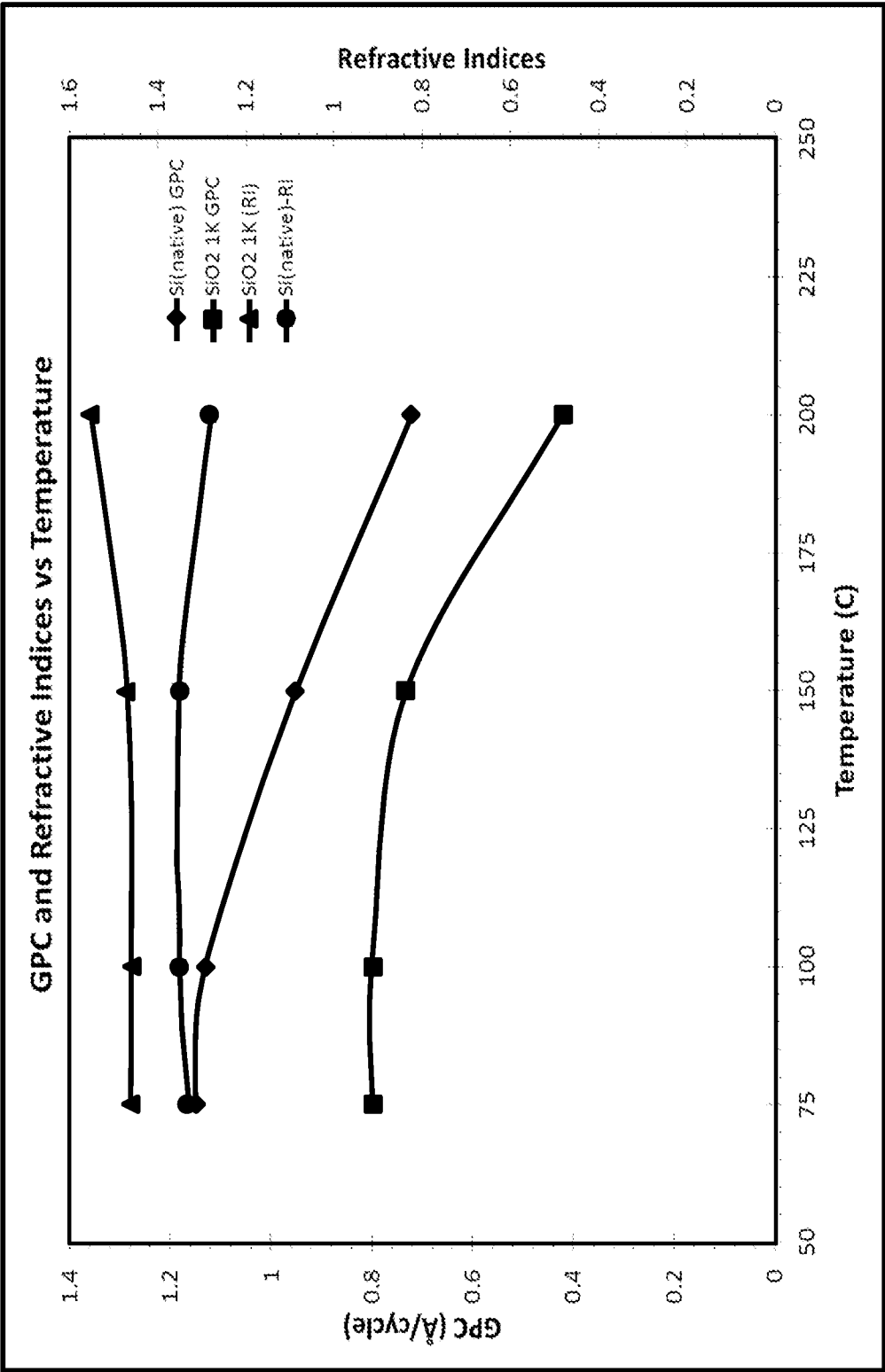


FIGURE 2

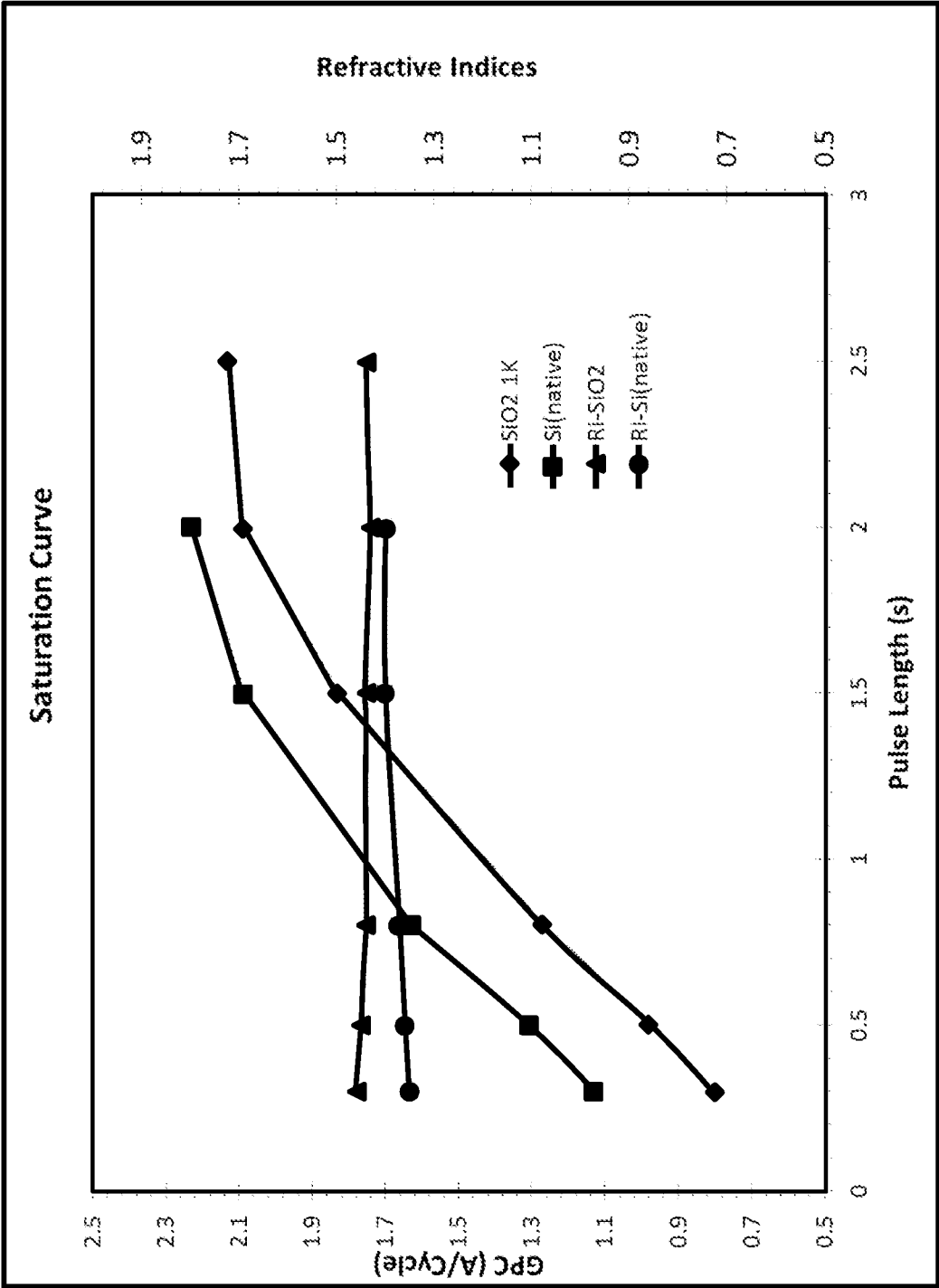


FIGURE 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/027899**A. CLASSIFICATION OF SUBJECT MATTER****H01L 21/205(2006.01)i**

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

B. FIELDS SEARCHEDMinimum documentation searched (classification system followed by classification symbols)
H01L 21/205; B32B 7/02; H01L 21/31; B32B 1/00; C08G 77/06; C08K 3/10; C23C 16/00Documentation 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 modelsElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & keywords: silicon, oxycarbide, co-reactant, disiloxane, hydrogen**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009-0075490 A1 (CHRISTIAN DUSSARRAT) 19 March 2009 See abstract, paragraphs [0039]-[0045] and claim 1.	1-3
X	US 2003-0064154 A1 (RAVI K. LAXMAN et al.) 03 April 2003 See abstract, paragraphs [0034]-[0037], [0091]-[0096], [0116]-[0118] and claims 1, 11-13, 25.	15
Y		8-10
Y	US 2001-0055672 A1 (MICHAEL A. TODD) 27 December 2001 See abstract, paragraph [0092] and claims 1, 10-11.	8-10
A	US 5162480 A (CURTIS L. SCHILLING, JR. et al.) 10 November 1992 See abstract, column 4, line 19 - column 6, line 61 and claim 14.	1-3, 8-10, 15
A	US 5023295 A (ERHARD BOSCH et al.) 11 June 1991 See abstract, column 3, line 7 - column 8, line 44 and claims 1, 7-8.	1-3, 8-10, 15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"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)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search
23 July 2014 (23.07.2014)Date of mailing of the international search report
24 July 2014 (24.07.2014)Name and mailing address of the ISA/KR
International Application Division
Korean Intellectual Property Office
189 Cheongsu-ro, Seo-gu, Daejeon Metropolitan City, 302-701,
Republic of Korea
Facsimile No. +82-42-472-7140Authorized officer
CHOI, Sang Won

Telephone No. +82-42-481-8291



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2014/027899**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-7, 11-14
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2014/027899

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009-0075490 A1	19/03/2009	CN 101889331 A EP 2193541 A1 JP 2010-539730 A KR 10-2010-0061733 A TW 200931520 A WO 2009-039251 A1	17/11/2010 09/06/2010 16/12/2010 08/06/2010 16/07/2009 26/03/2009
US 2003-0064154 A1	03/04/2003	AU 2002-323040 A1 AU 2002-323040 A8 WO 03-015129 A2 WO 2003-015129 A3	24/02/2003 09/11/2006 20/02/2003 14/09/2006
US 2001-0055672 A1	27/12/2001	EP 1123991 A2 EP 1123991 A3 JP 2001-298024 A US 2004-0161617 A1 US 2007-0032676 A1 US 6733830 B2 US 7144620 B2 US 7544827 B2	16/08/2001 13/11/2002 26/10/2001 19/08/2004 08/02/2007 11/05/2004 05/12/2006 09/06/2009
US 5162480 A	10/11/1992	AT 138953 T CA 2057660 A1 DE 69120040 D1 DE 69120040 T2 EP 0490401 A2 EP 0490401 B1 JP 04-353522 A JP 10-081750 A JP 2672225 B2 JP 3103826 B2 KR 10-0133943 B1 US 5275980 A US 5354830 A	15/06/1996 15/06/1992 11/07/1996 24/10/1996 17/06/1992 05/06/1996 08/12/1992 31/03/1998 05/11/1997 30/10/2000 20/04/1998 04/01/1994 11/10/1994
US 5023295 A	11/06/1991	DE 3831479 A1 EP 0359251 A3 EP 0359251 B1 JP 02-115268 A JP 06-058763 B2 JP 1927256 C	29/03/1990 06/02/1991 24/11/1993 27/04/1990 03/08/1994 25/04/1995