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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
28 August 2014 (28.08.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/130668 A1

(51) International Patent Classification:
H01L 21/205 (2006.01)

(21) International Application Number:
PCT/US2014/017391

(22) International Filing Date:
20 February 2014 (20.02.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/767,860 22 February 2013 (22.02.2013) US

(71) Applicant *(for all designated States except US)*: **APPLIED MATERIALS, INC.** [US/US]; 3050 Bowers Avenue, Santa Clara, California 95054 (US).

(72) Inventors; and
(71) Applicants *(for US only)*: **THOMPSON, David** [CA/US]; 2193 Bentley Ridge Drive, San Jose, California 95138 (US). **ANTHIS, Jeffrey W.** [US/US]; 1008 Empey Way, San Jose, California 95128 (US).

(74) Agent: **CRISTALDI, Michelle, A.**; Servilla Whitney LLC, 33 Wood Avenue South, Second Floor, Suite 210, Iselin, New Jersey 08830 (US).

(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, LT, 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, 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).

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

(54) **Title**: CATALYTIC ATOMIC LAYER DEPOSITION OF FILMS COMPRISING SIOC

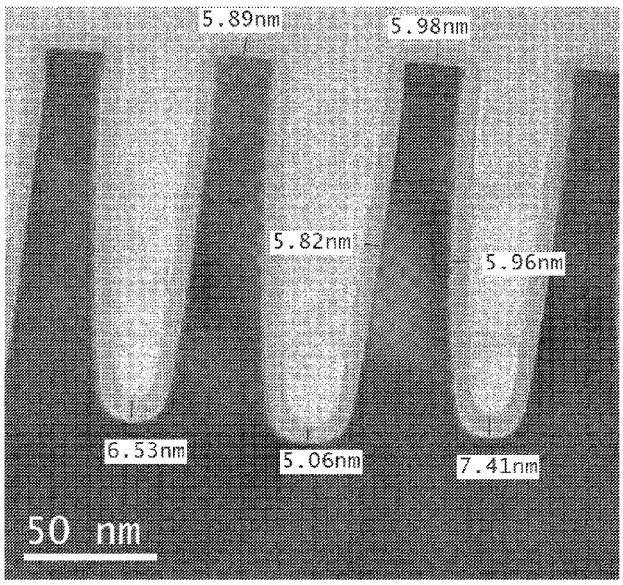


FIGURE 4

(57) **Abstract**: Provided are methods of for deposition of SiOC. Certain methods involve exposing a substrate surface to a first and second precursor in the presence of a catalyst comprising a neutral two electron donor base. The first precursor has formula $(X_yH_{3-y}Si)_zCH_{4-z}$ or $(X_yH_{3-y}Si)(CH_2)_n(SiX_yH_{3-y})$, wherein X is a halogen, y 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. The second precursor comprises water or a compound containing carbon and at least two hydroxyl groups. Certain other methods relate to exposing a substrate surface to a first and second precursor in the presence of a catalyst comprising a neutral two electron donor base, the first precursor comprising SiX_4 or $X_3Si\text{-}SiX_3$, wherein X is a halide, and the second precursor comprising carbon and at least two hydroxyl groups.

WO 2014/130668 A1

CATALYTIC ATOMIC LAYER DEPOSITION OF FILMS COMPRISING SiOC

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 SiOC 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 atomic layer deposition (ALD), which employs sequential, surface reactions to form layers of precise thickness. Most ALD processes are based on binary reaction sequences which deposit a binary compound film. Because the surface reactions are sequential, the two gas phase reactants are not in contact, and possible gas phase reactions that may form and deposit particles are limited.

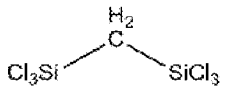
[0003] ALD has been used to deposit metals and metal compounds on substrate surfaces. Al_2O_3 deposition is an example of a typical ALD process illustrating the sequential and self-limiting reactions characteristic of ALD. Al_2O_3 ALD conventionally uses trimethylaluminum (TMA, often referred to as reaction "A" or the "A" precursor) and H_2O (often referred to as the "B" reaction or the "B" precursor). In step A of the binary reaction, hydroxyl surface species react with vapor phase TMA to produce surface-bound $AlOAl(CH_3)_2$ and CH_4 in the gas phase. This reaction is self-limited by the number of reactive sites on the surface. In step B of the binary reaction, $AlCH_3$ of the surface-bound compound reacts with vapor phase H_2O to produce AlOH bound to the surface and CH_4 in the gas phase. This reaction is self-limited by the finite number of available reactive sites on surface-bound $AlOAl(CH_3)_2$. Subsequent cycles of A and B, purging gas phase reaction products and unreacted vapor phase precursors between reactions and between reaction cycles, produces Al_2O_3 growth in an essentially linear fashion to obtain the desired film thickness.

[0004] In order to facilitate deposition, catalysts have been used during some ALD processes. The catalyst is used to activate a reaction between two or more species during the deposition process. One process involving catalytic ALD involves the deposition of SiO_2 using water and $SiCl_4$. However, new catalytic ALD methods for other films are desired.

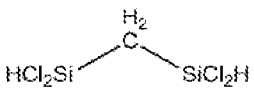
SUMMARY

[0005] One aspect of the invention relates to a method of depositing a film. The method comprises exposing a substrate surface to a first and second precursor in the presence of a catalyst comprising a neutral two electron donor base, the first precursor having a formula $(X_yH_{3-y}Si)_zCH_{4-z}$ or $(X_yH_{3-y}Si)(CH_2)_n(SiX_yH_{3-y})$, wherein X is a halogen, y 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, and the second precursor comprising water or a compound containing carbon and at least two hydroxyl groups. In one or more embodiments, each X is independently selected from Cl, Br and I.

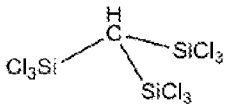
[0006] In some embodiments, the first precursor has a formula $(X_yH_{3-y}Si)_zCH_{4-z}$. In further embodiments, the first precursor has a structure represented by:

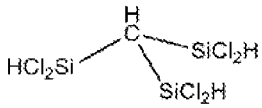


,



,





or .

In some embodiments, the first precursor comprises bis(trichlorosilyl)methane. In one or more embodiments, the first precursor 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.

[0007] In some embodiments, the catalyst comprises an amine. In one or more embodiments, the catalyst comprises pyridine or NH_3. In some embodiments, the second precursor comprises a diol. In one or more embodiments, the diol comprises ethylene glycol, propylene glycol and butane-1,4-diol. In some embodiments, a film comprising SiOC is provided.

[0008] Another aspect of the invention relates to a method of depositing a film, the method comprising exposing a substrate surface to a first and second precursor in the presence of a catalyst comprising a neutral two electron donor base, the first precursor comprising SiX_4 or $X_3Si\text{-}SiX_3$, wherein X is a halide, and the second precursor comprises a compound containing carbon and at least two hydroxyl groups to provide a film comprising SiOC. In one or more embodiments, X is selected from the group consisting of Cl, Br and I.

[0009] In some embodiments, the first precursor comprising SiX_4. In one or more embodiments, the catalyst comprises an amine. In some embodiments, the catalyst comprises pyridine or NH_3. In one or more embodiments, the second precursor is a diol. In some embodiments, the diol comprises ethylene glycol, propylene glycol and butane-1,4-diol.

[0010] A third aspect of the invention relates to a method of depositing a film, the method comprising exposing a substrate surface to a first and second precursor in the presence of a catalyst comprising an pyridine, the first precursor comprising bis(trichlorosilyl)methane and the second precursor comprising water.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] 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 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.

[0012] FIG. shows an exemplary pulse sequence according to one or more embodiments of the invention;

[0013] FIG. 2 shows a depth profile of the elemental content of a film deposited according to one or more embodiments of the invention;

[0014] FIG. 3 shows a transmission electron microscope image of a film deposited according to one or more embodiments of the invention over a photoresist substrate;

[0015] FIG 4 shows a transmission electron microscope image of a film deposited according to one or more embodiments of the invention over a silicon substrate; and

[0016] FIG 5 shows a transmission electron microscope image of a film deposited according to one or more embodiments of the invention over blanket Si(100).

DETAILED DESCRIPTION

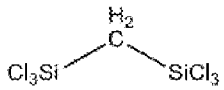
[0017] Before describing several exemplary embodiments of the invention, it is to be understood that the invention is not limited to the details of construction or process steps set forth in the following description. The invention is capable of other embodiments and of being practiced or being carried out in various ways. It is also to be understood that the complexes and ligands 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.

[0018] A "substrate" as used herein, 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.

[0019] It has been discovered that SiOC films can be deposited using certain silicon precursors which contain a halogen and a second precursor selected from water or a diol. Either the diol or silicon precursor may contain carbon, which ends up incorporated into the film. Such SiOC films can exhibit better dielectric constants than the conventional SiO_2 films. Specifically, the carbon content can lower the dielectric constant, which lowers leakage at a transistor level.

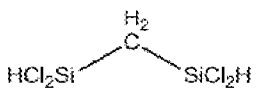
[0020] Accordingly, one aspect of the invention relates to method of depositing a film. The method comprises exposing a substrate surface to a first and second precursor in the presence of a catalyst comprising a neutral two electron donor base, the first precursor having a formula $(X_yH_{3-y}Si)_zCH_{4-z}$, or $(X_yH_{3-y}Si)(CH_2)_n(SiX_yH_{3-y})$, wherein X is a halogen, y 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, and the second precursor comprising water or a compound containing carbon and at least two hydroxyl groups. In one or more embodiments, a film comprising SiOC is provided.

[0021] The first precursor is a silicon precursor, and can act as both a silicon and carbon source. 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, 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:

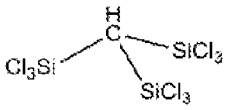


.

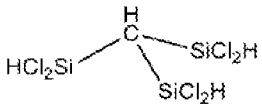
Other examples of suitable precursors include, but are not limited to those having a structure represented by:



,



or



.

[0022] In other embodiments, the first precursor 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, embodiments at least one of the X groups is Cl. In even further embodiments, all X groups are Cl.

[0023] In some embodiments, the second precursor may comprise water. In embodiments where the second precursor comprises water, the resulting film will still contain carbon from the first precursor.

[0024] In other embodiments, the second precursor comprises a compound containing carbon and at least two hydroxyl groups. In further embodiments, the second precursor 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 second precursors. Suitable second precursors, 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 second precursor, and then the second may be used for the next cycle to react with the Si-Cl in the first precursor. Films deposited using diols are thought to also have the advantage of being oxygen deficient.

[0025] Various first and second precursors 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. For example, in embodiments where the first precursor has formula $(X_yH_{3-y}Si)(CH_2)_n(SiX_yH_{3-y})$, longer carbon chains can be selected to result in a higher carbon content in the deposited film. In one or more embodiments, the carbon content of the film is about 10%.

[0026] The catalyst comprises a neutral two electron donor base. In one or more 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 NH_3. 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.

[0027] In an exemplary embodiment, the method comprises exposing a substrate surface to a first and second precursor in the presence of a catalyst comprising an amine, the first precursor comprising bis(trichlorosilyl)methane and the second precursor comprising water. In further embodiments, the catalyst comprises pyridine. In one or more embodiments, a film comprising SiOC is provided.

[0028] Another aspect of the invention relates to a method of depositing a film, the method comprising a substrate surface to a first and second precursor in the presence of a catalyst comprising a neutral two electron donor base, the first precursor comprising SiX_4 or $X_3Si\text{-}SiX_3$, wherein X is a halide, and the second precursor comprising a compound containing carbon and at least two diols.

[0029] Again, the first precursor is a silicon precursor. In some embodiments, the first precursor comprises SiX_4. In other embodiments, the first precursor comprises $X_3Si\text{-}SiX_3$. In one or more embodiments, each X is independently selected from Cl, Br and I. In further embodiments, embodiments at least one of the X groups is Cl. In even further embodiments, all X groups are Cl. In embodiments where the first precursor comprises $X_3Si\text{-}SiX_3$, and all X groups are chlorine, the compound is $Cl_3Si\text{-}SiCl_3$, also known as hexachlorodisilane. Accordingly, in one or more embodiments, the silicon precursor is selected from $SiCl_4$, $SiBr_4$, or SiI_4.

[0030] The second precursor comprises carbon and at least two hydroxyl groups. Carbon may be incorporated into the deposited film from the second precursor. Accordingly, in one or more embodiments, the resulting film comprises SiOC. In some embodiments, the second precursor may comprise a diol. Suitable second precursors, include, but are not limited to, ethylene glycol, propylene glycol and butane-1,4-diol. In further embodiments, the diol comprises ethylene glycol. Again, as discussed above, it is thought that at least two OH groups are needed to repeat the cycle and get additional deposition.

[0031] The catalyst comprises a neutral two electron donor base. In one or more 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 NH_3. 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.

[0032] The precursors may be flowed and/or exposed to the substrate surface either sequentially or substantially simultaneously. In embodiments where the substrate is exposed to the precursors sequentially, the process may be repeated up until a desired film thickness has been achieved. As used herein, "substantially simultaneously" refers to either co-flow or where there is merely overlap between exposures of the precursors. In one or more

embodiments, the catalyst is added with any one or more of the reactants. In other embodiments, the catalyst is added alone, before and/or after any of the precursors.

[0033] The reaction conditions for the ALD reaction will be selected based on the properties of the film precursors, substrate surface, and the catalyst. The deposition may be carried out at atmospheric pressure, but may also be carried out at reduced pressure. The vapor pressure of the catalyst 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 catalyst used and pressure. The properties of the specific substrate, film precursors, and catalyst may be evaluated using methods known in the art, allowing selection of appropriate temperature and pressure for the reaction.

[0034] In one or more embodiments, the deposition is carried out at a temperature less than about 400, 350, 300, 250, 200, 150, 125, or 100 °C. In some embodiments, the deposition is carried out at a temperature in the range of about 70 to about 100 °C, about 70 to about 125 °C or about 70 to about 125 °C.

[0035] According to one or more embodiments, the substrate is subjected to processing 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 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.

[0036] 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.

[0037] 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. 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.

[0038] 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.

[0039] 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.

[0040] The substrate can also be stationary or rotated during processing. A rotating substrate can be rotated continuously or in discreet steps. For example, a substrate may be rotated throughout the entire process, or the substrate can be rotated by a small amount between exposure 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.

[0041] 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.

[0042] 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

Example 1

[0043] A SiOC was deposited using hexachlorodisilylmethylene and water using a pyridine catalyst. The pressure and temperature of the chamber were 12 torr and 70 °C, respectively. The pulse sequence is shown in Figure 1, which shows alternating pyridine/hexachlorodisilylmethylene pulses followed by alternating pyridine/water pulses. The hexachlorodisilylmethylene pulse length was 2.0 seconds, surrounded by a curtain of 1.0 second pyridine pulses. The water pulse length was 0.2 seconds, also surrounded by a curtain of 1.0 second pyridine pulses. Purge length was 10 seconds. The cycle was repeated 150 times to arrive at a film thickness of 16.7nm, corresponding to 1.1 Angstroms growth per cycle.

Example 2

[0044] A SiOC was deposited using according to the methods of Example 1, except that the deposition was carried out to a film thickness of about 60-70 Angstroms. Figure 2 shows the X-ray photoelectron spectroscopy depth profile of the SiOC film. Table 1 below shows the average elemental content in the bulk film.

Table 1: Average Content in Bulk Film

O1s	C1s	Si2p-O/C	Si2p
41.14	9.69	28.36	20.83

[0045] As seen from Table 1 and Figure 2, no nitrogen or chlorine ends up deposited, showing that the precursor does not contaminate the film. The resulting carbon content was around 10%.

Examples 3-5

[0046] A SiOC was deposited using according to the methods of Example 1 over a photoresist, silicon substrate with features, and blanket Si(100). Transmission electron microscope photographs of the films were taken and are shown in Figures 3-5, respectively. Figures 3-5 also show measurements of the film thickness at various points of the films. As

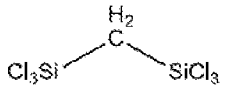
can be seen in the photographs, the deposited films are very conformal over a variety of substrates, even over features in the substrate.

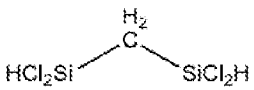
What is claimed is:

1. A method of depositing a film, the method comprising exposing a substrate surface to a first and second precursor in the presence of a catalyst comprising a neutral two electron donor base, the first precursor having a formula $(X_yH_{3-y}Si)_zCH_{4-z}$ or $(X_yH_{3-y}Si)(CH_2)_n(SiX_yH_{3-y})$, wherein each X is independently selected from Cl, Br and I, y 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, and the second precursor comprising water or a compound containing carbon and at least two hydroxyl groups.

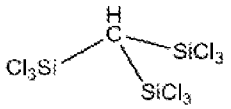
2. The method of claim 1, wherein the first precursor has a formula $(X_yH_{3-y}Si)_zCH_{4-z}$.

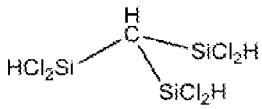
3. The method of claim 1 or 2, wherein the first precursor has a structure represented by:



,


,



or


.

4. The method of any of claims 1-3, wherein the first precursor comprises bis(trichlorosilyl)methane.

5. The method of any of claims 1-4, wherein the first precursor has a formula $(X_yH_{3-y}Si)(CH_2)_n(SiX_yH_{3-y})$.

6. The method of any of claims 1-5, wherein n has a value of 2 or 3.

7. The method of any of claims 1-6, wherein the catalyst comprises an amine, pyridine or NH_3.

8. The method of any of claims 1-7, wherein the second precursor comprises a diol.

9. The method of any of claims 1-8, wherein the diol comprises ethylene glycol, propylene glycol and butane-1,4-diol.

10. The method of any of claims 1-9, wherein a film comprising SiOC is provided.

11. A method of depositing a film, the method comprising exposing a substrate surface to a first and second precursor in the presence of a catalyst comprising a neutral two electron donor base, the first precursor comprising SiX_4 or $X_3Si\text{-}SiX_3$, wherein each X is independently selected from Cl, Br and I, and the second precursor comprises a compound containing carbon and at least two hydroxyl groups to provide a film comprising SiOC.

12. The method of claim 11, wherein the first precursor comprising SiX_4.

13. The method of claim 11 or 12, wherein the catalyst comprises an amine, pyridine or NH_3.

14. The method of any of claims 11-13, wherein the second precursor is a diol.

15. The method of any of claims 11-14, wherein the diol comprises ethylene glycol, propylene glycol and butane-1,4-diol.

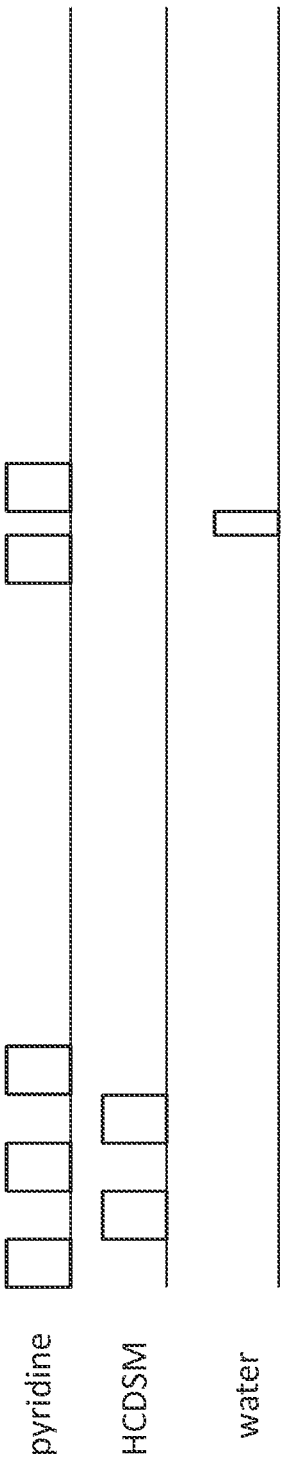


FIGURE 1

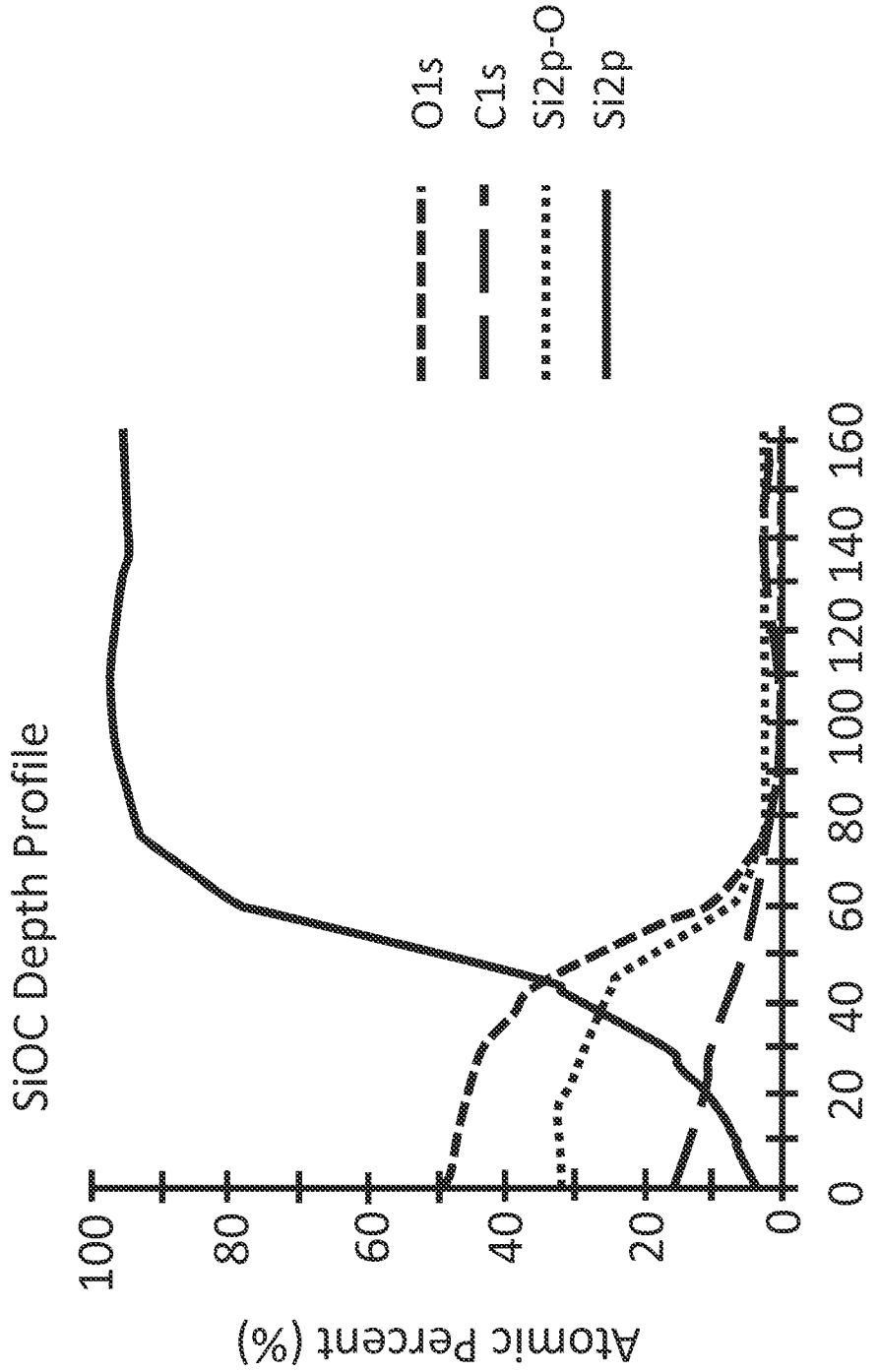

SiOC Depth Profile
Atomic Percent (%)
100
80
60
40
20
0
0 20 40 60 80 100 120 140 160
Etch Time (s)
O1s
C1s
Si2p-O
Si2p

FIGURE 2

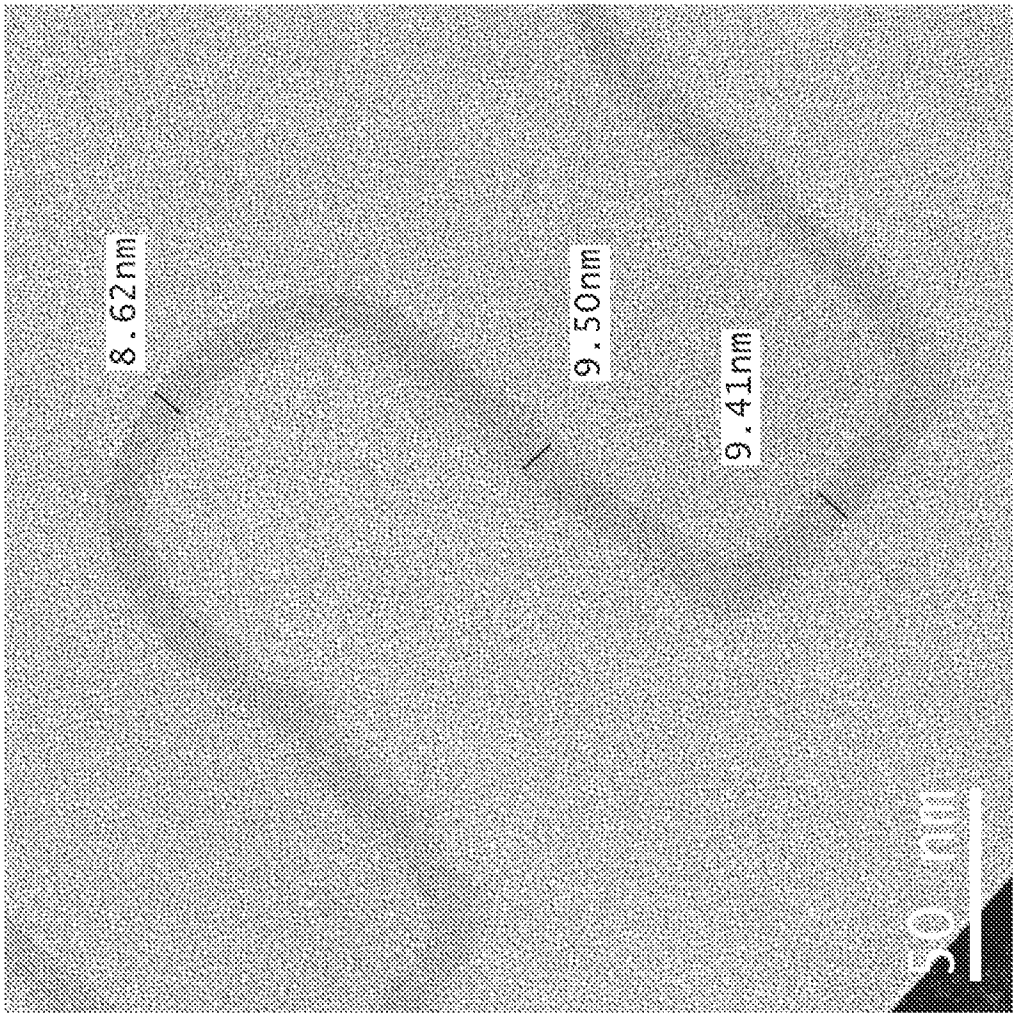


FIGURE 3

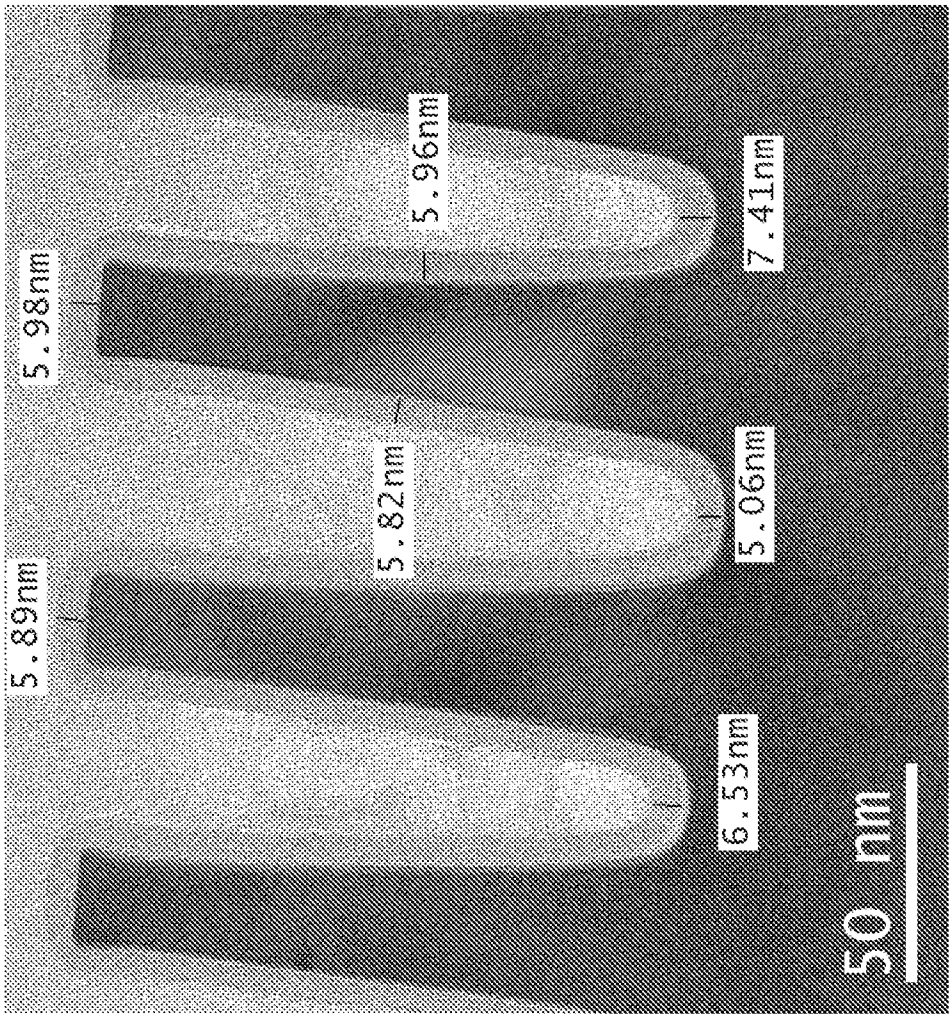


FIGURE 4

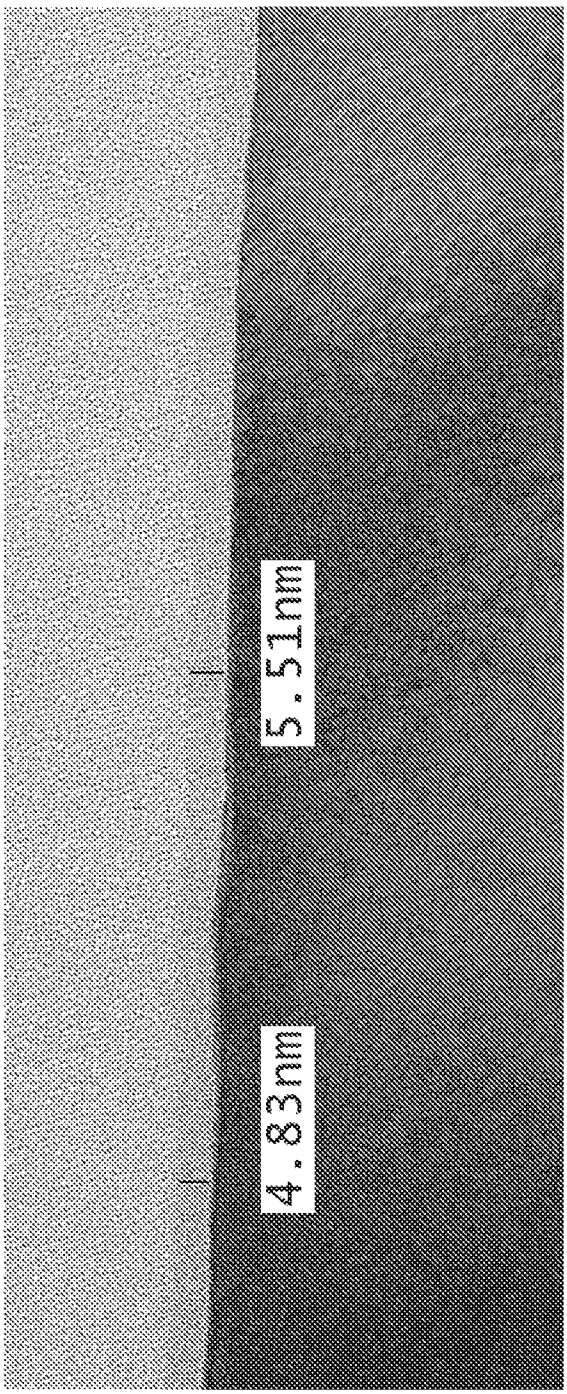


FIGURE 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/017391

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 SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01L 21/205; C23C 16/52; H01L 21/311; H01L 21/469; C23C 16/40; C23C 16/455; H01L 21/283

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & keywords: ALD, SIOC, methylenebis,bismethane,trichlorosilyl,trichlorosilane,diol, precursor

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1925692 A1 (APPLIED MATERIALS, INC.) 28 May 2008 See abstract, paragraphs [0010], [0023]-[0025] and claims 1-3.	1-3,11-13
A	US 2009-0081883 A1 (DIANE C. FREEMAN et al.) 26 March 2009 See abstract, paragraph [0054] and claim 7.	1-3,11-13
A	US 2012-0276306 A1 (SHINTARO UEDA) 01 November 2012 See abstract, paragraphs [0013], [0045] and claim 5.	1-3,11-13
A	US 2012-0052681 A1 (EUGENE P. MARSH) 01 March 2012 See abstract, paragraphs [0005], [0025] and claim 1.	1-3,11-13
A	KR 10-2001-0104285 A (SHARP KABUSHIKI KAISHA) 24 November 2001 See abstract, pages 2-5 and claims 1, 22.	1-3,11-13

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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

Date of the actual completion of the international search	Date of mailing of the international search report
30 May 2014 (30.05.2014)	**30 May 2014 (30.05.2014)**

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

Authorized officer
KIM, Young Jin
Telephone No. +042 481 5771

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/017391

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.: 4-10, 14-15
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 addtional 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/US2014/017391

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1925692 A1	28/05/2008	CN 101187012 A	28/05/2008
		CN 101187012 C0	28/05/2008
		JP 2008-142702 A	26/06/2008
		JP 5219466 B2	26/06/2013
		KR 10-0954027 B1	20/04/2010
		KR 10-2008-0043706 A	19/05/2008
		TW 200831696 A	01/08/2008
		TW I359877 B	11/03/2012
		US 2008-0113096 A1	15/05/2008
		US 7776395 B2	17/08/2010
US 2009-0081883 A1	26/03/2009	CN 102027603 A	20/04/2011
		CN 102027603 B	20/11/2013
		EP 2210270 A2	28/07/2010
		JP 2011-506758 A	03/03/2011
		US 7858144 B2	28/12/2010
		WO 2009-042051 A2	02/04/2009
		WO 2009-042051 A3	18/11/2010
US 2012-0276306 A1	01/11/2012	KR 10-2012-0121356 A	05/11/2012
		US 8592005 B2	26/11/2013
US 2012-0052681 A1	01/03/2012	None	
KR 10-2001-0104285 A	24/11/2001	JP 2002-016062 A	18/01/2002
		JP 3739081 B2	25/01/2006
		TW 506055 A	11/10/2002
		TW 506055 B	11/10/2002
		US 6410462 B1	25/06/2002