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- (81) **Designated States** (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, 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, 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.
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(54) **Title:** DEPOSITION OF FILMS CONTAINING ALKALINE EARTH METALS

(57) **Abstract:** Described are methods of depositing a metal film by chemical reaction on a substrate. The method comprises: exposing the substrate to flows of a first reactant gas comprising a group 2 metal and a second reactant gas comprising a halide to form a first layer containing a metal halide on the substrate; exposing the substrate to a third reactant gas comprising an oxidant to form a second layer containing a metal peroxide or metal hydroxide on the substrate during; exposing the substrate to heat or a plasma to convert the metal peroxide or metal hydroxide to metal oxide. The method may be repeated to form the metal oxide film absent any metal carbonate impurity.



DEPOSITION OF FILMS CONTAINING ALKALINE EARTH METALS

TECHNICAL FIELD

[0001] Embodiments of the present invention generally relate to metal film deposition, and specifically to the deposition of films comprising group 2 metals.

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, dielectrics for magnetic read/write heads, and random access memory. Metal oxide films incorporating transition metals are used in semiconductor applications including high K gate dielectric films, active materials for ferroelectric memories, thin film battery cathodes, materials in silicon based light emitting devices and memory cells. Many metal-oxygen condensed phase systems employ metal oxides that are known to be stable at different oxidation potentials and have well-defined stoichiometric phases. For these materials it is generally possible to consistently obtain a desired metal oxide once an oxidation potential threshold is exceeded, and equilibrium is reached.

[0003] Methods for deposition of thin films include chemical vapor deposition (CVD) and atomic layer deposition (ALD). CVD processes involve exposing a substrate to one or more volatile precursors which react and/or decompose onto the substrate to produce a film. Most ALD processes are based on binary reaction sequences, where each of the two surface reactions occurs sequentially. 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. Current methods for depositing metal oxide films, particularly strontium oxide films involve the use of ozone which results in the formation of SrCO_3 , which is undesirable. Thus, there is a need to develop methods of depositing thin SrO films without the formation of SrCO_3 .

SUMMARY

[0004] One aspect of the invention relates to a method of depositing a metal oxide film on a substrate. The method comprises (a) exposing a substrate surface to flows of a metal precursor and a halide precursor to provide a metal halide film on the substrate surface, wherein the metal comprises a group 2 metal; then (b) exposing a substrate surface containing the metal halide film to an oxidant; and (c) subsequently exposing the substrate surface to heat or a plasma to provide a metal oxide film on the substrate. In one or more embodiments, the method further comprises flowing a purge gas after each exposure. In one or more embodiments, (a), (b) or (c) is repeated one or more times.

[0005] In one or more embodiments, the metal precursor is selected from a strontium precursor, a calcium precursor and a magnesium precursor. In further embodiments, the metal precursor comprises Sr(thd)₂-bis(tetramethylheptanedionate), Sr(methd)₂-bis(bis(methoxyethoxytetramethylheptanedionate), and Sr(dpm)₂-bis(dipivaloylmethanate), Ca(C₁₁H₁₉O₂)₂ (bis(tetramethylheptanedionate) Calcium), C₁₀H₂F₁₂O₄Ca (calcium hexfluoropentanedionate), C₆H₁₄O₄Ca (calcium methoxyethoxide), Mg(C₂H₅)₂ (Bis(cyclopentadienyl)magnesium(II)), C₂OH₃OMg Bis(pentamethylcyclopentadienyl)magnesium, or combinations thereof.

[0006] In some, the halide precursor comprises, F₂, Cl₂, Br₂, and I₂. In one or more embodiments, the oxidant comprises one or more of H₂O, H₂O₂, O₂, O₃, N₂O, NO, NO_x, nitrates, alcohols, carboxylic acids, CO, CO₂, and HCOH. In one or more embodiments, the substrate is exposed to heat or a plasma.

[0007] A second aspect of the invention relates to a method of depositing a strontium oxide film on a substrate. The method comprises (a) exposing a substrate surface to alternating pulses of a strontium precursor and a halide precursor to provide a strontium halide film on the substrate surface; then (b) exposing the substrate surface containing a strontium halide film to an oxidant; and (c) exposing the substrate surface to heat or a plasma to provide a strontium oxide film on the substrate surface. In some embodiments, the strontium precursor comprises Sr(thd)₂-bis(tetramethylheptanedionate), Sr(methd)₂-bis(bis(methoxyethoxytetramethylheptanedionate), or Sr(dpm)₂-bis(dipivaloylmethanate). In one or more embodiments, the halide precursor is selected from the list comprising, F₂, Cl₂, Br₂, and I₂.

[0008] In one or more embodiments, the oxidant comprises one or more of H₂O, H₂O₂, O₂, O₃, N₂O, NO, NO_x, nitrates, alcohols, carboxylic acids, CO, CO₂, and HCOH. In one or more embodiments, the method further comprises flowing a purge gas after each exposure. In some embodiments, (a), (b) or (c) is repeated one or more times.

5 [0009] A third aspect of the invention relates to a method of depositing a strontium oxide metal film having no strontium carbonate incorporation on a substrate. The method comprises (a) disposing a substrate within a processing chamber; (b) performing a deposition process comprising: flowing a strontium precursor gas and Cl₂ gas to at least a portion of the substrate within the chamber under conditions which form a partial monolayer on the substrate, the partial monolayer
10 comprising strontium terminated with chlorine, flowing a purge gas, flowing water vapor to the substrate within the chamber under conditions which form a partial monolayer on the substrate, the partial monolayer comprising SrO₂ or Sr(OH)₂ and flowing a purge gas; (c) exposing the substrate having the SrO₂ or Sr(OH)₂ containing film thereon to heat or a plasma, flowing a purge gas; and (d) repeating (b) and (c), wherein the deposition process is selected from chemical vapor deposition
15 and atomic layer deposition or combinations thereof. In one or more embodiments, in (c), the substrate is exposed to heat.

DETAILED DESCRIPTION

[0010] 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
20 in the following description. The invention is capable of other embodiments and of being practiced or being carried out in various ways.

[0011] 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
25 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.

[0012] 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 is chemical vapor deposition (CVD) in which a gas phase chemical precursor molecule and a reactant gas are reacted on and/or above a temperature-controlled surface to form a thin film. The reactive species, energy, rate of chemical supply, substrate temperature and substrate itself contribute to determining the properties of the film. In a typical CVD process, the reactants are introduced into the reactor in gas phase and activated by heat, plasma or other means. The reactive species are then adsorbed onto the substrate surface, where they may undergo chemical reactions or react with other incoming species to form a solid film. Reaction by-products are desorbed from the substrate surface and removed or purged from the reactor.

[0013] A variation of chemical vapor deposition for deposition of thin films is atomic layer deposition (ALD), which employs sequential, self-limiting surface reactions to form layers of precise thickness controlled at the Ångstrom or monolayer level. Most ALD processes are based on binary reaction sequences which deposit a binary compound film. Each of the two surface reactions occurs sequentially, and because they are self-limiting, a thin film can be deposited with atomic level control. 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. The self-limiting nature of the surface reactions also allows the reaction to be driven to completion during every reaction cycle, resulting in films that are continuous and pinhole-free.

[0014] As used in this specification and the appended claims, the term “purge” is used to mean any process in which the contents of a system are removed. Purging can mean that the contents (e.g., a gaseous reactant) are removed by being replaced with another gas (e.g., an inert gas) or removed by introducing a vacuum (or partial vacuum) to the system.

[0015] According to one or more of the embodiments, the invention relates to a method of depositing a metal oxide film by chemical reaction. The methods, also referred to as processes, include sequentially exposing a substrate, or portion of a substrate, to various deposition gases containing chemical precursors or reactants including a first reactant gas, a second reactant gas and a third reactant gas. Between the exposures, a purge gas can be flowed. The first reactant gas and second reactant gas form at least a partial layer of metal halide on the substrate during a first

deposition process. The substrate is also exposed, sequentially, to a third reactant gas. The third reactant gas forms at least a partial layer of metal peroxide/metal hydroxide on the substrate during a second deposition process. The substrate is then exposed to heat or to a plasma to provide a metal oxide film on the substrate having a desired thickness. Skilled artisans will understand that the first deposition process can be repeated multiple times before the second deposition process, and that the second deposition process can be repeated multiple times before the first deposition process, and that either process can be performed first.

[0016] In a specific embodiment, the first reactant gas can include a metal precursor containing any suitable alkaline earth metal or Group 2 metal known to the skilled artisan. Suitable Group 2 metals include strontium, calcium, magnesium and the like. Such suitable metal species are those that form stable carbonates. A list of suitable alkaline earth metal precursors includes, Sr(thd)2-bis(tetramethylheptanedionate), Sr(methd)2-bis(bis(methoxyethoxy tetramethylheptanedionate), and Sr(dpm)2-bis(dipivaloylmethanate, $\text{Ca}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2$ (bis(tetramethylheptanedionate)Calcium), $\text{C}_{10}\text{H}_2\text{F}_{12}\text{O}_4\text{Ca}$ (calciumhexfluoropentanedionate), $\text{C}_6\text{H}_{14}\text{O}_4\text{Ca}$ (calciummethoxyethoxide), $\text{Mg}(\text{C}_2\text{H}_5)_2$ (Bis(cyclopentadienyl) magnesium(II)), $\text{C}_2\text{OH}_3\text{OMg}$ Bis(pentamethyl cyclopentadienyl) magnesium, and combinations thereof. In another embodiment, the second reactant gas can include any suitable halide containing gas known to the skilled artisan. Suitable halide species include, F_2 , Cl_2 , Br_2 , I_2 , and the like. In another embodiment the substrate is exposed to a third reactant gas comprising an OH containing species or an oxidant. In another embodiment, suitable oxidants include, but are not limited to, H_2O , H_2O_2 , O_2 , O_3 , N_2O , NO , NO_x , nitrates, alcohols, carboxylic acids, CO , CO_2 , and HCOH . Specifically, in some embodiments, the oxidant comprises water. In a specific embodiment, the methods of the invention form a first layer containing a metal halide on the substrate during a first deposition cycle and then during a second deposition cycle, the metal halide containing substrate is exposed to an oxidant to provide a layer containing a metal peroxide or metal hydroxide on the substrate. In another embodiment, the substrate is exposed to heat or to a plasma to provide the desired metal oxide film. Specifically, the methods include repeating the first, second, or third cycles to form the metal oxide film. Specifically, the metal oxide film is substantially free of any metal carbonate formation. More specifically, the metal oxide film contains no metal carbonate formation.

[0017] In detailed embodiments, the methods include exposing the substrate to heat or to a plasma to obtain the desired metal oxide film. In one embodiment, the substrate is heated.

[0018] Plasmas may be used for treating the films described herein. In one embodiment, the substrate is exposed to a plasma gas. Typical plasma gases may contain inert gases, such as for example, nitrogen, hydrogen, argon, neon, helium, or combinations thereof. The plasma may be generated externally from the processing chamber, such as by a remote plasma generator system. Typically, a plasma may be remotely generated from a microwave (MW) frequency generator or a radio frequency (RF) generator.

[0019] A list of suitable metal oxide films contemplated by the invention includes but is not limited to: SrO, MgO, CaO.

[0020] In detailed embodiments, the method comprises, disposing a substrate within a processing chamber and performing a first deposition cycle comprising first flowing a gas containing a strontium precursor and a gas containing halide precursor to at least a portion of the substrate within the chamber under conditions which form a partial monolayer on the substrate, the partial monolayer comprising strontium terminated with chlorine, followed by flowing a purge gas into the chamber. Then, water vapor may be flowed to the substrate within the chamber under conditions which form a partial monolayer on the substrate; the partial monolayer comprising strontium hydroxide, followed by flowing a purge gas into the chamber. This can then be followed by applying heat or flowing a plasma to at least a portion of the substrate within the chamber under conditions which form a layer comprising strontium oxide, followed by flowing a purge gas into the chamber. The first, second and third processes or cycles are then repeated until the desired thickness of the strontium oxide film is reached.

[0021] During the purge, typically an inert gas is introduced into the processing chamber to purge the reaction zone or otherwise remove any residual reactive compound or by-products from the reaction zone. Alternatively, the purge gas may flow continuously throughout the deposition process so that only the purge gas flows during a time delay between disposal of the reactant gases.

[0022] Thin metal oxide films are very desirable in the semiconductor industry. Specific embodiments are directed to methods of obtaining strontium oxide films. Previous methods involved using strontium precursors with ozone in a deposition cycle. This typically resulted in the

formation of strontium carbonate (SrCO_3) incorporation in the film, which is an undesirable impurity. To avoid strontium carbonate incorporation, in specific embodiments, a strontium precursor, selected from the list comprising, $\text{Sr}(\text{thd})_2$ -bis(tetramethylheptanedionate), $\text{Sr}(\text{methd})_2$ -bis(bis(methoxyethoxy)tetramethylheptanedionate), $\text{Sr}(\text{dpm})_2$ -bis(dipivaloylmethanato and the like, can be pulsed into a chamber containing a substrate. Then a halide precursor, such as, for example Cl_2 , can be pulsed in to the chamber to form a partial monolayer comprising strontium chloride (SrCl_2). This is followed by a purge gas. Then water vapor may be flowed to the substrate within the chamber under conditions which form a partial monolayer on the substrate; the partial monolayer comprising strontium hydroxide ($\text{Sr}(\text{OH})_2$) or strontium peroxide (SrO_2), followed by flowing a purge gas into the chamber. It should be understood that a variety of oxidants including water vapor, H_2O_2 , O_2 , O_3 , N_2O , NO , NO_x , nitrates, alcohols, carboxylic acids, CO , CO_2 , HCOH , and the like can be flowed into the chamber to provide the desired $\text{Sr}(\text{OH})_2$ or SrO_2 . Subsequently, the substrate can be exposed to heat or to a plasma to provide the required strontium oxide (SrO) containing film on the substrate. The pulse/purge cycles are repeated one or more times until the desired thickness of the strontium oxide containing film is achieved.

[0023] Whilst not wishing to be bound by theory, SrCl_2 is involatile and thus behaves like NaCl in that it has no vapor pressure and consists of large networks of anions and cations. When SrCl_2 is reacted with water vapor, SrO_2 is deposited with HCl as a byproduct. Unlike previous methods involving strontium precursors and ozone, which resulted in SrCO_3 formation, the use of involatile halides as intermediates such as in the methods of the invention, was previously unknown. Thus, the methods of the invention described herein, provide a marked improvement in strontium oxide film deposition.

[0024] In one embodiment of the invention the methods are carried out sequentially, in situ, without exposing the substrates to air.

[0025] Specific embodiments of the invention are directed to methods of obtaining metal oxide films absent of any metal carbonate impurity on a substrate. In particular, films such as SrO and CaO and MgO are prepared by vapor deposition such as CVD, ALD or plasma-enhanced CVD (PE-CVD) and plasma-enhanced ALD (PE-ALD). A processing chamber is configured to expose the substrate to a sequence of gases and/or plasmas during the deposition process.

[0026] In some embodiments, the substrate is exposed to a first reactant gas and a second reactant gas. The exposure to these first and second gases can be substantially simultaneously, as in a CVD reaction, or sequentially, as in an ALD reaction. As used in this specification and the appended claims, the term “substantially simultaneously” means that the two precursor gases are
5 flowed into the chamber to react with each other and the substrate surface together. It will be understood by those skilled in the art that there may be areas of the substrate which are briefly exposed to one precursor only until the other precursor diffuses to the same area.

[0027] In atomic layer deposition type chambers, the substrate can be exposed to the first and second reactant gases either spatially or by a time domain processes. Time domain ALD is a
10 traditional process in which the first reactant gas flows into the chamber to react with the surface. The first reactant gas is purged from the chamber before flowing the second reactant gas. In spatial ALD, both the first and second reactant gases are simultaneously flowed to the chamber but are separated spatially so that there is a region between the flows that prevents mixing of the gases. In spatial ALD, the substrate must be moved relative to the gas distribution plate, or vice-
15 versa.

[0028] In some embodiments, a plasma system and a processing chamber or system which may be used during methods described here for depositing or forming metal oxide materials include the TXZ® CVD, chamber available from Applied Materials, Inc., located in Santa Clara, Calif. Further disclosure of plasma systems and processing chambers is described in commonly
20 assigned U.S. Pat. Nos. 5,846,332, 6,079,356, and 6,106,625. In other embodiments, a PE-ALD processing chamber or system which may be used during methods described here for depositing or forming metal oxide materials is described in commonly assigned U.S. Ser. No. 12/494,901, filed on Jun. 30, 2009, published as United States patent application publication number 2010/0003406. An ALD processing chamber used in some embodiments described herein may contain a variety
25 of lid assemblies. Other ALD processing chambers may also be used during some of the embodiments described herein and are available from Applied Materials, Inc. A detailed description of an ALD processing chamber may be found in commonly assigned U.S. Pat. Nos. 6,821,563, 6,878,206, 6,916,398, and 7,780,785. In another embodiment, a chamber configured to operate in both an ALD mode as well as a conventional CVD mode may be used to deposit metal
30 oxide materials is described in commonly assigned U.S. Pat. No. 7,204,886.

[0029] Reference throughout this specification to "one embodiment," "certain embodiments," "one or more embodiments," "an embodiment," "one aspect," "certain aspects," "one or more embodiments" and "an aspect" 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," "in an embodiment," "according to one or more aspects," "in an aspect," etc., in various places throughout this specification are not necessarily referring to the same embodiment or aspect of the invention. Furthermore, the particular features, structures, materials, or characteristics may be combined in any suitable manner in one or more
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embodiments or aspects. The order of description of the above method should not be considered limiting, and methods may use the described operations out of order or with omissions or additions.

[0030] It is to be understood that the above description is intended to be illustrative, and not restrictive. Many other embodiments will be apparent to those of ordinary skill in the art upon
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reviewing the above description. The scope of the invention should, therefore, be determined with reference to the appended claims, along with the full scope of equivalents to which such claims are entitled.

What is claimed is:

1. A method of depositing a metal oxide film on a substrate comprising:
 - (a) exposing a substrate surface to flows of a metal precursor and a halide precursor to provide a metal halide film on the substrate surface, wherein the metal comprises a group 2 metal; then
 - (b) exposing a substrate surface containing the metal halide film to an oxidant; and
 - (c) subsequently exposing the substrate surface to heat or a plasma to provide a metal oxide film on the substrate.
2. The method of claim 1, further comprising flowing a purge gas after each exposure.
3. The method of claim 1 or 2, wherein (a), (b) or (c) is repeated one or more times.
4. The method of any of claims 1-3 wherein the metal precursor is selected from a strontium precursor, a calcium precursor and a magnesium precursor.
5. The method of any of claims 1-4 wherein the metal precursor comprises Sr(thd)₂-bis(tetramethylheptanedionate), Sr(methd)₂-bis(bis(methoxyethoxytetramethylheptanedionate), and Sr(dpm)₂-bis(dipivaloylmethanate), Ca(C₁₁H₁₉O₂)₂ (bis(tetramethylheptanedionate) Calcium), C₁₀H₂F₁₂O₄Ca (calcium hexfluoropentane-dionate), C₆H₁₄O₄Ca (calcium methoxyethoxide), Mg(C₂H₅)₂ (Bis(cyclopentadienyl) magnesium(II)), C₂₀H₃₀Mg Bis(pentamethylcyclopentadienyl)magnesium, or combinations thereof.
6. The method of any of claims 1-5, wherein the halide precursor comprises, F₂, Cl₂, Br₂, and I₂.
7. The method of any of claims 1-6, wherein the oxidant comprises one or more of H₂O, H₂O₂, O₂, O₃, N₂O, NO, NO_x, nitrates, alcohols, carboxylic acids, CO, CO₂, and HCOH.
8. The method of any of claims 1-7, wherein the metal oxide film has a thickness up to about 500 Å.
9. The method of any of claims 1-8, wherein the substrate is exposed to heat.
10. The method of any of claims 1-9, wherein the substrate is exposed to a plasma.
11. A method of depositing a strontium oxide film on a substrate, the method comprising:

- (a) exposing a substrate surface to alternating pulses of a strontium precursor and a halide precursor to provide a strontium halide film on the substrate surface; then
- (b) exposing the substrate surface containing a strontium halide film to an oxidant; and
- (c) exposing the substrate surface to heat or a plasma to provide a strontium oxide film on the substrate surface.

12. The method of claim 11, wherein the strontium precursor comprises $\text{Sr}(\text{thd})_2$ -bis(tetramethylheptanedionate), $\text{Sr}(\text{methd})_2$ -bis(bis(methoxyethoxytetramethylheptanedionate), or $\text{Sr}(\text{dpm})_2$ -bis(dipivaloylmethanate).
13. The method of claim 11 or 12, wherein the halide precursor is selected from the list comprising, F_2 , Cl_2 , Br_2 , and I_2 .
14. The method of any of claims 11-13, wherein the oxidant comprises one or more of H_2O , H_2O_2 , O_2 , O_3 , N_2O , NO , NO_x , nitrates, alcohols, carboxylic acids, CO , CO_2 , and HCOH .
15. The method of any of claims 11-14, further comprising flowing a purge gas after each exposure.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/048420**A. CLASSIFICATION OF SUBJECT MATTER****C23C 16/44(2006.01)i, C23C 16/06(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)

C23C 16/44; B05D 5/12; C07F 3/00; H01M 8/10; C23C 16/40; C01B 13/22; C23C 16/00; C23C 16/30; C23C 16/06

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: metal oxide film, deposition, strontium, halide, oxidant, and heat

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5447909 A (TAKAHASHI et al.) 5 September 1995 See column 3, line 48 - column 4, line 13 and claims 6,10,13.	1-3,11-13
A	US 4931425 A (KIMURA et al.) 5 June 1990 See column 5, line 22 - column 6, line 22 and claims 1,5.	1-3,11-13
A	WO 2009-086263 A1 (SIGMA-ALDRICH CO.) 9 July 2009 See paragraphs [0020],[0023]-[0025] and claims 1,15-17.	1-3,11-13
A	JP 02-088773 A (FUJITSU, LTD.) 28 March 1990 See abstract, column 10, line 9 - column 11, line 7, and claims 1,2.	1-3,11-13
A	US 2005-0095480 A1 (BEATTY et al.) 5 May 2005 See paragraph [0036] and claims 1,7.	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 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

03 September 2013 (03.09.2013)

Date of mailing of the international search report

04 September 2013 (04.09.2013)

Name and mailing address of the ISA/KR

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/048420

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 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 fee, this Authority did not invite payment of any additional fee.
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.

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