



(43) International Publication Date
28 March 2013 (28.03.2013)

(10) International Publication Number
WO 2013/043501 A1

- (51) **International Patent Classification:**
H01L 21/205 (2006.01) *C23C 16/44* (2006.01)
- (21) **International Application Number:**
PCT/US2012/055490
- (22) **International Filing Date:**
14 September 2012 (14.09.2012)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
61/538,600 23 September 2011 (23.09.2011) US
13/616,903 14 September 2012 (14.09.2012) US
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- (81) **Designated States (unless otherwise indicated, for every kind of national protection available):** AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, 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.

- (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, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) **Title:** METAL-ALUMINUM ALLOY FILMS FROM METAL AMIDINATE PRECURSORS AND ALUMINUM PRECURSORS

(57) **Abstract:** Described are methods for deposition of metal- aluminum films using metal amidinate precursors and aluminum precursors. Such metal- aluminum films can include metal aluminum carbide, metal aluminum nitride and metal aluminum carbonitride films. The aluminum precursors may be alkyl aluminum precursors or amine alanes.



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METAL-ALUMINUM ALLOY FILMS FROM METAL AMIDINATE PRECURSORS AND ALUMINUM PRECURSORS

TECHNICAL FIELD

[0001] The present invention relates generally to methods of depositing thin films of metal-aluminum alloys and to films deposited using such methods. In particular, the invention relates to deposition of metal-aluminum, metal aluminum carbide, metal aluminum nitride and metal aluminum carbonitride 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 atomic layer control and conformal deposition 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.

[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 $\text{AlOAl}(\text{CH}_3)_2$ 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 $\text{AlOAl}(\text{CH}_3)_2$. Subsequent cycles of A and B, purging gas phase reaction products and unreacted vapor phase precursors between reactions and between reaction cycles, produces

5 Al_2O_3 growth in an essentially linear fashion to obtain the desired film thickness.

[0004] While perfectly saturated monolayers are often desired, this goal is very difficult to achieve in practice. The typical approach to further ALD development has been to determine whether or not currently available chemistries are suitable for ALD. Although a few processes have been developed that are effective for deposition of certain transition metal-

10 aluminum layers using transition metal halides and alkyl aluminum precursors, in general ALD processes for deposition of meta-aluminum layers have not been sufficiently successful to be adopted commercially. There is a need for new deposition chemistries that are commercially viable with a wide range of metals. The present invention addresses this problem by providing novel precursor combinations which are specifically designed and optimized to take advantage

15 of the atomic layer deposition process.

SUMMARY

[0005] One aspect of the invention pertains to a method of depositing a metal-aluminum layer, the method comprising exposing a substrate surface to pulses of a metal amidinate precursor and an aluminum precursor to form a metal-aluminum layer on the

20 substrate surface, wherein the metal amidinate precursor comprises a p or f-block metal and the aluminum precursor comprises an alkyl aluminum precursor or an amine alane. In various embodiments, the substrate surface is not exposed to an oxidant during formation of the metal-aluminum layer.

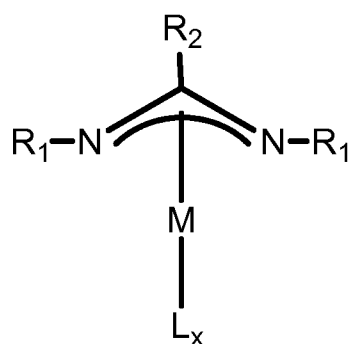
[0006] In one or more embodiments of this aspect, the metal-aluminum layer comprises

25 a metal aluminum carbide layer, a metal aluminum nitride layer, or a metal aluminum carbonitride layer. In some embodiments, the metal-aluminum layer comprises less than 5, 4, 3, 2, 1, 0.5, 0.25, 0.1, 0.05 or 0.01 weight % oxygen.

[0007] In certain embodiments of this aspect, the substrate is heated to a temperature of about 100 °C to about 500 °C.

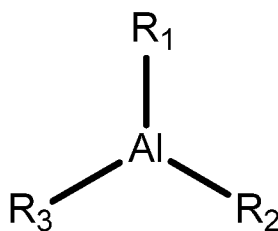
[0008] According to one or more embodiments, the substrate surface is exposed to the pulses sequentially, simultaneously, or substantially simultaneously. In some embodiments, the deposition process is an atomic layer deposition process.

[0009] In one or more embodiments, the metal amidinate precursor has a structure represented by:



wherein R_1 and R_2 are each independently hydrogen or a C_{1-8} straight or branched alkyl, M is a p or f-block metal, L_x are x ligands, x is a number from 1-4, and with each L independently being the same or different ligand as another L . In some embodiments, one or more L 's is an amidinate ligand. In a further embodiment, the metal amidinate precursor comprises lanthanum tris(N,N' -diisopropylformamidinate).

[0010] One or more embodiments of this aspect use an alkyl aluminum precursor has a structure represented by:



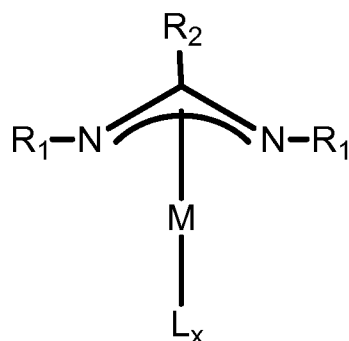
wherein R_1 , R_2 and R_3 are each independently hydrogen or a C_1-C_8 straight or branched alkyl. In one embodiment, R_1 , R_2 and R_3 are the same. In other embodiments, the alkyl aluminum precursor comprises one or more of trimethyl aluminum, triethyl aluminum and dimethylaluminumhydride. According to some embodiments, the alkyl aluminum precursor comprises trimethyl aluminum.

[0011] In one or more embodiments, the aluminum precursor is an amine alane. The amine alane may be alane coordinated to a tertiary amine. In some embodiments, the tertiary amine has a molecular weight less than 250 g/mol.

[0012] According to one or more embodiments, the deposition process further comprises exposing the substrate surface to a second metal amidinate precursor comprising a second p or f-block metal. In some embodiments, the second metal amidinate precursor comprises an f-block metal.

[0013] Another aspect of the invention pertains to a method of depositing a metal-aluminum layer by atomic layer deposition, the method comprising sequentially exposing a substrate surface to alternating pulses of a metal amidinate precursor and an aluminum precursor to form a metal-aluminum layer on the substrate surface. According to one or more embodiments of this aspect, the substrate surface is not exposed to an oxidant during formation of the metal-aluminum layer. In some embodiments, the metal-aluminum layer is oxide-free.

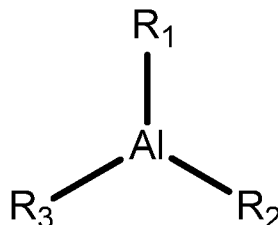
[0014] In one or more embodiments of this aspect, the metal amidinate precursor has a structure represented by:



wherein R_1 and R_2 are each independently hydrogen or a C_{1-8} straight or branched alkyl, M is p or f-block metal, L_x are x ligands, x is a number from 1-4, and with each L independently being the same or different ligand as another L. In some embodiments, M is an f-block metal.

According to one or more embodiments, the aluminum precursor is an alkyl aluminum precursor having a structure represented by:

5



wherein R_1 , R_2 and R_3 are each independently hydrogen or a C_1 - C_8 straight or branched alkyl.

[0015] In one or more embodiments, the aluminum precursor is an amine alane. The amine alane may be alane coordinated to a tertiary amine. In some embodiments, the tertiary amine has a molecular weight less than 250 g/mol.

[0016] In some embodiments of this aspect, the metal-aluminum layer comprises a metal aluminum carbide layer, a metal aluminum nitride layer, or a metal aluminum carbonitride layer. According to one or more embodiments, the substrate is heated to a temperature of about 100 °C to about 500 °C.

[0017] According to some embodiments, one or more L's is an amidinate ligand. In further embodiments, the metal amidinate precursor comprises lanthanum tris(N,N' -diisopropylformamidinate).

[0018] In one or more embodiments, the alkyl aluminum precursor comprises one or more of trimethyl aluminum, triethyl aluminum and dimethylaluminum-hydride. In some embodiments, the alkyl aluminum precursor comprises trimethyl aluminum.

[0019] Yet another aspect of the invention pertains to a method of depositing a lanthanum-aluminum layer by atomic layer deposition, the method comprising sequentially exposing a surface of a substrate to alternating pulses of lanthanum tris(N,N' -diisopropylformamidinate) and trimethyl aluminum to form on the surface a lanthanum-aluminum layer. In some embodiments, the lanthanum-aluminum layer comprises lanthanum aluminum carbide. In one or more embodiments, the substrate is heated to a temperature of about 100 °C to about 500 °C.

[0020] Another aspect of the present invention pertains to a metal-aluminum layer deposited by one of the methods described herein. In one or more embodiments, metal-aluminum layer has a thickness in the range from about 1 to about 10 nm. In some embodiments, the metal-aluminum layer is less than 5 weight % oxygen.

DETAILED DESCRIPTION

[0021] 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.

[0022] 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.

[0023] In one or more embodiments, a film composed largely of metal and aluminum, and in some embodiments, carbon and/or nitrogen, is deposited on a substrate. Such films can have n-metal film characteristics and can be used as metal gate materials. Thus, according to one or more embodiments, the metal-aluminum film is oxide-free, as the presence of oxygen increases the dielectric constant of the film and makes it unsuitable for use as a metal gate material.

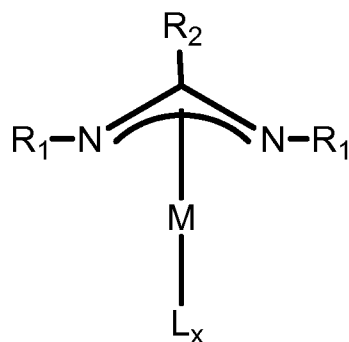
[0024] As used herein, "oxide-free" means that the oxygen content of the metal-aluminum film is below a certain tolerability threshold. In one embodiment, an "oxide-free" film is less than 5 weight % oxygen. In some embodiments, the metal-aluminum layer comprises less than 5, 4, 3, 2, 1, 0.5, 0.25, 0.1, 0.05 or 0.01 weight % oxygen.

[0025] As used herein, "substantially simultaneously" refers to either co-flow or where there is merely overlap between exposures of the two components.

[0026] According to one aspect of the invention, a metal-aluminum film is deposited on a substrate surface using metal amidinate precursors and aluminum precursors. In one or more embodiments, the substrate surface is exposed to the pulses sequentially, simultaneously, or substantially simultaneously. In some embodiments, the film may be deposited by sequentially exposing the substrate surface to alternating pulses of the metal amidinate precursor and the aluminum precursor

[0027] Metal amidinate precursors typically have better vapor pressure than corresponding metal halide precursors. For many metals, metal chlorides do not have sufficient vapor pressure to allow delivery of the metal. Thus, use of metal amidinate precursors increases the range of metals that can be deposited through atomic layer deposition or other deposition processes.

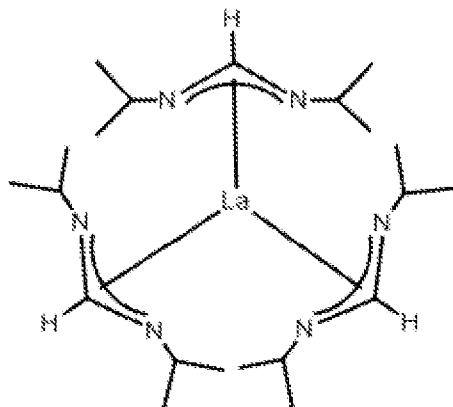
[0028] In one embodiment, the metal amidinate precursor comprises a metal coordination complex that may be represented by formula (I):



wherein R_1 and R_2 are each independently hydrogen or a C_{1-8} straight or branched alkyl. M is any p or f-block metal. L_x can be any ligand set, where x is a number from 1-4, and with each L being the same or different ligand as another L . In one embodiment, L_x comprises additional amidinate ligands. In some embodiments, M is an f-block metal.

[0029] In all the above ligands of formula (I), the R group substituents may be selected to control characteristics of the metal coordination complex. R_1 may be selected to tune the sterics of the precursor. Sterics should be selected such that the precursor does not become too bulky, and the vapor pressure will drop to an unusable level for vapor deposition.

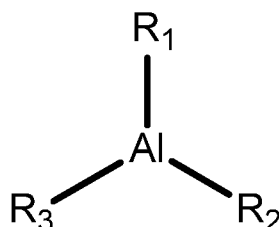
[0030] According to some embodiments, the metal amidinate precursor comprises lanthanum tris(N,N' -diisopropylformamidinate), which has the structure of formula (II):



Lanthanum tris(N,N'-diisopropylformamidinate) is available from the Dow Chemical Company.

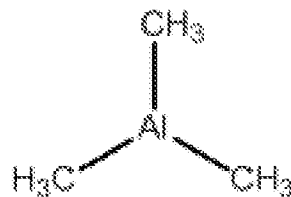
[0031] In addition to the metal amidinate precursor, a second precursor is used in the deposition process. This second precursor is an aluminum precursor, which is used to supply the aluminum for the film. The aluminum precursor can also be a carbon source if the metal-aluminum film comprises a metal aluminum carbide or metal aluminum carbonitride film. In one or more embodiments, the aluminum precursor may be an alkyl aluminum precursor or an amine alane.

[0032] According to one or more embodiments, the aluminum precursor is an alkyl aluminum precursor that may be represented by formula (III):



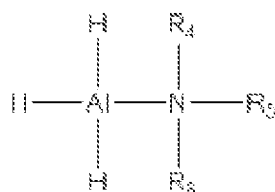
wherein R_1 , R_2 and R_3 are each independently hydrogen or a C_1 - C_8 straight or branched alkyl.

[0033] In one embodiment, R_1 , R_2 and R_3 are the same functional group, i.e. are all hydrogen or are all the same alkyl group. In some embodiments, the alkyl aluminum precursor comprises one or more of trimethyl aluminum (TMA), triethyl aluminum (TEA) and diisobutylaluminumhydride (DMAH). TMA, TEA and DMAH are all commercially-available compounds. In some embodiments, the alkyl aluminum precursor comprises trimethyl aluminum, which has the structure of formula (IV):



[0034] The aluminum precursor may also be an amine alane. In one or more embodiments, the amine alane is alane coordinated to a tertiary amine. In some embodiments, the amine is a tertiary amine. Some embodiments provide that the tertiary amine has a molecular weight less than or equal to 250 g/mol.

[0035] In one or more embodiments, the amine alane is represented by the structure of formula (V):

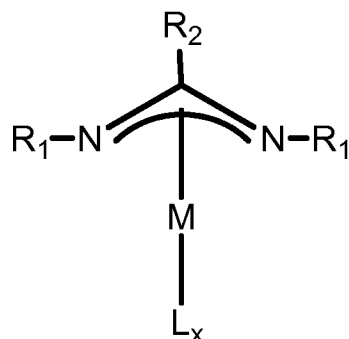


wherein R_4 , R_5 and R_6 are each independently a C_1 - C_8 straight or branched alkyl. In one or more embodiments, two or more of R_4 , R_5 and R_6 may form a cyclic structure, such as with N-methylpyrrolidine.

[0036] According to one or more embodiments, the deposition process further comprises exposing the substrate surface to a second metal amidinate precursor comprising a second p or f-block metal. In some embodiments, the second metal amidinate precursor comprises an f-block metal. When two or more metal amidinate precursors are used, the substrate may be exposed to the two precursors sequentially, simultaneously, or substantially simultaneously.

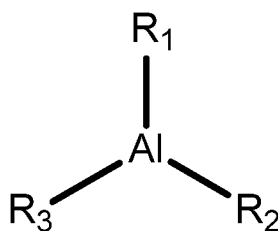
[0037] Certain embodiments pertain to a metal-aluminum layer that comprises nitrogen, such as a metal aluminum nitride or metal aluminum carbonitride film. In such embodiments, the nitrogen incorporated into the film can originate from the amidinate ligands in the metal amidinate precursor.

[0038] Another aspect of the invent relates to a method of depositing a metal-aluminum layer by atomic layer deposition, the method comprising sequentially exposing a surface of a substrate to alternating pulses of a metal amidinate precursor and an aluminum precursor to form a metal-aluminum layer on the substrate surface. In accordance with embodiments of this aspect, the metal amidinate precursor has a structure represented by formula (I):



wherein R_1 and R_2 are each independently hydrogen or a C_{1-8} straight or branched alkyl. M is any p or f-block metal. L_x are x ligands, where x is a number from 1-4, and with each L being the same or different ligand as another L . In one or more embodiments, L_x comprises additional amidinate ligands. In some embodiments, M is an f-block metal.

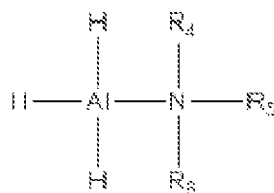
[0039] The aluminum precursor in accordance with this aspect may be an alkyl aluminum precursor having a structure represented by formula (III):



wherein R_1 , R_2 and R_3 are each independently hydrogen or a C_1 - C_8 straight or branched alkyl.

[0040] The aluminum precursor may also be an amine alane. In one or more embodiments, the amine alane is alane coordinated to a tertiary amine. In some embodiments, the amine is a tertiary amine. Some embodiments provide that the tertiary amine has a molecular weight less than or equal to 250 g/mol.

[0041] In one or more embodiments, the amine alane is represented by the structure of formula (V):



wherein R₄, R₅ and R₆ are each independently a C₁-C₈ straight or branched alkyl. In one or more embodiments, two or more of R₄, R₅ and R₆ may form a cyclic structure, such as with N-methylpyrrolidine.

[0042] In one or more embodiments, the metal-aluminum layer comprises a metal aluminum carbide layer, a metal aluminum nitride layer, or a metal aluminum carbonitride layer. According to one or more embodiments, the metal-aluminum layer is oxide-free.

[0043] In some embodiments, one or more L's is an amidinate ligand. The metal amidinate precursor may comprise lanthanum tris(N,N'-diisopropylformamidinate).

[0044] According to one or more embodiments, the alkyl aluminum precursor comprises one or more of trimethyl aluminum, triethyl aluminum and dimethylaluminumhydride. In some embodiments, the alkyl aluminum precursor comprises trimethyl aluminum.

[0045] Another aspect of the invention relates to a method of depositing a lanthanum-aluminum layer by atomic layer deposition, the method comprising sequentially exposing a surface of a substrate to alternating pulses of lanthanum tris(N,N'-diisopropylformamidinate) and trimethyl aluminum to form on the surface a lanthanum-aluminum layer. In one or more embodiments, the lanthanum-aluminum layer is oxide-free. In some embodiments, the lanthanum-aluminum layer comprises lanthanum aluminum carbide.

[0046] The reaction conditions for the ALD reaction will be selected based on the properties of the selected ligands for the metal amidinate and the properties of the aluminum precursor. The deposition can be carried out at a reduced pressure. The vapor pressure of the metal amidinate should be low enough to be practical in such applications. The substrate temperature should be high enough to keep the bonds between the metal atoms at the surface intact and to prevent thermal decomposition of gaseous reactants. However, the substrate temperature should also be high enough to keep the source materials (i.e., the reactants) in the

gaseous phase and to provide sufficient activation energy for the surface reaction. The appropriate temperature depends on the specific precursors used and the pressure. According to one or more embodiments, the substrate is heated to a temperature of about 100 °C to about 500 °C.

5 **[0047]** The properties of a precursor for use in the ALD deposition methods of the invention can be evaluated using methods known in the art, allowing selection of appropriate temperature and pressure for the reaction. In general, lower molecular weight and the presence of functional groups that increase the rotational entropy of the ligand sphere result in a melting point that yields liquids at typical delivery temperatures and increased vapor pressure.

10 **[0048]** An optimized metal amidinate precursor for use in the deposition methods of the invention will have all of the requirements for sufficient vapor pressure, sufficient thermal stability at the selected substrate temperature and sufficient reactivity to produce a self-limiting reaction on the surface of the substrate without unwanted impurities in the thin film or condensation. Sufficient vapor pressure ensures that molecules of the source compound are
15 present at the substrate surface in sufficient concentration to enable a complete self-saturating reaction. Sufficient thermal stability ensures that the source compound will not be subject to the thermal decomposition which produces impurities in the thin film.

[0049] Any metal amidinate, including but not limited to complexes represented by formula (I) and/or (II), and having suitable vapor pressure properties may be used in the thin
20 layer film deposition methods of the invention.

[0050] In an exemplary embodiment of an ALD process, a first chemical precursor ("A") is pulsed, for example, delivering a metal species containing substituents to the substrate surface in a first half reaction. A first chemical precursor "A" is selected so its metal reacts with suitable underlying species to form new self-saturating surface. Excess unused reactants
25 and the reaction by-products are removed, typically by an evacuation-pump down and/or by a flowing inert purge gas. Then a second chemical precursor ("B"), is delivered to the surface, wherein the second chemical precursor "B" also forms self-saturating bonds with the underlying reactive species to provide another self-limiting and saturating second half reaction. A second purge period is typically utilized to remove unused reactants and the reaction by-
30 products.

[0051] To form another layer, a second pulse of the first chemical precursor "A" is delivered to the layer from the first deposition cycle, which then reacts with the layer on the substrate surface. The deposition cycle of pulses of the A precursor, B precursor, A precursor, B precursor (typically including purges between each pulse) is then repeated used to build a metal-aluminum layer of the desired thickness. It will be understood that the "A", "B", and purge gases can flow simultaneously, and the substrate and/or gas flow nozzle can oscillate such that the substrate is sequentially exposed to the A, purge, and B gases as desired.

[0052] In some embodiments, the first chemical precursor "A" is a metal amidinate precursor and the second chemical precursor "B" is an aluminum precursor, but it is possible to begin the cycle with either precursor.

[0053] The precursors and/or reactants may be in a state of gas, plasma, vapor or other state of matter useful for a vapor deposition process. 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 pulses of precursor and reactants.

[0054] In one or more embodiments, at least two different types of metal-containing precursors can be utilized. Thus, a "C" metal-containing precursor may be utilized, wherein the "C" metal-containing precursor is different from the "A" metal-containing precursor thereby providing ALD cycle A, B, C, B, A, B, C, B, A, B, C, B . . . (with purges in between each pulse). Likewise a different type of second reactant (a "D" reactant) may be utilized in a reaction sequence, in which "B" and "D" reactants are different to provide a reaction sequence in which the following pulsed ALD cycle is utilized A, B, C, D, A, B, C, D . . . (with purges between each pulse). As noted above, instead of pulsing the reactants, the gases can flow simultaneously from a gas delivery head or nozzle and the substrate and/or gas delivery head can be moved such that the substrate is sequentially exposed to the gases.

[0055] Of course, the aforementioned ALD cycles are merely exemplary of a wide variety of ALD process cycles in which a deposited layer is formed.

[0056] A deposition gas or a process gas as used herein refers to a single gas, multiple gases, a gas containing a plasma, combinations of gas(es) and/or plasma(s). A deposition gas may contain at least one reactive compound for a vapor deposition process. The reactive

compounds may be in a state of gas, plasma, vapor, during the vapor deposition process. Also, a process may contain a purge gas or a carrier gas and not contain a reactive compound.

[0057] A "substrate surface," as used herein, refers to any substrate or material surface formed on a substrate upon which film processing is performed during a fabrication process.

5 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. Barrier layers, metals or metal nitrides on a substrate surface
10 include titanium, titanium nitride, tungsten nitride, tantalum and tantalum nitride, aluminum, copper, or any other conductor or conductive or non-conductive barrier layer useful for device fabrication. Substrates may have various dimensions, such as 200 mm or 300 mm diameter wafers, as well as, rectangular or square panes. Substrates on which embodiments of the invention may be useful include, but are not limited to semiconductor wafers, such as
15 crystalline silicon (e.g., Si<100> or Si<111>), silicon oxide, strained silicon, silicon germanium, doped or undoped polysilicon, doped or undoped silicon wafers, III-V materials such as GaAs, GaN, InP, etc. and patterned or non-patterned wafers. Substrates may be exposed to a pretreatment process to polish, etch, reduce, oxidize, hydroxylate, anneal and/or bake the substrate surface.

20 [0058] The reactants are typically in vapor or gas form. The reactants may be delivered with a carrier gas. A carrier gas, a purge gas, a deposition gas, or other process gas may contain nitrogen, hydrogen, argon, neon, helium, or combinations thereof. Plasmas may be useful for depositing, forming, annealing, treating, or other processing of the materials described herein.

25 [0059] In one or more embodiments, the various gases for the process may be pulsed into an inlet, through a gas channel, from various holes or outlets, and into a central channel. In one or more embodiments, the deposition gases may be sequentially pulsed to and through a showerhead. Alternatively, as described above, the gases can flow simultaneously through gas supply nozzle or head and the substrate and/or the gas supply head can be moved so that the
30 substrate is sequentially exposed to the gases.

[0060] Another aspect of the invention pertains to an apparatus for deposition of a film on a substrate to perform a process according to any of the embodiments described above. In one embodiment, the apparatus comprises a deposition chamber for CVD or ALD of a film on a substrate. The chamber comprises a process area for supporting a substrate. The apparatus include a first inlet in fluid communication with a supply of metal amidinate precursor. The apparatus further includes a second inlet in fluid communication with a purge gas. The apparatus further includes a third inlet in fluid communication with a supply of aluminum precursor. The apparatus can further include a vacuum port for removing gas from the deposition chamber. The apparatus can further include a fourth inlet for supplying one or more auxiliary gases such as inert gases to the deposition chamber. The apparatus can further include a means for heating the substrate by radiant and/or resistive heat.

[0061] Another aspect of the invention pertains to a metal-aluminum layer deposited by any of the methods described herein. In one or more embodiments, metal-aluminum layer has a thickness in the range from about 1 to about 10 nm. In some embodiments, the metal-aluminum layer is less than 5 weight % oxygen.

[0062] In one or more embodiments, the metal-aluminum layer comprises a metal aluminum carbide layer, a metal aluminum nitride layer, or a metal aluminum carbonitride layer.

EXAMPLES

Example 1 – ALD of lanthanum tris(*N,N'*-diisopropylformamidinate) and trimethyl aluminum

[0063] A lanthanum-aluminum carbide layer was produced on a substrate by atomic layer deposition of lanthanum tris(*N,N'*-diisopropylformamidinate) and trimethyl aluminum. The substrate was heated to a temperature of about 400 °C and the pressure of the deposition chamber was about 5 torr.

[0064] 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.

What is claimed is:

1. A method of depositing a metal-aluminum layer, the method comprising:

exposing a substrate surface to pulses of an amidinate precursor and an aluminum precursor to form a metal-aluminum layer on the substrate surface, wherein the amidinate precursor comprises a p or f-block metal and the aluminum precursor comprises an alkyl aluminum precursor or an amine alane, and with the proviso that the substrate surface is not exposed to an oxidant during formation of the metal-aluminum layer.

2. The method of claim 1, wherein the substrate surface is exposed to the pulses sequentially, simultaneously, or substantially simultaneously.

3. The method of claim 1 or 2, wherein the metal amidinate precursor comprises an f-block metal.

4. The method of any of claims 1-3, further comprising exposing the substrate surface to a second metal amidinate precursor comprising a second p or f-block metal.

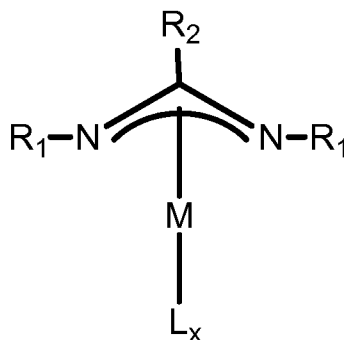
5. The method of any of claims 1-4, wherein the metal-aluminum layer comprises a metal aluminum carbide layer, a metal aluminum nitride layer, or a metal aluminum carbonitride layer.

6. The method of any of claims 1-5, wherein the metal-aluminum layer is less than 5 weight % oxygen.

7. The method of any of claims 1-6, wherein the substrate is heated to a temperature of about 100 °C to about 500 °C.

8. The method of any of claims 1-7, wherein the metal amidinate precursor has a structure represented by:

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wherein R_1 and R_2 are each independently hydrogen or a C_{1-8} straight or branched alkyl, M is p or f-block metal, L_x are x ligands, x is a number from 1-4, and with each L independently being the same or different ligand as another L.

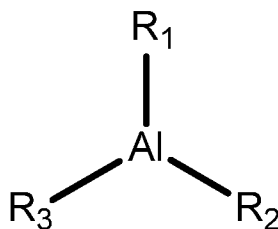
5

9. The method of any of claims 1-8, wherein one or more L's is an amidinate ligand.

10. The method of any of claims 1-9, wherein the metal amidinate precursor comprises lanthanum tris(*N,N'*-diisopropylformamidinate).

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11. The method of any of claims 1-10, wherein the aluminum precursor comprises an alkyl aluminum precursor having a structure represented by:



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wherein R_1 , R_2 and R_3 are each independently hydrogen or a C_1 - C_8 straight or branched alkyl.

12. The method of any of claims 1-11, wherein the alkyl aluminum precursor comprises one or more of trimethyl aluminum, triethyl aluminum and dimethylaluminumhydride.

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13. The method of any of claims 1-12, wherein the aluminum precursor comprises alane coordinated to a tertiary amine having a molecular weight less than or equal to 250 g/mol.

5 14. A metal-aluminum layer deposited by the method of any of claims 1-13.

15. The metal-aluminum layer of claim 14, wherein the metal-aluminum layer has a thickness in the range from about 1 to about 10 nm.

A. CLASSIFICATION OF SUBJECT MATTER***H01L 21/205(2006.01)i, C23C 16/44(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; C01F 17/00; H01L 21/469; H01L 29/78; C07F 1/08; H01L 21/31; C23C 16/18; C23C 16/00; H01L 21/285

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-aluminum layer,deposition,precursor

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2007-0237697 A1 (ROBERT D. CLARK) 11 October 2007 See paragraphs [0035], [0056]; and claims 1-2.	1-3
A	US 2009-0315093 A1 (DONG LI et al.) 24 December 2009 See claims 1, 7; and figure 1.	1-3
A	US 7053009 B2 (JOHN F. CONLEY, JR. et al.) 30 May 2006 See column 9, line 49 - column 10, line 10; and figure 3.	1-3
A	US 7867919 B2 (KIE Y. AHN et al.) 11 January 2011 See column 8, line 43 - column 9, line 45; and figure 2.	1-3
A	KR 10-2010-0017170 A (L'AIR LIQUIDE SOCIETE ANONYME POUR L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGES CLAUDE) 16 February 2010 See paragraphs [0018]-[0039]; and claims 1, 5.	1-3
A	CHARLES B. MUSGRAVE et al., "Precursors For Atomic Layer Deposition Of High-k Dielectrics", Future Fab International, January 2005, Vol 18, pages 126-128 See 3rd page, 2nd and 3rd column.	1-3



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

28 FEBRUARY 2013 (28.02.2013)

Date of mailing of the international search report

04 MARCH 2013 (04.03.2013)

Name and mailing address of the ISA/KR



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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2012/055490**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.: 15
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:
Claim [15] is not clear, since this claim refers to multiple dependent claim [14] which does not comply with PCT Rule 6.4(a).
3. ☒ Claims Nos.: 4-14
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 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.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2012/055490

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