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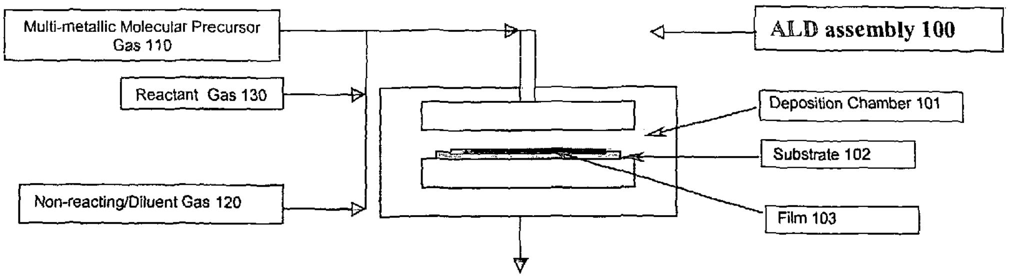

(57) Abstract: Atomic layer deposition methods for depositing conformal homogeneous multi-component films on substrates are provided. In one method, a pulse of multi-metallic molecular precursor is introduced into a deposition chamber where a substrate is located. The multi-metallic molecular precursor contains the metallic elements necessary to form a mono-layer of the multi-metallic film. In another method, a mixture of two or more metallic precursors is pulsed into a deposition chamber where a substrate is located. The mixture of metallic precursors contains the metallic elements necessary to form a mono-layer of the multi-metallic film. In both methods, subsequent reactants are pulsed into the chamber to convert the precursors into the desired mono-layer. The cycle is repeated as many times as necessary to achieve a film of desired thickness. Illustrative films that may be formed by these processes include metallic alloy films, multi-metallic oxide films, multi-metallic nitride films and multi-metallic oxynitride films. By introducing the multiple metallic components in a single pulse in per cycle, throughput is increased. In addition, by introducing the multiple metallic components in a single pulse, a homogeneous film is formed that does not require subsequent annealing.

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MOLECULAR LAYER DEPOSITION OF THIN FILMS WITH MIXED COMPONENTS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is related to, and claims priority to, United States Provisional Patent Application No. 60/397,029, entitled Molecular Layer Deposition Of Thin Films With Mixed Components, filed July 18, 2002, the entire disclosure of which is hereby incorporated by reference.

FIELD OF THE INVENTION

The present invention relates to the field of semiconductors. More specifically, the present invention relates to the atomic layer deposition (ALD) of thin conformal homogeneous multi-metallic films onto semiconductor devices and wafers.

BACKGROUND OF THE INVENTION

The next generation of semiconductor devices will require thinner dielectric films for metal-oxide-silicon (MOS) transistor gates and capacitor dielectrics. However, as oxides are scaled down, the tunneling leakage current becomes more significant and limits the useful range for gate oxides to a thickness of about 1.8 nm or more. Accordingly, extensive research is being done to identify high-k materials that, when made ultra-thin, provide the dielectric properties of silicon dioxide minus the leakage.

Thin multi-metallic films are of increasing interest in the microelectronic industry. For example, hafnium silicate (Hf-Si-O) films are considered a possible alternative gate oxide film to silicon oxide (Si-O) films. Similarly, tantalum silicon nitride (Ta-Si-N) films are reported to have better properties than tantalum nitride (TaN) films as a barrier for copper interconnect.

Current deposition techniques for forming films onto semiconductor devices and wafers include chemical vapor deposition (CVD). In CVD, two or more reactant gases are mixed together in a deposition chamber where the gases either react in the gas phase and precipitate a film onto a substrate's surface or react directly on the substrate's surface. Deposition by CVD occurs for a specified length of time, based on the desired thickness of the deposited film. Since the specified time is a function of the flux of reactants into the chamber, the required time may vary from chamber to chamber.

CVD is increasingly unable to meet the requirements for making advanced thin films. CVD requires high processing temperatures and makes inefficient use of reactants. In addition, CVD results in the presence of a relatively high level of impurities in the resultant film. Finally, CVD is limited in its ability to deposit ultra-thin homogeneous conformal films for high k gate dielectrics onto wafers.

Atomic layer deposition (ALD) is an alternative to traditional CVD for depositing thin films. In a conventional ALD deposition cycle, each reactant gas is introduced sequentially into the chamber, so that no gas phase intermixing occurs. A monolayer of a first reactant (*i.e.*, precursor) is physi- or chemisorbed onto the substrate's surface. Excessive first reactant is then evacuated, usually with the aid of an inert purge gas and/or pumping. A second reactant is then introduced to the deposition chamber and reacts with the first reactant to form a mono-layer of the desired film through a self-limiting surface reaction. The self-limiting reaction stops once the initially adsorbed first reactant fully reacts with the second reactant. Excessive second reactant is evacuated usually with the aid of an inert purge gas and/or pumping. A desired film thickness is obtained by repeating the deposition cycle as necessary. The film thickness can be controlled to atomic layer (i.e., angstrom scale) accuracy by counting the number of deposition cycles.

ALD has several advantages over traditional CVD. First, ALD can be performed at lower temperatures. Second, ALD can produce ultra-thin conformal films. In fact, ALD can control film thickness on an atomic scale and be used to "nano-engineer" complex thin films. Third, ALD provides conformal coverage of thin films on non-planar substrates.

However, one problem with conventional ALD processes is the low throughput that results from long cycle times. Conventional ALD processes perform a relatively slow "layer-by layer" growth using alternating doses of precursor and reactant. This problem is exacerbated when the deposited film is a multi-metallic film, since multiple precursors are employed. The deposition rate of multi-metallic films is typically less than 1 Å per cycle. To be useful in semiconductor manufacturing, an ALD process must demonstrate an acceptable throughput.

Another difficulty in the production of multi-metallic films using conventional ALD processes is the non-homogeneity of the resultant film. Homogenous films are desired, for example, in MOS device applications. Conventional ALD processes, due to the use of alternating doses of chemical sources, form films that are a series of phase separated nano-laminates. Subsequent high temperature annealing is required to inter-diffuse the multiple elements to form a homogeneous composition. Accordingly, there is a significant need in the industry for further developments.

SUMMARY OF THE INVENTION

The present invention provides new ALD methods for depositing conformal homogeneous multi-metallic films onto substrates. Films that may be deposited by the ALD method of the present invention include metallic alloy films, multi-metallic oxide films, multi-metallic nitride films, and multi-metallic oxynitride films. ALD depositions embraced by the method of the present invention include thermal ALD, photo-assisted ALD, laser assisted ALD, plasma-assisted ALD and radical assisted ALD.

A first ALD method for forming a multi-metallic film on a substrate comprises at least one cycle that comprises the step of introducing a multi-metallic molecular precursor gas into a deposition chamber that contains the substrate. Preferably, the multi-metallic molecular precursor comprises all of the metallic elements necessary to make a homogeneous mono-layer of the film. By introducing the metallic elements in a single pulse per cycle, as part of a single precursor, the metallic elements are mixed uniformly on a molecular level and the need to for alternate doses of multiple precursors is eliminated. One example of a multi-metallic molecular precursor is tri-(tert-butoxy)siloxy-tri(tert-butoxy)titanium - $(tBuO)_3Si$-O-

$Ti(OtBu)_3$ - which can be used to deposit titanium silicate (Ti-Si-O) films when the subsequent reactant is an oxygen source.

In one embodiment, the first ALD method includes at least one cycle that comprises the following steps: (i) introducing a multi-metallic molecular precursor gas into a deposition chamber that contains a substrate; (ii) purging the deposition chamber; (iii) introducing one or more reactant gases to the deposition chamber; and (iv) purging the deposition chamber. By this method, the multi-metallic molecular precursor is physi-or chemisorbed onto the substrate's surface and the subsequent reactant cleaves any undesirable ligands from the precursor, leaving a mono-layer of the desired multi-metallic film. The reactant can be any oxidizing or reducing agent or mixture thereof and is selected to convert the physi-or chemisorbed precursor into the type of multi-metallic film desired. Each time the cycle is repeated, another mono-layer is added. In this manner, a conformal homogeneous film of the desired thickness and composition can be nano-engineered.

In another aspect of the invention, a second ALD method is provided for forming a multi-metallic film on a substrate comprising at least one cycle that comprises the step of introducing a mixture of metallic molecular precursor gases into a deposition chamber that contains the substrate. Preferably, the mixture of precursors comprises all of the metallic elements necessary to make a homogeneous mono-layer of the film. By introducing the metallic elements in a single pulse per cycle, as part of a cocktail of precursors, the metallic elements are mixed uniformly on a molecular level and the need to for alternate doses of multiple precursors is eliminated. One example of a suitable precursor cocktail is a mixture of the two compounds $Hf(NEtMe)_2$ and $Si(NEtMe)_2$ – which can be used to deposit hafnium silicate (Hf-Si-O) films when the subsequent reactant is an oxygen source.

In one embodiment, the first ALD method comprises at least one cycle that comprises the following steps: (i) introducing a mixture of at least two different metallic molecular precursors to a deposition chamber; (ii) purging the deposition chamber; (iii) introducing a reactant gas to the deposition chamber; and (iv) purging the deposition chamber. By this method, the mixture, or cocktail, of metallic molecular precursors is first physi- or chemisorbed onto the substrate's surface and the subsequent reactant cleaves any undesirable ligands from the precursors, leaving a mono-layer of the desired multi-metallic film. Once again, the reactant can be any oxidizing or reducing agent or combination thereof and is selected to convert the physi- or chemisorbed precursors into the type of multi-metallic film desired. Each time the cycle is repeated, another mono-layer is added. In this manner, a conformal homogeneous film of the desired thickness and composition can be nano-engineered.

Both methods permit all of the metallic elements necessary to make the multi-metallic film to be supplied in a single dose, or pulse, in each deposition cycle. Thus, the inventions provide several benefits. First, the inventions significantly reduce ALD process cycle time and, thereby, increase throughput. Second, the inventions form homogeneous films as-deposited, which eliminates the need for subsequent annealing. Third, the inventions increase efficiency by reducing the number of particles generated in the gas phase during the film deposition process.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention is described in detail below and with reference to the following figures, in which:

FIGS. 1A, 1B and **1C** illustrate schematic diagrams of an ALD systems and method according to various embodiments of the present invention;

FIGS. 2A, 2B, 2C and **2D** also illustrates ALD systems and methods according to additional embodiments of the present invention;

FIG. 3 illustrates a schematic diagram of an ALD system and method of the present invention; and

FIG. 4 is a TEM cross section image of a 45Å $Hf_{0.58}Si_{0.42}O_2$ film made in accordance with one of the ALD methods of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

"Metal" as used herein is an element selected the following elements in the periodic table: Li; Be; Na; Mg; Al; K; Ca; Sc; Ti; V; Cr; Mn; Fe; Co; Ni; Cu; Zn; Ga; Ge; Rb; Sr; Y; Zr; Nb; Mo; Tc; Ru; Rh; Pd; Ag; Cd; In; Sn; Sb; Cs; Ba; La; Hf; Ta; W; Re; Os; Ir; Pt; Au; Hg; Tl; Pb; Bi; Po; Fr; Ra; Ac; Ce; Pr; Nd; Pm; Sm; Eu; Gd; Tb; Dy; Ho; Er; Tm; Yb; Lu; Th; Pa; U; Np; Pu; Am; Cm; Bk; Cf; Es; Fm; Md; No; and Lr.

"Metalloid" as used herein is an element selected from the following elements in the periodic table: B; Si; Ge; As; Sb; Te and At.

"Metallic" as used herein indicates the presence of at least one element selected from metals and metalloids as defined above.

"Multi-metallic" as used herein indicates the presence of two or more elements selected from metals and metalloids as defined above.

"Molecular precursor" as used herein is a reactant used to introduce atoms or chemical groups onto a substrate to form a film. The molecular precursor is physi- or chemisorbed onto the surface of a substrate and must be modified by a subsequent reactant or reactants to produce the desired film.

"Metallic molecular precursor" as used herein is a molecular precursor that contains at least one element selected from metals and metalloids as defined above.

"Multi-metallic molecular precursor" as used herein is a molecular precursor that contains at least two elements selected from metals and metalloids as defined above.

"Leaving groups" and "ligands," as used interchangeably herein, refer to atoms or chemical groups in a metallic molecular precursor that are attached, covalently or non-covalently, to the metallic components therein.

"Hydrogen source" means any compound that contains within its structure reactive hydrogen and includes but is not limited to hydrogen gas and the like.

"Oxygen source" means any compound that contains within is structure a reactive oxygen including but not limited to atomic oxygen, oxygen gas, ozone, water, alcohols, hydrogen peroxide and the like.

"Nitrogen source" means any compound that contains within its structure a reactive nitrogen and includes but is not limited to atomic nitrogen, nitrogen gas, ammonia, hydrazine, alkylhydrazine, alkylamine and the like.

"Multi-metallic film" as used herein is any film whose components, not counting any contaminants, includes two or more elements selected from metals and metalloids as defined above. Illustrative multi-metallic films include but are not limited to metallic alloy films, multi-metallic oxide films, multi-metallic nitride films and multi-metallic oxynitride films.

"Metallic alloy film" as used herein is a film formed principally from metal and/or metalloid elements as defined above.

"Oxide film" as used herein is a film formed principally from oxygen and at least one type of metal or metalloid as defined above.

"Nitride film" as used herein is a film formed principally from nitrogen and at least one type of metal or metalloid as defined above.

"Oxynitride film" as used herein is a film formed principally from oxygen, nitrogen, and at least one type of metal or metalloid as defined above.

Overview

In one aspect of the present invention, a multi-metallic molecular precursor is utilized in an ALD process to deposit conformal homogeneous multi-metallic films onto substrates. In another aspect, a mixture, or cocktail, of two or more metallic molecular precursors is utilized in an ALD process to deposit conformal homogeneous multi-metallic films onto substrates. Preferably, in both embodiments, all of the metallic elements necessary to make the multi-metallic films are introduced in a single dose or pulse in each deposition cycle.

Accordingly, the present invention eliminates the need to alternate pulses of two or more metallic precursors and, thereby, increases throughput. Furthermore, the present invention generates a homogeneous film as deposited, thereby eliminating the need to subsequently anneal the film. The invention reduces the particles generated in the gas phase during the film deposition, among other advantages.

Multi-Metallic Molecular Precursor Compounds

A first ALD method for forming multi-metallic films on a substrate comprises at least one cycle that comprises the step of introducing a multi-metallic molecular precursor gas into a deposition chamber that contains a substrate. In one embodiment, the method for forming multi-metallic films on a substrate comprises at least one cycle that comprises the following steps: (i) introducing a multi-metallic molecular precursor gas into a deposition chamber that contains a substrate; (ii) purging the deposition chamber; (iii) introducing one or more reactant gases to the deposition chamber; and (iv) purging the deposition chamber.

The multi-metallic molecular precursor contains, within each molecule, the different metallic elements required to make the desired film. In one embodiment, the multi-metallic molecular precursor comprises the following formula:

$$(L^1)_aM^1GM^2(L^2)_b$$

where M^1 and M^2 are different metallic elements, where each L^1 and L^2 is a leaving group (ligand) and may be the same or different, where a and b are integers less than a valence number for M^1 and M^2, respectively, and where G is selected from a single bond, double bond, bridging atom and bridging group.

M^1 and M^2 can be any metallic element as long as M^1 and M^2 are not identical. Preferred metallic elements for use as M^1 and M^2 include Si, Li, Be, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Ba, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Tl, Pb, Bi, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Th.

G can be a single bond, double bond, bridging atom or bridging group. Preferred selections for G include a single bond (-), an oxygen bridge (-O-), a nitrogen bridge (-N=), a secondary or tertiary amine bridge ($-NR^s-$), a sulfur bridge (-S-) and a secondary or tertiary phosphorous bridge ($-PR^s$), where R^s is can be hydrogen or any known substituent. Preferably, R^s is selected from hydrogen and C1-C6 alkyls.

L^1 and L^2 is selected, independently, from ligands and may be the same or different. Suitable ligands are readily ascertainable by those of ordinary skill in the art and include those ligands known to be useful in precursors for ALD processes. Undesirable ligands are removed during the course of film deposition due to their relatively weak chemical bonds. Preferred ligands include alkyls, alkoxides, halides, hydrides, amides, imides, azides, nitrates, cyclopentadienyls, carbonyls, carboxylates, diketonates, as well as substituted analogs thereof and combinations thereof. It is preferable, but not necessary to use relatively small ligands having, *e.g.*, 1-12 atoms. Compounds that contain small relatively small ligands tend to volatilize more readily at lower temperatures than compounds that contain relatively larger ligands. Specific preferred ligands include dimethylamide ($-N(CH_3)_2$), diethylamide ($-N(CH_2CH_3)_2$), methylethylamide ($-N(CH_3)(CH_2CH_3)$), methoxide ($-OCH_3$), ethoxide ($-OCH_2CH_3$), and butoxide ($-O(CH_2)_3CH_3$).

Variables a and b are integers less than a valence number for M^1 and M^2, respectively. Preferably, a an b are integers one less than a valence number for M^1 and M^2, respectively. More preferably, a and b are selected, independently, from 1, 2 and 3.

In one embodiment, the multi-metallic precursor comprises the following formula:

$$(R^1O)_x(R^2R^3N)_{3-x}Si\text{-}O\text{-}M(OR^4)_y(NR^5R^6)_{v-y},$$

where R^1, R^2, R^3, R^4, R^5 and R^6 are, independently, selected from H, F, C1-C6 alkyls and substituted C1-C6 alkyls, where M is selected from Si, Li, Be, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Ba, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Tl, Pb, Bi, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Th, where x is selected from 1, 2 and 3, where y is an integer less than or equal to v and where v is an integer one less than a valance number for M. Preferred selections for R^2, R^3, R^5 and R^6 are methyl and ethyl. Preferred selections for R^1 and R^4 are methyl, ethyl, propyl, and butyl. Preferred selections for M are Ti, Zr, and Hf and, in such cases, v is selected from the integers 1, 2 and 3.

A specific example of a suitable multi-metallic molecular precursor is tri-(tert-butoxy)siloxy-tri(tert-butoxy)titanium ($(tBuO)_3Si\text{-}O\text{-}Ti(OtBu)_3$), which can be used to deposit a titanium silicate (Ti-Si-O).

FIGS. 1A, 1B and 1C show various ways in which the multi-metallic molecular precursors can be utilized to deposit a homogeneous conformal film on a substrate. **FIGS. 1A, 1B and 1C** show a simplified cross sectional schematic view of an ALD assembly **100.** The ALD assembly **100** comprises a deposition chamber **101**. Positioned within the deposition chamber **101** is a substrate or wafer **102.** It is on the surface of the wafer **102** that a homogenous conformal film **103** of desired thickness will be deposited. Connected to the deposition chamber **101** are one or more supply lines for providing multi-metallic molecular precursor vapor **110**, diluent gas **120** and reactant gas **130** to the deposition chamber **101**.

The substrate **102** can be any material with a metallic or hydrophilic surface which is stable at the processing temperatures employed. Suitable materials will be readily evident to those of ordinary skill in the art. Preferred substrates **102** include silicon wafers. The substrate **102** may be pretreated to instill, remove, or standardize the chemical makeup and/or properties of the substrate's **102** surface. For example, silicon wafers form silicon dioxide on exposed surfaces. Silicon dioxide in small amounts is desirable because it attracts the metal precursor to the surface. However, in large quantities, silicon dioxide is undesirable. This is especially true if the layer being formed is intended to be a substitute for silicon dioxide. Accordingly, silicon dioxide on the surface of silicon wafers is often stripped away, for example, by treatment with hydrogen fluoride (HF) gas prior to film formation. A thin standardized silicon dioxide surface layer, only a few Å thick, is then reintroduced prior to film formation by standard oxidation methods, for example, by exposure to ozone.

The multi-metallic molecular precursor vapor **110** comprises a vaporized compound having the formula $(L^1)_aM^1GM^2(L^2)_b$, wherein M^1, M^2, G, L^1, L^2, a and b are as previously described. The compound is a liquid or solid at room temperature. The compound may be dissolved in a solid. Preferably, the compound is, or is dissolved in, a liquid. The precursor vapor **110** can be generated by direct vaporization of the solid or liquid compound in a vaporizer, with or without solvent, or by using a bubbler.

The diluent gas **120** can be any non-reactive gas or mixture of non-reactive gases, including any noble gas or gases. Typical non-reactive gases include Ar, He, Ne, Xe, and N_2.

The reactant gas **130** can be any reducing agent or oxidizing agent or a mixture thereof. Thus, in **FIG. 1B**, the reactant gas **130** is reducing agent **130'** and in **FIG. 1C** the reactant gas **130** is oxidizing agent **130"**. The reducing agent **130'** or oxidizing agent **130"** may be a gas or a liquid at room temperature but it is introduced to the deposition chamber **101** as a gas. The nature of the reactant gas **130** is selected based on the nature of the multi-metallic film desired.

In **FIGS. 1A, 1B and 1C**, a multi-metallic film **103** is formed to a desired thickness on wafer **102** under conditions of ALD. The multi-metallic molecular precursor gas **110** reacts with the reactant gas **130** (which may be oxidizer **130'** or reducer **130"**) to form film **103**.

More specifically, when wafer **102** is placed in deposition chamber **101**, the deposition chamber **101** is evacuated of gases and the wafer **102** is heated to a set deposition temperature. The deposition temperature can range anywhere from approximately 100 °C to 600 °C, but is preferably from approximately 300 °C to 500 °C. A steady flow of a diluent gas **120**, *e.g.*, Ar, He, Ne, Xe, or N_2, is then introduced. The pressure is raised by the introduction of the diluent gas **120** to a set process pressure, which can range anywhere from approximately 100 mTorr to 10 Torr, but is preferably from approximately 200 mTorr to 1.5 Torr. After a steady state pressure has been achieved and after sufficient time has been provided to allow residual gases to be evacuated from the surface of the wafer, the ALD cycle begins.

In the first step, a pulse of the multi-metallic molecular precursor vapor **110** is introduced into the deposition chamber **101** by opening appropriate valves. The vapor flow for the precursor gas **110** can range anywhere from approximately 1 sccm to 1000 sccm, but is preferably in the range of from approximately 5 sccm to 100 sccm. The precursor vapor **110** can be diluted by diluent gas **120**. In such cases, the flow rate for the diluent gas **120** can range anywhere from approximately 100 sccm to 1000 sccm. The precursor vapor **110** can be generated using a bubbler or by direct vaporization of liquid or solid in a vaporizer. The pulse time for the precursor gas **110** can range anywhere from approximately 0.01 s to 10 s, but is preferably in the range of from approximately 0.05 s to 2 s. At the end of the pulse, the flow of precursor vapor **110** into the chamber is terminated either by directing the flow of precursor vapor **110** into an exhaust line (for direct vaporization of the liquid) or by diverting the flow of precursor vapor **110** around the bubbler.

In the second step, the deposition chamber **101** is purged for an appropriate time. Preferably, during the purge, non-reactive gas **120** flows into the chamber **101** through the vapor delivery line. For example, the non-reacting diluent gas **120** can be He, Ne, Ar, Xe, or N_2. The amount of non-reacting gas **120** utilized in this step is preferably the same as the total flow of precursor gas **110** during the precursor vapor **110** pulse step. The vapor purge time can be from approximately 0.1 s to 10 s but is preferably from approximately 0.5 s to 5 s. Alternatively, the purge can be accomplished by pumping excess precursor gas **110** out of the chamber **101** in addition to, or in lieu of, pulsing non-reacting gas **120** into the chamber **101**. Pumping generally entails the use vacuum or low pressure to cause evacuation.

In the third step, at the end of the vapor purge, a flow of reactant gas **130** is directed into the deposition chamber **101**. The reactant gas **130** is chosen depending on the desired material to be deposited and may, for example, be a reducing agent **130'** or an oxidizing agent **130"**. The flow of reactant gas **130** can range from approximately 100 sccm to 2000 sccm but is preferably in the range approximately 200 sccm to 1000 sccm. The pulse time for the reactant gas **130** can range anywhere from 0.1 s to 10 s, but is preferably from 0.5 s to 3 s.

In the fourth and final step of the cycle, after the pulse of the reactant gas **130** is completed, the chamber **101** is purged using a flow of non-reacting gas **120**. For example, the non-reacting gas **120** can be He, Ne, Ar, Xe, or N_2. The purge flow for the non-reacting gas **120** is preferably the same as the total flow of reactant gas **130** through the reactant delivery line during the pulse of the reactant gas **130**. Alternatively, the purge can be accomplished by pumping excess reactant gas **130** out of the chamber **101** in addition to, or in lieu of, pulsing non-reacting gas **120** into the chamber **101**.

This completes one cycle in the ALD process and generates a conformal homogeneous mono-layer of the desired film. The cycle is then repeated as many times as necessary to achieve the desired film thickness.

As stated, the reactant gas **130** is chosen depending on the desired material to be deposited and may, for example, be a reducing agent **130'** or an oxidizing agent **130"**. This is illustrated in more detail with reference to **FIGS. 2A**, **2B**, **2C** and **2D**.

FIGS. 2A, **2B**, **2C** and **2D** are identical with **FIG. 1** with three exceptions. First, the multi-metallic molecular precursor **210** has the following formula:

$$(R^1O)_u(R^2R^3N)_{t-u}M^1\text{-}O\text{-}M^2(OR^4)_y(NR^5R^6)_{v-y},$$

where M^1, M^2, R^1, R^2, R^3, R^4, R^5, R^6, v and y are as previously defined, where u is an integer less than or equal to t and where t is an integer one less than a valence number for M^1. Second, the reactant gases employed are a hydrogen source **231**, an oxygen source **232**, a nitrogen source **233** or a combination of a oxygen source **232** and nitrogen source **233**, respectively. Third, the films deposited are a metallic alloy film **204**, a multi-metallic oxide film **205**, a multi-metallic nitride film **206** and a multi-metallic oxynitride film **207**, respectively.

In **FIG. 2A**, a metallic alloy film **204** is produced from pulses of precursor **210** and a hydrogen source **231**. Suitable hydrogen sources **231** include hydrogen (H_2) gas. Each cycle in this process deposits a mono-layer of metallic alloy film **204**. In one embodiment, M^2 in the formula for precursor **210** is silicon, so the resultant film has the formula (M^1-Si) where M^1 is as previously defined. For example, if the metallic elements selected for M^1 and M^2 in the formula for precursor **210** are hafnium and silicon, respectively, then a hafnium silicide (Hf-Si) film is deposited. This process should work equally well if the B in the multi-metallic precursor is a covalent bond.

In **FIG. 2B**, a multi-metallic oxide film **205** is produced from pulses of precursor **210** and an oxygen source **232**. Suitable oxygen sources **232** include but are not limited to atomic oxygen (O), oxygen gas (O_2), ozone (O_3), steam (H_2O), hydrogen peroxide (H_2O_2), alcohols, nitric oxide (NO) and nitrous oxide (N_2O). Ozone is a preferred oxygen source due to its ability to react at lower temperatures and minimize the amount of contaminants in the resultant film. Each cycle deposits a mono-layer of oxide film **205**. In one embodiment, M^2 in the formula for precursor **210** is silicon, so the resultant film has the formula (M^1-Si-O) where M^1 is as previously defined. For example, if the metallic elements selected for M^1 and M^2 in the formula for precursor **210** are hafnium and silicon, respectively, then a hafnium silicate (Hf-Si-O) film is deposited. This method should work equally well if the B in the multi-metallic precursor is a covalent bond.

In **FIG. 2C**, a multi-metallic nitride film **206** is produced from pulses of precursor **210** and a nitrogen source **233**. Suitable nitrogen sources include but are not limited to atomic nitrogen (N), nitrogen gas (N_2), ammonia (NH_3), hydrazine (H_2NNH_2), alkylhydrazine, alkylamine, and mixtures thereof. In one embodiment, M^2 in the formula for precursor **210** is silicon, so the resultant film has the formula (M^1-Si-N) where M^1 is as previously defined. For example, if the metallic elements selected for M^1 and M^2 in the formula for precursor **210** are tantalum and silicon, respectively, then a tantalum silicon nitride (Ta-Si-N) film is deposited. This method should work equally well if the B in the multi-metallic precursor is a covalent bond or a secondary or tertiary amine.

In **FIG. 2D**, a multi-metallic oxynitride film **207** is produced from pulses of precursor **210**, an oxygen source **232** and a nitrogen source **233**. Suitable oxygen and nitrogen sources include those discussed above with reference to **FIGS. 2B** and **2C**. In one embodiment, M^2 in the formula for precursor **210** is silicon, so the resultant film has the formula (M^1-Si-O-N) where M^1 is as previously defined. For example, if the metallic elements selected from M^1 and M^2 in the formula for precursor **210** are titanium and silicon, respectively, then a titanium silicon oxynitride (Ti-Si-O-N) film is deposited.

The multi-metallic molecular precursors of the instant invention may comprise more than two metallic elements. For example, multi-metallic molecular precursors having three and four metallic elements can be represented by the following respective formulae:

$$(L^1)_aM^1G^1M^2(L^2)_bG^2M^3(L^3)_c;$$

and

$$(L^1)_aM^1G^1M^2(L^2)_bG^2M^3(L^3)_cG^3M^4(L^4)_d$$

where M^1, M^2, L^1, L^2, a and b are as previously defined, where M^3 and M^4 are metallic elements which may be the same and/or may be identical to either M^1 or M^2, where L^3 and L^4

are ligands, where c and d are selected from integers less than a valence number for M^3 and M^4, respectively, and where G^1, G^2 and G^3 are each, independently, selected from a single bond, double bond, bridging atom and bridging group. In general, however, as the precursor becomes larger it is harder to keep in solution and vaporize. Furthermore, as the precursor gets larger, its stability becomes a bigger concern. Accordingly, it is preferable to use multi-metallic precursors that contain only two metallic elements.

Multi-metallic molecular precursors can be mixed with other multi-metallic and/or metallic precursors to create homogenous films with controlled ratios of metallic components. For example, a 50:50 mixture of $(tBuO)_3Si-O-Ti(OtBu)_3$ and $(tBuO)_3Si-O-Si(OtBu)_3$ should yield a homogenous film that contains a 4:1 ratio of silicon to titanium. Alternatively, a 50:50 mixture of a 50:50 $(tBuO)_3Si-O-Ti(OtBu)_3$ and $(tBuO)_4Si$ should yield a homogeneous film that contains a 3:1 ratio of silicon to titanium. Preferably, in such embodiments, the precursors are mixed either in the solvent phase, prior to vaporization, or in the gas phase, after vaporization, and introduced to the deposition chamber simultaneously. In addition, it is preferable in such embodiments to select similar, and even more preferably identical, ligands for the different precursors. The use of similar or identical ligands facilitates the ability to dissolve the different precursors uniformly in a single solvent under similar conditions.

In addition, the multi-metallic molecular precursors can be utilized in an ALD process that introduce other precursors in separate pulses. This is not a preferred embodiment, as it fails to embrace the full benefit of the invention which permits the precursor introduction to be consolidated into a single step. Nonetheless, the use of multi-metallic molecular precursors in any ALD process will consolidate the number of pulses necessary and further the homogeneity of the resultant film. Accordingly, ALD processes that introduce other precursors in separate pulses are also embraced if they utilize a multi-metallic molecular precursor.

Multi-Metallic Molecular Precursor Cocktails

In another aspect of the present invention, a second ALD method for forming a multi-metallic film on a substrate comprises at least one cycle that comprises the step of introducing a mixture of metallic molecular precursor gases into a deposition chamber that contains the substrate. In one embodiment, the second ALD method comprises at least one cycle that comprises the following steps: (i) introducing a mixture of at least two different metallic molecular precursors to a deposition chamber; (ii) purging the deposition chamber; (iii) introducing a reactant gas to the deposition chamber; and (iv) purging the deposition chamber.

This embodiment of the method is visually illustrated by **FIG. 3**. In **FIG. 3** is identical to **FIG. 1A**, with the exception that a vapor mixture of metallic precursors **310** is utilized instead of a multi-metallic molecular precursor vapor **110**. Similarly, the steps in the second method are the same as those employed in the first method with the exception that a vapor mixture of metallic precursors **310** is utilized in the first step of the cycle rather than a multi-metallic molecular precursor **110**.

Each metallic precursor contains, within its molecules, a metallic element required to make the desired film. In one embodiment, the metallic precursors in the mixture have the following formulae:

$$(L^1)_wM^1;$$

and

$$M^2(L^2)_z$$

where M^1 and M^2 are different metallic elements, where each L^1 and L^2 a ligand and may be the same or different and where w and z are integers less than or equal to a valence number for M^1 and M^2, respectively.

As stated, M^1 and M^2 can be any metallic element as long as M^1 and M^2 are not identical. Preferred metallic elements for use as M^1 and M^2 include Si, Li, Be, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Ba, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Tl, Pb, Bi, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Th.

As stated, each L^1 and L^2 is selected, independently, from ligands and may be the same or different. Suitable ligands are readily ascertainable by those of ordinary skill in the art and include those ligands known to be useful in precursors for ALD processes. Undesirable ligands are removed during the course of film deposition due to their relatively weak chemical bonds. Preferred ligands include but are not limited to a double bonded nitrogen, alkyls, alkoxides, halides, hydrides, amides, imides, azides, nitrates, cyclopentadienyls, carbonyls, carboxylates, diketonates, as well as substituted analogs thereof and combinations thereof. It is preferable, but not necessary to use relatively small ligands having, *e.g.*, 1-12 atoms. Compounds that contain small relatively small ligands tend to volatilize more readily at lower temperatures than compounds that contain relatively larger ligands. Furthermore, compounds that contain relatively smaller ligands tend to be more stable. Specific preferred ligands include a double bonded nitrogen (=N), dimethylamide ($-N(CH_3)_2$), diethylamide ($-N(CH_2CH_3)_2$), methylethylamide ($-N(CH_3)(CH_2CH_3)$), methoxide ($-OCH_3$), ethoxide ($-OCH_2CH_3$), and butoxide ($-O(CH_2)_3CH_3$). It is also preferably, but not necessary to use similar, and more preferably identical, ligands in both precursors. The use of identical ligands facilitates the ability to dissolve the different precursors uniformly in the same solvent under the similar conditions.

As stated, w and z are integers less than or equal to a valence number for M^1 and M^2, respectively. In one embodiment, either at least one of w and z is an integer one less than a valence number for metallic element due to the presence of a double bond between one of the ligands and the metallic element. In another embodiment, w and z are integers equal to a valence number for their respective metallic elements. Preferably, w and z are selected, independently, from 1, 2, 3 and 4.

The precursor vapors **310** can be mixed in the deposition zone, or a mixture of precursor gases **310** can be delivered to the deposition zone by direct liquid injection (DLI) of a mixture of precursors in liquid phase. When delivering by direct liquid injection, the liquid precursors are vaporized in a separate vaporization step. In one embodiment the vapor of the individual precursors is mixed in the delivery manifold and deposition chamber **101** during the precursor pulse step. In another embodiment an alternating precursor pulse sequence is used.

The diluent gas **120** can be any non-reactive gas or mixture of non-reactive gases, including any noble gas or gases. Typical non-reactive gases include Ar, He, Ne, Xe, and N_2.

The reactant gas **130** can be any reducing agent or oxidizing agent or a mixture thereof. Thus, in **FIG. 1B**, the reactant gas **130** is reducing agent **130'** and in **FIG. 1C** the reactant gas **130** is oxidizing agent **130"**. The reducing agent **130'** or oxidizing agent **130"** may be a gas or a liquid at room temperature but it is introduced to the deposition chamber **101** as a gas. The nature of the reactant gas **130** is selected based on the nature of the multi-metallic film desired. Suitable reactant gases **130** include hydrogen sources, oxygen sources and/or nitrogen sources.

In one embodiment, the mixture of precursors is a mixture of the two compounds $M(NR^8R^9)_q$ and $Si(NR^{10}R^{11})_2$ where R^8, R^9, R^{10} and R^{11} are, independently, selected from H, F, C1-C6 alkyls, and substituted C1-C6 alkyls, where M is selected from Si, Li, Be, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Ba, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Tl, Pb, Bi, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Th, and q is less than or equal to a valence number for M. Preferred selections for R^8, R^9, R^{10} and R^{11} are methyl and ethyl. Preferred selections for M are Ti, Zr, and Hf and, in such cases, q equals 2, 3 or 4.

In one such embodiment, the precursor cocktail is a mixture of $N{=}Ta(NR'R'')_3$ and $Si(NRR')_4$. This cocktail is especially useful for depositing a tantalum silicon nitride layer.

In another such embodiment the precursor cocktail is a mixture of $Hf(NR^{12}R^{13})_4$ and $Si(NR^{14}R^{15})_4$, where R^{12}, R^{13}, R^{14} and R^{15} are selected from methyl and ethyl groups. This mixture can be used to deposit a number of different halfnium-silicon films depending on the nature of the reactant utilized. For example, if the reactant is an oxygen source, then the multi-component film will be a hafnium silicate (Hf-Si-O) film. Alternatively, if the reactant is a nitrogen source, a hafnium silicon nitride (Hf-Si-N) film will be formed. Alternatively, if a mixture of oxygen and nitrogen sources is utilized, the resultant film will be a hafnium oxynitride (Hf-Si-O-N) film. Finally, if a hydrogen source is utilized, a hafnium silicon alloy (Hf-Si) film will be formed. Suitable oxygen sources, nitrogen sources, and hydrogen sources are identical to those identified previously.

When depositing HfSiO films from a precursor cocktail comprising $Hf(NR^{12}R^{13})_4$ and $Si(NR^{14}R^{15})_4$ using ALD, the mixture can range anywhere from 10:1 to 1:10 by volume and the vapor flow rate can range anywhere from approximately 0.01 g/min to 10 g/min. When the oxidizer is ozone, which is preferred, the total O_2/O_3 flow can range anywhere from approximately 100 sccm to 1000 sccm and the ozone concentration can range anywhere from 1% to 20% by volume. During the deposition, the process pressure can range anywhere from approximately 50 mTorr to 10 Torr and the substrate temperature can range anywhere from approximately 200 °C to 600 °C, with the preferred substrate temperature being from approximately 300 °C to 400 °C. The dilution gas flow rate can range anywhere from approximately 100 sccm to 2000 sccm, but preferably ranges from approximately 500 sccm to 2000 sccm.

A specific example of a mixture of precursors for deposition of HfSiO films using a cocktail comprising $Hf(NR^{12}R^{13})_4$ and $Si(NR^{14}R^{15})_4$ is the case where R^{12} and R^{14} are methyl and R^{13} and R^{15} are ethyl. The resulting hafnium and silicon precursors are tetrakis(ethylmethylamino) hafnium (*i.e.*, TEMAHf) and tetrakis(ethylmethylamino) silicon (*i.e.*, TEMASi). In this example, a solventless precursor mixture of TEMAHf and TEMASi was delivered to the deposition region using a direct liquid injection system equipped with a vaporizer. Ozone was used as an oxygen source for depositing the metal oxide films. Various precursor mixtures were used, ranging from a 99:1 Hf:Si molar ratio mixture to a 1:99 Hf:Si molar ratio mixture. In this example, the liquid flow rate can range from approximately 0.01 to 1 g/min, but the flow rate is preferably in the range approximately 0.02 to 0.1 g/min. The oxygen flow can range from approximately 100 sccm to 1000 sccm. The deposition temperature can range from approximately 250 °C to 450 °C. Using a flow rate of 0.04 g/min and an oxygen flow of 300 sccm with 12% by volume O_3 at temperatures from 300 °C to 450 °C it is possible to obtain HfSiO films with varying composition (see Table 1 below).

Table 1

Rutherford Back Scattering Spectroscopy/Hydrogen Forward Scattering (RBS/HFS) composition analysis of Hf-Si-O films

Wafer Temperature (°C)	O	Si	Hf	O/(Hf+Si)	H	C	N	RI @ 633nm for 500Å films
300	61.9	6.9	23.5	2.04	3.5	3.3	0.9	1.83
350	63.4	10.9	20.3	2.03	1.4	3	1	1.77
400	62.7	13.3	18.5	1.97	1.8	2.5	1.2	1.72
450	63.8	13.7	18.8	1.96	1	2.1	0.6	1.68

A transmission electron microscope cross section image of 45Å $Hf_{0.58}Si_{0.42}O_2$ is shown in **FIG. 4** for the HfSiO film deposited at 400°C. A polysilicon cap layer was also deposited followed by a thermal anneal at 700°C for 30 s. The amorphous state of the film was maintained after the anneal with an interfacial oxide layer thickness of approximately 7Å.

ALD depositions embraced by these methods include thermal ALD, photo-assisted ALD, laser assisted ALD, plasma-assisted ALD and radical assisted ALD.

The preceding description is illustrative rather than limiting and is intended to provide a written description of the inventions sufficient to enable one of ordinary skill in the art to practice the full scope and any best mode of the inventions to which patent rights are claimed. Other embodiments and modifications may be readily apparent to those skilled in the art. All such embodiments and modifications should be considered part of the inventions if they fall within the scope of the appended claims and any equivalents thereto.

What is claimed:

1. An atomic layer deposition method for depositing a multi-metallic film on a substrate, characterized in that at least one cycle is performed that comprises the step of introducing a multi-metallic molecular precursor gas into a deposition chamber that contains the substrate.

2. A method of forming a multi-metallic film on a substrate comprising at least one cycle that comprises the following steps:

(i) introducing a multi-metallic molecular precursor gas into a deposition chamber that contains the substrate;

(ii) purging the deposition chamber;

(iii) introducing one or more reactant gases into the deposition chamber; and

(iv) purging the deposition chamber.

3. The method of claim 2 where the multi-metallic molecular precursor has the following formula:

$$(L^1)_aM^1GM^2(L^2)_b$$

where M^1 and M^2 are different metallic elements, where each L^1 and L^2 is a leaving group that may be the same or different, where a and b may be the same or different and are integers less than a valence number for M^1 and M^2, respectively, and where G is selected from a single bond, double bond, bridging atom and bridging group.

4. The method of claim 3 where G is oxygen.

5. The method of claim 3 where M^1 and M^2 are different metallic elements selected from Si, Li, Be, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Ba, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Tl, Pb, Bi, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Th..

6. The method of claim 3 where each L^1 and L^2 is a leaving group selected from alkyls, alkoxides, halides, hydrides, amides, imides, azides, nitrates, cyclopentadienyls, carbonyls, carboxylates, diketonates, and substituted analogs thereof.

7. The method of claim 6 where each L^1 and L^2 is a leaving group selected from dimethylamide, diethylamide, methylethylamide, methoxide, ethoxide and butoxide.

8. The method of claim 3 where a and b are selected, independently, from the integers 1, 2 and 3.

9. The method of claim 3 where the multi-metallic molecular precursor has the following formula:

$$(R^1O)_x(R^2R^3N)_{3-x}Si\text{-}O\text{-}M(OR^4)_y(NR^5R^6)_{v-y},$$

where R^1, R^2, R^3, R^4, R^5 and R^6 are, independently, selected from H, F, C1-C6 alkyls and substituted C1-C6 alkyls, where M is selected from Si, Li, Be, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Ba, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Tl, Pb, Bi, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Th, where x is selected from 1, 2 and 3, where y is an integer less than or equal to v and where v is an integer one less than a valance number for M.

10. The method of claim 9 where the M is selected from Ti, Zr and Hf.

11. The method of claim 10 where the multi-metallic molecular precursor is tri-(tert-butoxy)siloxy-tri(tert-butoxy)titanium.

12. The method of claim 9 wherein R^2, R^3, R^5 and R^6 are selected from methyl and ethyl, where R^1 and R^4 are selected from methyl, ethyl, propyl, and butyl, where M is selected from Ti, Zr, and Hf and where v is selected from the integers 1, 2 and 3.

13. The method of any one of claim 2, 3, and 4 where the reactant gas is an oxidizing agent.

14. The method of any one of claims 2, 3 and 4 where the reactant gas is a reducing agent.

15. The method of any one of claim 2, 3 and 4 where the reactant gas is a hydrogen source and the multi-metallic film is a metallic alloy film.

16. The method of any one of claims 2, 3 and 4 where the reactant gas is an oxygen source and the multi-metallic film is multi-metallic oxide film.

17. The method of any one of claims 2, 3 and 4 where the reactant is a nitrogen source and the multi-metallic film is a multi-metallic nitride film.

18. The method of any one of claims 2, 3 and 4 where the reactant gas is a mixture of an oxygen source and a nitrogen source and the multi-metallic film is a multi-metallic oxynitride film.

19. The method of any one of claims 2, 3 and 4 where the purging steps are accomplished by pulsing diluent gas into the reaction chamber, or pumping gas out of the reaction chamber, or a combination of pulsing diluent gas into the reaction chamber and pumping gas out of the reaction chamber.

20. An atomic layer deposition method for forming a multi-metallic film on a substrate characterized in that at least one cycle is performed that comprises the step of introducing a mixture of metallic molecular precursor gases into a deposition chamber that contains the substrate.

21. A method of forming a multi-metallic film on a substrate comprising at least one cycle comprising the following steps:

(i) introducing a mixture of at least two different metallic molecular precursors into a deposition chamber that contains the substrate;

(ii) purging the deposition chamber;

(iii) introducing a reactant gas to the deposition chamber; and

(iv) purging the deposition chamber.

22. The method of claim 21 where the two metallic molecular precursors comprise the following respective formulae:

$$(L^1)_w M^1;$$

and

$$M^2(L^2)_z$$

where M^1 and M^2 are different metallic elements, where each L^1 and L^2 are ligands which may be the same or different, where w and z are integers less than or equal to a valence numbers for M^1 and M^2, respectively.

23. The method of claim 22 where M^1 and M^2 are different metallic elements selected from Si, Li, Be, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Ba, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Tl, Pb, Bi, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Th..

24. The method of claim 22 where each L^1 and L^2 is a leaving groups, which may be the same or different, selected from a double bonded nitrogen, alkyls, alkoxides, halides, hydrides, amides, imides, azides, nitrates, cyclopentadienyls, carbonyls, carboxylates, diketonates, and substituted analogs thereof.

25. The method of claim 22 where each L^1 and L^2 is a leaving group selected from a double bonded nitrogen, dimethylamide, diethylamide, methylethylamide, methoxide, ethoxide and butoxide.

26. The method of claim 22 where each L^1 and L^2 is the same.

27. The method of claim 22 where w and z are selected, independently, from 1, 2, 3 and 4.

28. The method of claim 22 where the two metallic precursors comprise the following respective formulae:

$$M(NR^8R^9)_q;$$

and

$$Si(NR^{10}R^{11})_2$$

where R^8, R^9, R^{10} and R^{11} are, independently, selected from H, F, C1-C6 alkyls, and substituted C1-C6 alkyls, where M is selected from Si, Li, Be, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Ba, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Tl, Pb, Bi, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Th, and where q is less than or equal to a valence number for M.

29. The method of claim 28 where M is selected from Ti, Zr and Hf.

30. The method of claim 28 where the two metallic precursors are $N{=}Ta(NR'R'')_3$ and $Si(NRR')_4$.

31. The method of claim 28 wherein the two metallic precursors are tetrakis(ethylmethylamino) hafnium and tetrakis(ethylmethylamino) silicon.

32. The method of any one of claims 21 and 22 where the reactant gas is an oxidizing agent.

33. The method of any one of claims 21 and 22 where the reactant gas is a reducing agent.

34. The method of any one of claims 21 and 22 where the reactant gas is a hydrogen source and the multi-metallic film is a metallic alloy film.

35. The method of any one of claims 21 and 22 where the reactant gas is an oxygen source and the multi-metallic film is multi-metallic oxide film.

36. The method of any one of claims 21 and 22 where the reactant has is a nitrogen source and the multi-metallic film is a multi-metallic nitride film.

37. The method of any one of claims 21 and 22 where the reactant gas is a mixture of an oxygen source and a nitrogen source and the multi-metallic film is a multi-metallic oxynitride film.

38. The method of any one of claims 21 and 22 where the purging steps are accomplished by pulsing diluent gas into the reaction chamber, or pumping gas out of the reaction chamber, or a combination of pulsing diluent gas into the reaction chamber and pumping gas out of the reaction chamber.

39. The method of any one of claims 1 and 20 where said method for atomic layer deposition is a method selected from thermal atomic layer deposition, photo-assisted atomic layer deposition, laser assisted atomic layer deposition, plasma assisted atomic layer deposition and radical enhanced atomic layer deposition.

FIG. 1A

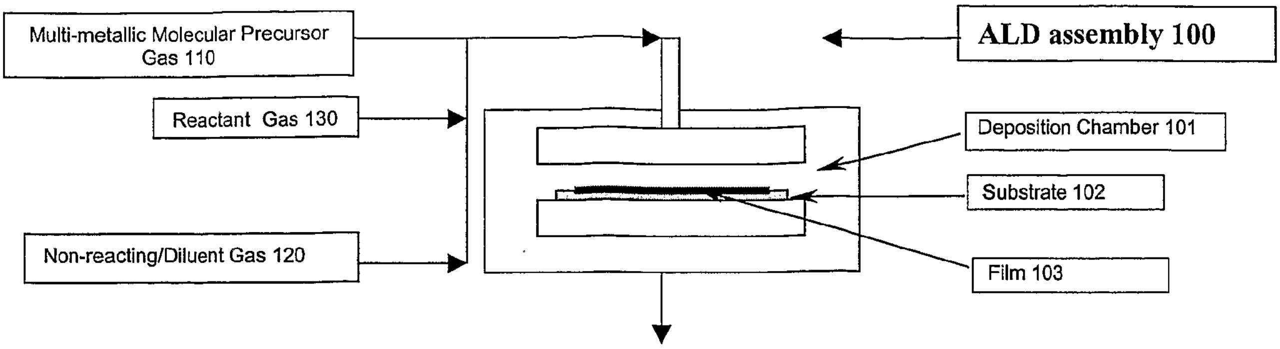

FIG. 1B

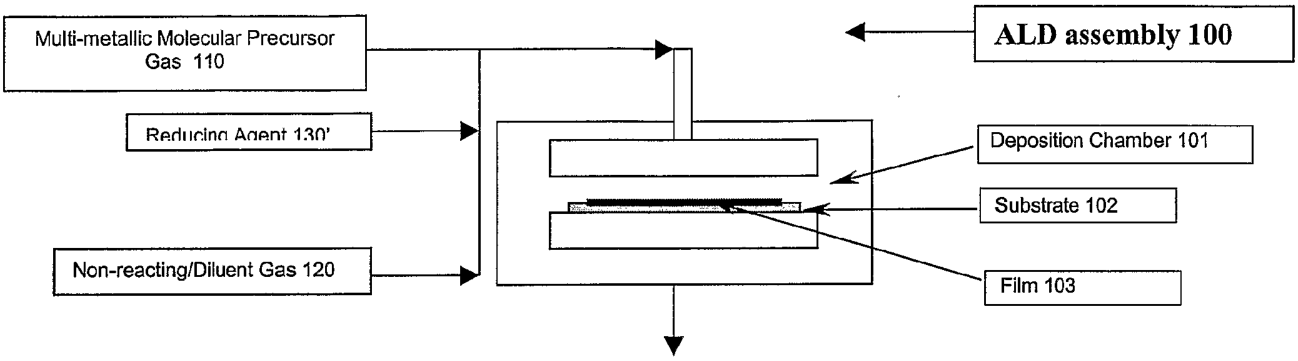

FIG. 1C

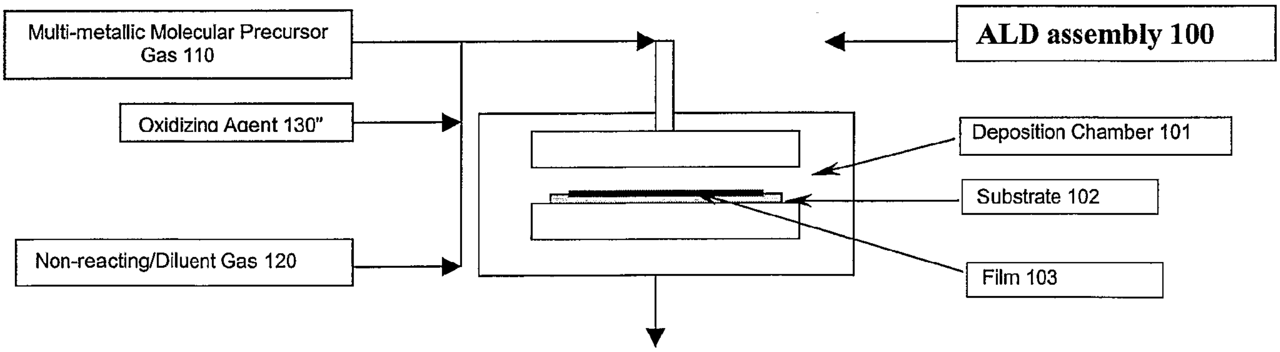

FIG. 2A

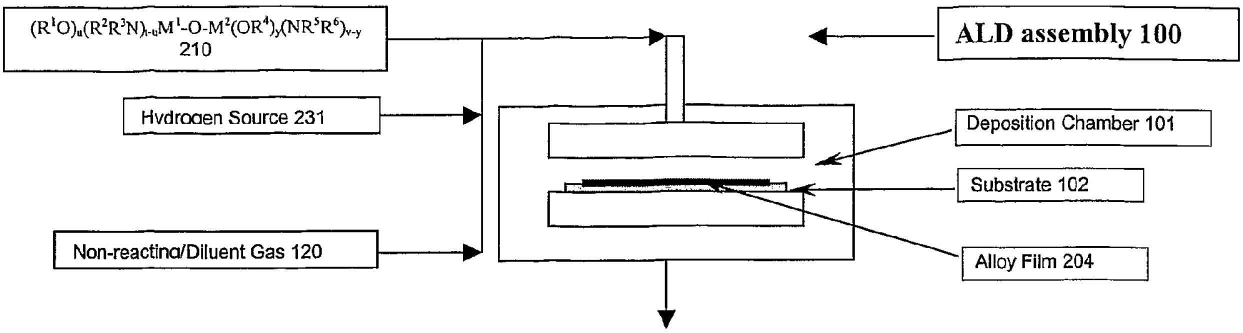

FIG. 2B

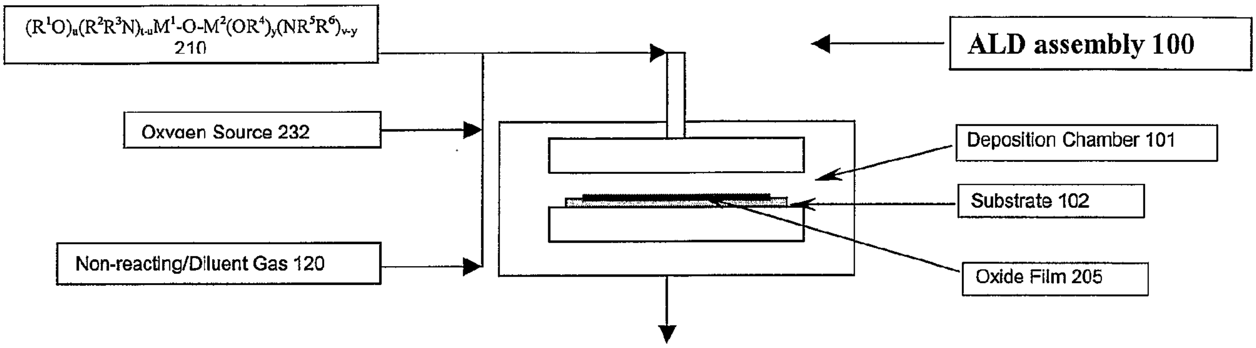

FIG. 2C

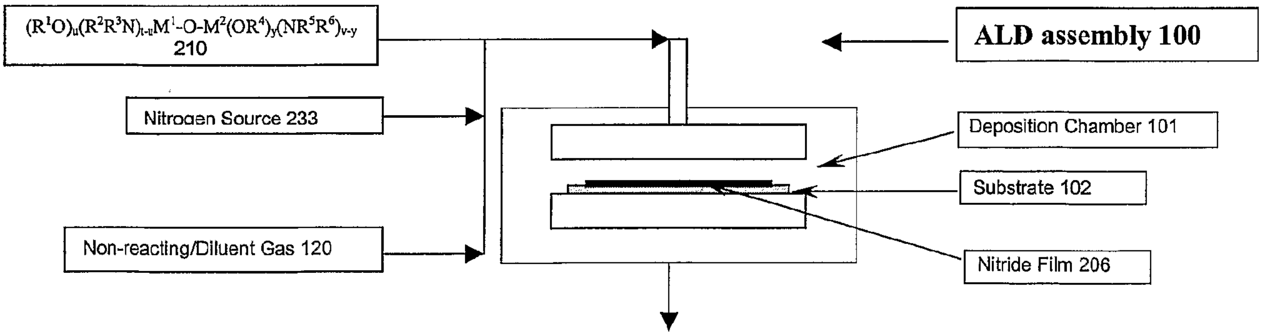

FIG. 2D

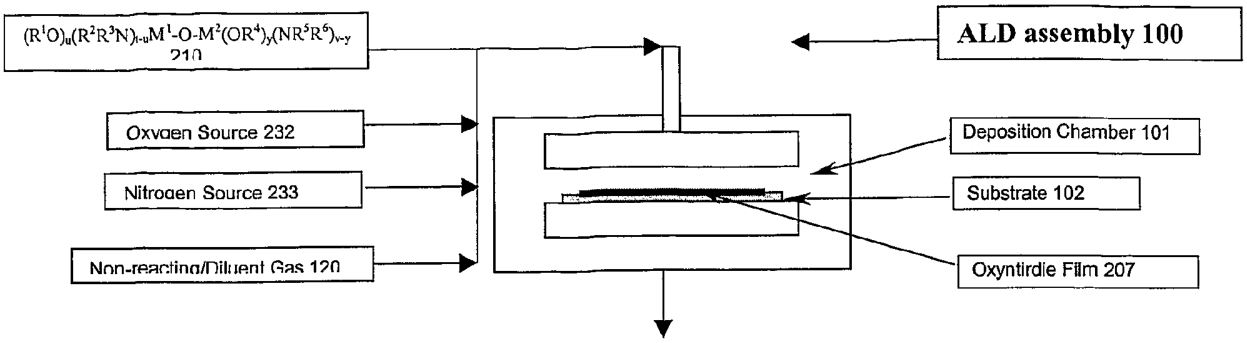
$(R^1O)_u(R^2R^3N)_{t-u}M^1\text{-}O\text{-}M^2(OR^4)_y(NR^5R^6)_{v-y}$ 210
Oxygen Source 232
Nitrogen Source 233
Non-reacting/Diluent Gas 120
ALD assembly 100
Deposition Chamber 101
Substrate 102
Oxyntirdie Film 207

FIG. 3.

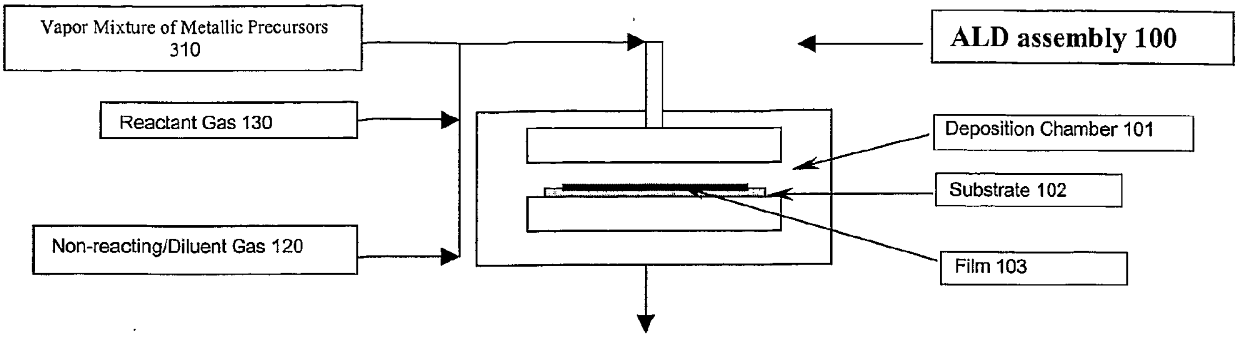
Vapor Mixture of Metallic Precursors 310
Reactant Gas 130
Non-reacting/Diluent Gas 120
ALD assembly 100
Deposition Chamber 101
Substrate 102
Film 103

FIG. 4