DEPOSITION METHODS FOR HIGH ASPECT RATIO STRUCTURES USING AN INHIBITOR MOLECULE

Cross Reference to Related Applications

[0001] The present application claims the benefit of U.S. Application No. 17,072,882 filed October 16, 2020, being incorporated herein by reference in its entirety for all purposes.

Technical Field

[0002] Disclosed are deposition methods for high aspect ratio structures using an inhibitor molecule in addition to precursors in semiconductor applications. In particular, the disclosed methods relates to vapor deposition processes using organometallic precursors and the inhibitor molecule containing O, N, S, P, B, C, F, Cl, Br, or I to improve thickness control including step coverage and gap filing in a substrate.

Background

[0003] As a device gets scaling down in semiconductors, precise thickness control is a key challenge. Atomic layer deposition (ALD) may be preferable to chemical vapor deposition (CVD) in a sense that growth per cycle (GPC) of ALD is much lower than the growth rate per unit time of CVD so that it will be relatively easy to achieve the desirable thickness, which is limited by layer by layer depositions resulting in very clear linearity of thickness vs. number of ALD cycles. However, even in ALD, GPC is highly dependent on a kind of precursor, process types, and which materials are deposited. Up to date, it has not been reported that universal or easy way to control the deposition rate or thickness in a given process, while maintaining the ALD behavior. In order to lower GPC in ALD, low amount of a precursor or a co-reactant could be applied to lead sub-ALD regime, but it would cause a very unstable process due to shortage of a precursor, because GPC can be varied significantly depending on a process temperature.

[0004] As a device sizes continue to be scaled down in semiconductors, step coverage is a key factor of integration for high aspect ratio (HAR) structures. For example, a narrow and deep trench is formed in a semiconductor substrate and a gap fill is performed using an insulating material to form an insulating film to be sequentially deposited from the bottom surface of the trench so that the trench is completely covered. Deposition onto HAR stepped surfaces faces the challenge of non-uniform gap filling, which may produce a poor step coverage and may contain voids and/or weakpoints.

[0005] As a device sizes continue to be scaled down in semiconductors, a vapor deposition is one of the most important techniques to deposit thin films of new materials. Especially, ALD becomes a key enabler to have highly conformal depositions as well as gap fillings. A big challenge for the gap filling is to seal two layers without any empty space in between, so called, a void or a seam which is a narrow line of openings during the deposition process. Normally, it will be even more challenging to fill a gap in a high aspect ratio structure or a complicated 3D structure.

[0006] There are various attempts to improve the thickness control, the step coverage and the gap fill.

[0007] US 20070141779 to Abelson et al. discloses methods for coating and filling high aspect ratio (HAR) recessed features and conformally or superconformally coating and/or uniformly filling structures with a continuous, conformal layer or superconformal layer, in which a bottom up growth of CrB_2 film is deposited on a trench substrate with a help of hydrogen plasma as a suppressor by conventional chemical vapor deposition (CVD) methods.

[0008] US 9564312 to Henri et al. discloses selective inhibition in atomic layer deposition (ALD) of silicon-containing films, e.g., SiN_x film. The selective inhibition involves an exposure of an adsorbed layer of a silicon-containing precursor to a hydrogen-containing inhibitor, prior to the exposure of the adsorbed layer to a second reactant. The exposure to a hydrogen-containing inhibitor may be performed with a plasma.

[0009] US 10103026 and US 20170040172 to Moon et al. discloses methods of forming a material layer, and more particularly, methods of forming a material layer, by which a material layer having good step coverage may be stably manufactured despite variations in other process parameters.

[0010] Talukdar T K (Doctoral dissertation, University of Illinois at Urbana-Champaign, 2018) discloses coating and filling of nanometer-scale structure using CVD, in which oxide is used to afford bottom-up filling of trenches by superconformal CVD method.

[0011] KR102095710 to Jin et al. discloses a method for forming a thin film using a surface protection material to achieve a good step coverage, which comprises a surface protection material supply step of supplying the surface protection material to adsorb the same on the substrate.

[0012] In the semiconductor process field, development of a process having good step coverage has attracted attention, and use of atomic layer deposition (ALD) processes has received specific attention.

Summary

[0013] Disclosed is a deposition method for improving thickness control of a film deposited on high aspect ratio (HAR) apertures in a substrate, the method comprising:

i) sequentially or simultaneously exposing the substrate to a vapor of an inhibitor, a vapor of a precursor and a vapor of a co-reactant; and

ii) depositing the film on the HAR apertures that has a desired thickness control through a vapor deposition process,

wherein the inhibitor contains O, N, S, P, B, C, F, Cl, Br, or I.

[0014] The disclosed deposition method may include one or more of the following aspects:

- further comprising maintaining a temperature of the substrate in a range of from room temperature to 650°C;
- the inhibitor being selected from one or more of
  a) oxygen based aliphatic and aromatic inhibitors including alcohols, diols, ethers, epoxides, aldehydes, ketones, carboxylic acids, enols, esters, anhydrides, phenols, substituted phenols;
  b) nitrogen based aliphatic and aromatic inhibitors including amines, imines, imides, amides, azides, cyanates, nitrile, nitrate, nitrite, nitrogen containing heterocycles;
  c) sulfur based aliphatic and aromatic inhibitors including thiols, sulfides, disulfide, sulfonxide, sulfone, thiocyanates, isothiocyanates, thioesters;
  d) phosphorus based aliphatic and aromatic inhibitors including phosphines, phosphonic acid, phosphodiesters;
  e) boron based aliphatic and aromatic inhibitors including boronic acid, boronic ester, borinic esters; carbon based aliphatic inhibitors including alkanes, alkenes, alkynes and benzene derivatives;
  f) halide containing organic molecules and inorganic halides including I_2; or
  g) H_2O vapor, H_2 gas, CO gas, CS gas and nitrogen oxide (NO_x) gases;
  h) and combinations of a)-g);
- the inhibitor being a radical form of a vapor or gas of the inhibitor at a temperature ranging from room temperature to approximately 650°C generated with or without plasma;
- the inhibitor being selected from tetrahydrofuran (THF), dimethoxyethane (DME), triethylamine (TEA), tetramethylethylenediamine (TMEDA),

dimethylethylenediamine (DMEDA) or tris(2-aminoethyl)amine;

- the inhibitor being THF;
- the inhibitor being DME;
- the inhibitor being TEA;
- tetramethylethylenediamine (TMEDA);
- dimethylethylenediamine (DMEDA);
- tris(2-aminoethyl)amine;
- the precursor being an organometallic precursor selected from alkylamino and cyclopendadiendyl derivatives of transition metals and main group elements that contain homoleptic or heteroleptic ligands selected from alkylamines, alkoxy, amidinates, or halides;
- the transition metals and main group elements being selected from Hf, Zr, Nb, Ti, lanthanides, rare earths, Al or Si;
- the precursor being $ZrCp(NMe_2)_3$;
- the precursor being $HfCp(NMe_2)_3$;
- the precursor being $Nb(=NtBu)Cp(NMe_2)_2$;
- the precursor being $TiCp^*(OMe)_3$;
- the thickness control being a step coverage control;
- the thickness control being a gap fill control;
- the desired thickness control being a desired step coverage;
- the desired thickness control being a desired gap fill;
- a step coverage being $\geq$ 100%;
- the step coverage being larger than the step coverage with the absence of the inhibitor;
- the film being a gap fill of the HAR aperture without a seam;
- the gap fill being formed by a bottom up deposition;
- the HAR ranging from 5:1 to 200:1;
- the substrate being a patterned or 3D structure;
- the aperture being a hole, a via, a trench, a gap or an opening formed in the substrate from a previous manufacturing step;
- the films deposited on the HAR structures being metal films, metal oxide films, silicon-containing films, alloys, and so on;
- the film deposited on the HAR structures being ZrO_2;
- the film deposited on the HAR structures being HfO_2;

- the film deposited on the HAR structures being Nb_2O_5;
- the film deposited on the HAR structures being TiO_2;
- the vapor deposition process being ALD, CVD or combination thereof;
- the vapor deposition process being a spatial ALD, a thermal ALD, a plasma enhanced ALD and a plasma enhanced CVD;
- the vapor deposition process being a spatial ALD;
- the vapor deposition process being a thermal ALD;
- the vapor deposition process being a plasma enhanced ALD;
- the vapor deposition process being a plasma enhanced CVD;
- the co-reactant being O_3, O_2, H_2O, H_2O_2, D_2O, alcohols, NH_3, N_2, N_2H_2, H_2, or radicals thereof generated by plasma;
- the co-reactant being O_3 or O_3 radicals generated by plasma;
- an order of exposing the substrate to the inhibitor, the precursor and the co-reactant including
    i) the inhibitor, the precursor and the co-reactant sequentially;
    ii) the precursor, the inhibitor and the co-reactant sequentially;
    iii) the precursor, the co-reactant and the inhibitor sequentially; or
    iv) the inhibitor and the precursor simultaneously and then the co-reactant;
- an order of exposing the substrate to the inhibitor, the precursor and the co-reactant being the inhibitor, the precursor and the co-reactant sequentially;
- an order of exposing the substrate to the inhibitor, the precursor and the co-reactant being the precursor, the inhibitor and the co-reactant sequentially;
- an order of exposing the substrate to the inhibitor, the precursor and the co-reactant being the precursor, the co-reactant and the inhibitor sequentially;
- an order of exposing the substrate to the inhibitor, the precursor and the co-reactant being the inhibitor and the precursor simultaneously and then the co-reactant; and
- further comprising
  purging and removing one or more of an excess inhibitor, an excess precursor and an excess co-reactant after each exposure using a purge gas,
  wherein the purge gas is an inert gas selected from N_2, Ar, Kr or combinations thereof;
- a consistent decrease in a growth rate of the film with a precursor dose time;
- a consistent decrease in a growth rate of the film versus the amount of a precursor;
- a growth rate of the film decreasing comparing to a growth rate of the film with an

absence of the inhibitor;

- a growth rate of the film versus the amount of the precursor decreasing comparing to that with an absence of the inhibitor;
- the precursor, the inhibitor or both are plasma activated; and
- the precursor, the inhibitor or both are not plasma activated.

[0015] Also disclosed is a deposition method for improving thickness control of a ZrO_2, HfO_2, Nb_2O_5 or TiO_2 film deposited on apertures therein with an aspect ratio of about 5:1 to about 200:1 in a substrate, the method comprising:

i) exposing the substrate to a vapor of an inhibitor selected from the group consisting of tetrahydrofuran (THF), dimethoxyethane (DME) and triethylamine (TEA), tetramethylethylenediamine (TMEDA); dimethylethylenediamine (DMEDA) and tris(2-aminoethyl)amine;

ii) exposing the substrate to a vapor of a precursor selected from the group consisting of $ZrCp(NMe_2)_3$, $HfCp(NMe_2)_3$, $Nb(=NtBu)Cp(NMe_2)_2$ and $TiCp^*(OMe)_3$;

iii) exposing the substrate to a vapor of a co-reactant O_3; and

iv) repeating the steps of i) to iii) until a desired thickness control of the ZrO_2, HfO_2, Nb_2O_5 or TiO_2 film deposited on the apertures is formed through an ALD process in a temperature ranging from room temperature to 650°C,

wherein a step coverage of the ZrO_2, HfO_2, Nb_2O_5 or TiO_2 film is $\geq$ 100%;

wherein a growth per cycle (GPC) of the ZrO_2, HfO_2, Nb_2O_5 or TiO_2 film versus the amount of a precursor decreases;

wherein the ZrO_2, HfO_2, Nb_2O_5 or TiO_2 film is a gap fill without a seam,

wherein, after each exposure, excess inhibitor, excess precursor and excess co-reactant is purged and removed using N_2, respectively.

[0016] Also disclosed is a deposition method for improving thickness control of a ZrO_2 film deposited on apertures therein with an aspect ratio of about 5:1 to about 200:1 in a substrate, the method comprising:

i) exposing the substrate to a vapor of an inhibitor selected from the group consisting of tetrahydrofuran (THF), dimethoxyethane (DME) and triethylamine (TEA), tetramethylethylenediamine (TMEDA); dimethylethylenediamine (DMEDA) and tris(2-aminoethyl)amine;

ii) exposing the substrate to a vapor of a precursor selected from the group consisting of $ZrCp(NMe_2)_3$;

iii) exposing the substrate to a vapor of a co-reactant O_3; and

iv) repeating the steps of i) to iii) until a desired thickness control of the ZrO_2 film deposited on the apertures is formed through an ALD process in a temperature ranging from room temperature to 650°C,

wherein a step coverage of the ZrO_2 film is ≥ 100%;

wherein a growth per cycle (GPC) of the ZrO_2 film versus the amount of a precursor decreases;

wherein the ZrO_2 film is a gap fill without a seam,

wherein, after each exposure, excess inhibitor, excess precursor and excess co-reactant is purged and removed using N_2, respectively.

[0017] Also disclosed is a deposition method for improving thickness control of a HfO_2 film deposited on apertures therein with an aspect ratio of about 5:1 to about 200:1 in a substrate, the method comprising:

i) exposing the substrate to a vapor of an inhibitor selected from the group consisting of tetrahydrofuran (THF), dimethoxyethane (DME) and triethylamine (TEA), tetramethylethylenediamine (TMEDA); dimethylethylenediamine (DMEDA) and tris(2-aminoethyl)amine;

ii) exposing the substrate to a vapor of a precursor selected from the group consisting of $HfCp(NMe_2)_3$;

iii) exposing the substrate to a vapor of a co-reactant O_3; and

iv) repeating the steps of i) to iii) until a desired thickness control of the HfO_2 film deposited on the apertures is formed through an ALD process in a temperature ranging from room temperature to 650°C,

wherein a step coverage of the HfO_2 film is ≥ 100%;

wherein a growth per cycle (GPC) of the HfO_2 film versus the amount of a precursor decreases;

wherein the HfO_2 film is a gap fill without a seam,

wherein, after each exposure, excess inhibitor, excess precursor and excess co-reactant is purged and removed using N_2, respectively.

[0018] Also disclosed is a deposition method for improving thickness control of a Nb_2O_5 film deposited on apertures therein with an aspect ratio of about 5:1 to about 200:1 in a substrate, the method comprising:

i) exposing the substrate to a vapor of an inhibitor selected from the group consisting of tetrahydrofuran (THF), dimethoxyethane (DME) and

triethylamine (TEA), tetramethylethylenediamine (TMEDA); dimethylethylenediamine (DMEDA) and tris(2-aminoethyl)amine;

ii) exposing the substrate to a vapor of a precursor selected from the group consisting of $Nb(=NtBu)Cp(NMe_2)_2$;

iii) exposing the substrate to a vapor of a co-reactant O_3; and

iv) repeating the steps of i) to iii) until a desired thickness control of the Nb_2O_5 film deposited on the apertures is formed through an ALD process in a temperature ranging from room temperature to 650°C,

wherein a step coverage of the Nb_2O_5 film is ≥ 100%;

wherein a growth per cycle (GPC) of the Nb_2O_5 film versus the amount of a precursor decreases;

wherein the Nb_2O_5 film is a gap fill without a seam,

wherein, after each exposure, excess inhibitor, excess precursor and excess co-reactant is purged and removed using N_2, respectively.

[0019] Also disclosed is a deposition method for improving thickness control of a TiO_2 film deposited on apertures therein with an aspect ratio of about 5:1 to about 200:1 in a substrate, the method comprising:

i) exposing the substrate to a vapor of an inhibitor selected from the group consisting of tetrahydrofuran (THF), dimethoxyethane (DME) and triethylamine (TEA), tetramethylethylenediamine (TMEDA); dimethylethylenediamine (DMEDA) and tris(2-aminoethyl)amine;

ii) exposing the substrate to a vapor of a precursor selected from the group consisting of $TiCp^*(OMe)_3$;

iii) exposing the substrate to a vapor of a co-reactant O_3; and

iv) repeating the steps of i) to iii) until a desired thickness control of the TiO_2 film deposited on the apertures is formed through an ALD process in a temperature ranging from room temperature to 650°C,

wherein a step coverage of the TiO_2 film is ≥ 100%;

wherein a growth per cycle (GPC) of the TiO_2 film versus the amount of a precursor decreases;

wherein the TiO_2 film is a gap fill without a seam,

wherein, after each exposure, excess inhibitor, excess precursor and excess co-reactant is purged and removed using N_2, respectively.

Notation and Nomenclature

[0020] The following detailed description and claims utilize a number of abbreviations, symbols, and terms, which are generally well known in the art, and include:

[0021] As used herein, the indefinite article "a" or "an" means one or more.

[0022] As used herein, "about" or "around" or "approximately" in the text or in a claim means ±10% of the value stated.

[0023] As used herein, "room temperature" in the text or in a claim means from approximately 20°C to approximately 25°C.

[0024] As used in the disclosed embodiments, the term "independently" when used in the context of describing R groups should be understood to denote that the subject R group is not only independently selected relative to other R groups bearing the same or different subscripts or superscripts, but is also independently selected relative to any additional species of that same R group. For example in the formula $MR^1_x(NR^2R^3)_{(4-x)}$, where x is 2 or 3, the two or three R^1 groups may, but need not be identical to each other or to R^2 or to R^3. Further, it should be understood that unless specifically stated otherwise, values of R groups are independent of each other when used in different formulas.

[0025] The standard abbreviations of the elements from the periodic table of elements are used herein. It should be understood that elements might be referred to by these abbreviation (*e.g.*, Si refers to silicon, N refers to nitrogen, O refers to oxygen, C refers to carbon, H refers to hydrogen, F refers to fluorine, *etc.*).

[0026] As used herein, the abbreviation "Me" refers to a methyl group; the abbreviation "Et" refers to an ethyl group; the abbreviation "Pr" refers to a propyl group (i.e., n-propyl or isopropyl); the abbreviation "iPr" refers to an isopropyl group; the abbreviation "Bu" refers to any butyl group (n-butyl, iso-butyl, tert-butyl, sec-butyl); the abbreviation "tBu" refers to a tert-butyl group; the abbreviation "sBu" refers to a sec-butyl group; the abbreviation "iBu" refers to an iso-butyl group; the abbreviation "Ph" refers to a phenyl group.

[0027] The term "substrate" refers to a material or materials on which a process is conducted. The substrate may refer to a wafer having a material or materials on which a process is conducted. The substrates may be any suitable wafer used in semiconductor, photovoltaic, flat panel, or LCD-TFT device manufacturing. The substrate may also have one or more layers of differing materials already deposited upon it from a previous manufacturing step. For example, the wafers may include silicon layers (e.g., crystalline, amorphous, porous, etc.), silicon-containing layers (e.g., SiO_2, SiN, SiON, SiCOH, etc.), metal containing layers (e.g., copper, cobalt, molybdenum, tungsten, platinum, palladium, nickel, ruthenium, gold, etc.), an organic layer such as amorphous carbon, or a photoresist,

or combinations thereof. Furthermore, the substrate may be planar or patterned. The substrate may include layers of oxides which are used as dielectric materials in MEMS, 3D NAND, MIM, DRAM, or FeRam device applications (for example, ZrO_2 based materials, HfO_2 based materials, TiO_2 based materials, rare earth oxide based materials, ternary oxide based materials, etc.) or nitride-based films (for example, TaN, TiN, NbN) that are used as electrodes. One of ordinary skill in the art will recognize that the terms "film" or "layer" used herein refer to a thickness of some material laid on or spread over a surface and that the surface may be a trench or a line. Throughout the specification and claims, the wafer and any associated layers thereon are referred to as substrates.

[0028] The term "wafer" or "patterned wafer" refers to a wafer having a stack of silicon-containing films on a substrate and a patterned hardmask layer on the stack of silicon-containing films formed for pattern etch. The term "wafer" or "patterned wafer" may also refers to a trench wafer having an aspect ratio.

[0029] The term "aspect ratio" refers to a ratio of the height of a trench (or aperture) to the width of the trench (or the diameter of the aperture).

[0030] Note that herein, the terms "aperture", "gap", "via", "hole", "opening", "trench" and "structure" may be used interchangeably to refer to an opening formed in a semiconductor substrate.

[0031] Note that herein, the terms "film" and "layer" may be used interchangeably. It is understood that a film may correspond to, or related to a layer, and that the layer may refer to the film. Furthermore, one of ordinary skill in the art will recognize that the term "film" or "layer" used herein refers to a thickness of some material laid on or spread over a surface and that the surface may range from as large as the entire wafer to as small as a trench or a line. Furthermore, the term "film" or "layer" used herein may also refer to a gap fill, more specifically, a gap fill formed by a bottom up deposition process. Herein, the "gap" refers to an aperture, a via, a hole, an opening, a trench, or the like.

[0032] Note that herein, the terms "deposition temperature", "substrate temperature" and "process temperature" may be used interchangeably. It is understood that a substrate temperature may correspond to, or be related to a deposition temperature or a process temperature, and that the deposition temperature or process temperature may refer to the substrate temperature.

[0033] Note that herein, the terms "precursor" and "deposition compound" and "deposition gas" may be used interchangeably when the precursor is in a gaseous state at room temperature and ambient pressure. It is understood that a precursor may correspond to, or be related to a deposition compound or deposition gas, and that the deposition

compound or deposition gas may refer to the precursor.

[0034] As used herein, the abbreviation "NAND" refers to a "Negated AND" or "Not AND" gate; the abbreviation "2D" refers to 2 dimensional gate structures on a planar substrate; the abbreviation "3D" refers to 3 dimensional or vertical gate structures, wherein the gate structures are stacked in the vertical direction.

[0035] The term "inhibitor" used herein refers to a modifier, a suppressor or a promoter, etc., which includes concepts of inhibition, suppression or promotion to improve the step coverage. The inhibitor is an additive or an inserted chemical during vapor deposition processes, which is removed after depositing a film. The inhibitor enhances conformality of a film deposited on a HAR structure and/or helps to remove voids or weakpoints in a gapfill application. The thickness of the inhibitor on the HAR structure may be a very thin layer, possibly one monolayer or less.

[0036] Please note that the silicon-containing films, such as SiN and SiO, are listed throughout the specification and claims without reference to their proper stoichiometry. The silicon-containing films may include pure silicon (Si) layers, such as crystalline Si, poly-silicon (p-Si or polycrystalline Si), or amorphous silicon; silicon nitride (Si_kN_l) layers; or silicon oxide (Si_nO_m) layers; or mixtures thereof, wherein k, l, m, and n, inclusively range from 0.1 to 6. Preferably, silicon nitride is Si_kN_l, where k and l each range from 0.5 to 1.5. More preferably silicon nitride is Si_3N_4. Herein, SiN in the following description may be used to represent Si_kN_l containing layers. Preferably silicon oxide is Si_nO_m, where n ranges from 0.5 to 1.5 and m ranges from 1.5 to 3.5. More preferably, silicon oxide is SiO_2. Herein, SiO in the following description may be used to represent Si_nO_m containing layers. The silicon-containing film could also be a silicon oxide based dielectric material such as organic based or silicon oxide based low-*k* dielectric materials such as the Black Diamond II or III material by Applied Materials, Inc. with a formula of SiOCH. Silicon-containing film may also include $Si_aO_bN_c$ where a, b, c range from 0.1 to 6. The silicon-containing films may also include dopants, such as B, C, P, As and/or Ge.

[0037] Ranges may be expressed herein as from about one particular value, and/or to about another particular value. When such a range is expressed, it is to be understood that another embodiment is from the one particular value and/or to the other particular value, along with all combinations within said range. Any and all ranges recited in the disclosed embodiments are inclusive of their endpoints (*i.e.*, x=1 to 4 or x ranges from 1 to 4 includes x=1, x=4, and x=any number in between), irrespective of whether the term "inclusively" is used.

[0038] Reference herein to "one embodiment" or "an embodiment" means that a

particular feature, structure, or characteristic described in connection with the embodiment may be included in at least one embodiment of the invention. The appearances of the phrase "in one embodiment" in various places in the specification are not necessarily all referring to the same embodiment, nor are separate or alternative embodiments necessarily mutually exclusive of other embodiments. The same applies to the term "implementation."

[0039] As used in this application, the word "exemplary" is used herein to mean serving as an example, instance, or illustration. Any aspect or design described herein as "exemplary" is not necessarily to be construed as preferred or advantageous over other aspects or designs. Rather, use of the word exemplary is intended to present concepts in a concrete fashion.

[0040] "Comprising" in a claim is an open transitional term which means the subsequently identified claim elements are a nonexclusive listing i.e. anything else may be additionally included and remain within the scope of "comprising." "Comprising" is defined herein as necessarily encompassing the more limited transitional terms "consisting essentially of" and "consisting of"; "comprising" may therefore be replaced by "consisting essentially of" or "consisting of" and remain within the expressly defined scope of "comprising".

[0041] Additionally, the term "or" is intended to mean an inclusive "or" rather than an exclusive "or". That is, unless specified otherwise, or clear from context, "X employs A or B" is intended to mean any of the natural inclusive permutations. That is, if X employs A; X employs B; or X employs both A and B, then "X employs A or B" is satisfied under any of the foregoing instances. In addition, the articles "a" and "an" as used in this application and the appended claims should generally be construed to mean "one or more" unless specified otherwise or clear from context to be directed to a singular form.

Brief Description of the Drawings

[0042] For a further understanding of the nature and objects of the present invention, reference should be made to the following detailed description, taken in conjunction with the accompanying drawings, in which like elements are given the same or analogous reference numbers and wherein:

FIG. 1 is a schematic diagram showing a poor step coverage of a HAR aperture;

FIG. 2 is a schematic diagram showing the inhibitor effect on step coverage of a HAR aperture with an inhibitor according to the disclosed methods;

FIG. 3a is a schematic diagram showing a perfect conformal step coverage of 100% film thickness ratio (bottom thickness/top thickness*100%) of a HAR aperture;

FIG. 3b is a schematic diagram showing a superconformal step coverage of >100% film thickness ratio of a HAR aperture;

FIG. 3c is a schematic diagram showing a gap fill up process through bottom up deposition;

FIG. 3d is a schematic diagram showing a gap fill through bottom up deposition;

FIG. 4a is an exemplary timing diagram for an order of introducing an inhibitor, a precursor and a co-reactant according to the disclosed methods;

FIG. 4b is another exemplary timing diagram for an order of introducing an inhibitor, a precursor and a co-reactant according to the disclosed methods;

FIG. 4c is another exemplary timing diagram for an order of introducing an inhibitor, a precursor and a co-reactant according to the disclosed methods;

FIG. 4d is another exemplary timing diagram for an order of introducing an inhibitor, a precursor and a co-reactant according to the disclosed methods;

FIG. 5 is a SEM image showing about 60% of step coverage of an aspect ratio 20:1 aperture without an inhibitor;

FIG. 6 is a SEM image showing about 100% of step coverage of an aspect ratio 25:1 aperture with the inhibitor dimethoxyethane (DME);

FIG. 7 is a SEM image showing about 100% of step coverage of an aspect ratio 25:1 aperture with the inhibitor triethylamine (TEA);

FIG. 8 is a SEM image showing about 100% of step coverage of an aspect ratio 20:1 hole with the inhibitor tetrahydrofuran (THF);

FIG. 9 is a consistent decrease in the growth rate with precursor dose time at 300°C within a saturation regime;

FIG. 10 is a comparison of GPC with and without inhibitor (DMEDA) within an ALD saturation regime;

FIG. 11 is a bottom up growth in 11:1 aspect ratio structure at 300°C; and

FIG. 12 is a full gap filling in 25:1 aspect ratio patterned structure.

Description of Preferred Embodiments

[0043] Disclosed are deposition methods for high aspect ratio (HAR) structures using an inhibitor molecule in addition to precursors in semiconductor applications. More specifically, the disclosed inhibitor deposition methods relates to vapor deposition processes using organometallic precursors and the inhibitor molecule containing O, N, S, P, B, C, F, Cl, Br, or I to improve thickness control of the deposited film, such as step coverage of a film in a substrate and a gap fill in the substrate. The disclosed inhibitor

deposition methods include the vapor deposition processes involving the inhibitors to improve thickness control, step coverage and gap fill. Furthermore, the disclosed inhibitor deposition methods include ALD processes involving the inhibitors to improve thickness control, step coverage and gap fill. The disclosed inhibitors include concepts of deposition inhibition, suppression or promotion to improve the resulting thickness of the deposited film including step coverage and gap fill. More specifically, the disclosed inhibitor deposition methods include a selection of inhibitor molecules and a selection of inhibitor doses to improve the thickness control of the deposited films, e.g., step coverage, gap fill, to prevent overhang films in the HAR structures, so called "pinch off", and to prevent voids and/or weakpoints formed in the deposited films and/or gap fills. The HAR structures include HAR apertures, gaps, holes, vias, trenches, openings and the like, manufactured in a substrate from a previous manufacturing process. The substrate generally has one or more layers of differing materials already deposited upon it from a previous manufacturing process.

[0044] The disclosed deposition precursors may be organometallic precursors. More specifically, the disclosed precursors may include alkylamino and cyclopendadiendyl derivatives of transition metals and main group elements that contain homoleptic or heteroleptic ligands selected from alkylamines, alkoxy, amidinates, or halides. The transition metals and main group elements may be Hf, Zr, Nb, Ti, lanthanides, rare earths, Al, Si, and so on. The disclosed precursors are suitable for the vapor deposition processes.

[0045] The disclosed deposition precursors include typical and well-known precursors applied to the vapor depositions, for example,

$M(CpR^1R^2R^3R^4R^5)(NR'_2)_3$, wherein M = Group 4 element, R^1, R^2, R^3, R^4 and R^5 each is independently H or a C_1 to C_6 linear or branched alkyl group, R′ is a C_1 to C_4 linear or branched alkyl group;

$M(CpR^1R^2R^3R^4R^5)(OR')_3$, wherein M = Group 4 element, R^1, R^2, R^3, R^4 and R^5 each is independently H or a C_1 to C_6 linear or branched alkyl group, R′ is a C_1 to C_4 linear or branched alkyl group;

$M(CpR^1R^2R^3R^4R^5)X_3$, wherein M = Group 4 element, R^1, R^2, R^3, R^4 and R^5 each is independently H or a C_1 to C_6 linear or branched alkyl group, X = halides;

$M(=NtBu)(NR_2)_3$, wherein M = Group 5 element, R = C_1 to C_6 alkyls;

$M(=NtBu)(CpR^1R^2R^3R^4R^5)(NR'_2)_3$, wherein M = Group 5 element, R^1, R^2, R^3, R^4 and R^5 each is independently H or a C_1 to C_6 linear or branched alkyl group, R′ is a C_1 to C_4 linear or branched alkyl group;

$M(NR_2)_5$, wherein M = Group 5 element, R = C_1 to C_6 alkyls;

AlR_3, wherein R = C_1 to C_6 alkyls;

$Ln(CpR^1R^2R^3R^4R^5)_3$, wherein Ln = Lanthanide elements, R^1, R^2, R^3, R^4 and R^5 each is independently H or a C_1 to C_6 linear or branched alkyl group;

$Ln(CpR^1R^2R^3R^4R^5)_2(R'\text{-amd})$, wherein Ln = Lanthanide elements, R^1, R^2, R^3, R^4 and R^5 each is independently H or a C_1 to C_6 linear or branched alkyl group, R′ is a C_1 to C_4 linear or branched alkyl group;

$Ln(CpR^1R^2R^3R^4R^5)_2(R'\text{-fmd})$, wherein Ln = Lanthanide elements, R^1, R^2, R^3, R^4 and R^5 each is independently H or a C_1 to C_6 linear or branched alkyl group, R′ is a C_1 to C_4 linear or branched alkyl group;

$Ln(NR_2)_3$, wherein Ln = Lanthanide elements, R = C_1 to C_6 alkyls;

hexacarbonyl(3,3-dimethyl-1-butyne)dicobalt (CCTBA, CAS No.: 56792-69-9);

$Ru(CpR^1R^2R^3R^4R^5)_2$, wherein R^1, R^2, R^3, R^4 and R^5 each is independently H or a C_1 to C_6 linear or branched alkyl group;

Ru(R-cyclohexadiene)$(CO)_3$, wherein R = C_1 to C_6 alkyls;

compounds of oxygen and chlorine with molybdenum MoO_xCl_y, wherein $x > 0$, $y > 0$;

organometallic molybdenum compounds; and

other Silicon-containing precursors.

[0046] Exemplary examples of the disclosed deposition precursors include an organometallic precursor selected from alkylamino and cyclopendadiendyl derivatives of transition metals and main group elements that contain homoleptic or heteroleptic ligands selected from alkylamines, alkoxy, amidinates, or halides, wherein the transition metals and main group elements is selected from Hf, Zr, Nb, Ti, lanthanides, rare earths, Al or Si.

[0047] Exemplary examples of the disclosed deposition precursors include $HfCp(NMe_2)_3$, $ZrCp(NMe_2)_3$, $NbCp(NMe_2)_3$, and $TiCp(NMe_2)_3$.

[0048] The most important feature of the disclosed inhibitor deposition methods is a selection of an inhibitor. The inhibitor should not react with a precursor that is used in the deposition process and should be physisorbed on the surface of HAR structures yet not so strongly (mild absorption), so that the physisorbed inhibitor may be subsequently purged and removed by a following purge step. In addition, in order to avoid any unnecessary reactions with an incoming co-reactant, the inhibitor dose and the following purge steps should be separated from the precursor dose and purge steps. In a HAR structure, the inhibitor layer may form a vertical gradient adsorption along the aperture, high adsorption near to the top entrance, low adsorption deep at the bottom (see **FIG. 1**), which may

compete with the incoming precursors for active binding sites of the surface, resulting in an improved step coverage and/or a perfect step coverage, for example, a step coverage of ≥ 100%, see **FIG. 2** and **FIG. 3a** and **FIG. 3b**.

[0049] The disclosed inhibitors may contain O, N, S, P, B, C, or a halogen element (e.g., F, Cl, Br, I).

[0050] The disclosed inhibitors include oxygen based inhibitors, nitrogen based inhibitors, sulfur based inhibitors, phosphorus based inhibitors, boron based inhibitors, carbon based inhibitors, halide containing organic molecules and inorganic halides, H_2O vapor, H_2 gas, CO gas, CS gas, nitrogen oxide (NO_x) gases, and any radical forms of gases at room temperature or higher.

[0051] The disclosed oxygen based inhibitors include aliphatic and aromatic inhibitors, such as, alcohols, diols, ethers, epoxides, aldehydes, ketones, carboxylic acids, enols, esters, anhydrides, phenols, substituted phenols, and the like. Exemplary examples of the disclosed oxygen based inhibitors include tetrahydrofuran (THF), dimethoxyethane (DME), diethylether and dioxane.

[0052] The disclosed nitrogen based inhibitors include aliphatic and aromatic inhibitors, such as, amines, imines, imides, amides, azides, cyanates, nitrile, nitrate, nitrite, nitrogen containing heterocycles, and the like. Exemplary examples of the disclosed nitrogen based inhibitors include triethylamine (TEA), trimethylamine, dimethylethylenediamine (DMEDA), tetramethylethylenediamine (TMEDA) and NH_3.

[0053] The disclosed sulfur based inhibitors include aliphatic and aromatic inhibitors, such as, thiols, sulfides, disulfide, sulfonxide, sulfone, thiocyanates, isothiocyanates, thioesters, and the like. Exemplary examples of the disclosed sulfur based inhibitors include H_2S, Me_2S, Et_2S, Me_2S-SMe_2 and Et_2S-SEt_2.

[0054] The disclosed phosphorus based inhibitors include aliphatic and aromatic inhibitors, such as, phosphines, phosphonic acid, phosphodiesters, and the like. Exemplary examples of the disclosed phosphorus based inhibitors include PH_3, PMe_3 and $P(OMe)_3$.

[0055] The disclosed boron based inhibitors include aliphatic and aromatic inhibitors, such as, boronic acid, boronic ester, borinic esters, and the like. Exemplary examples of the disclosed boron based inhibitors include BMe_3, BEt_3, borazine, $B(OMe)_3$ and $B(OEt)_3$.

[0056] The disclosed carbon based inhibitors include aliphatic inhibitors, such as, alkanes, alkenes, alkynes and benzene derivatives, and the like. Exemplary examples of the disclosed carbon based inhibitors include acetylene and alkene.

[0057] The disclosed halide containing organic molecules and inorganic halides include I_2.

[0058] The disclosed inhibitors may be radical forms of gases at room temperature. The disclosed inhibitors are any radical forms of gases at a temperature range from room temperature to approximately 650°C; preferably, the disclosed inhibitors are compounds that may interact with surface having relatively high electron negativity or lone pair electrons. For example, THF, DME, TEA, and the like.

[0059] Purity of the disclosed precursors and inhibitors is greater than 95% w/w (i.e., 95.0% w/w to 100.0% w/w), preferably greater than 98% w/w (i.e., 98.0% w/w to 100.0% w/w), and more preferably greater than 99% w/w (i.e., 99.0% w/w to 100.0% w/w). One of ordinary skill in the art will recognize that the purity may be determined by H NMR and gas liquid chromatography with mass spectrometry. The disclosed precursors and inhibitors may contain impurities of organic, inorganic and metal-containing molecules. The total quantity of these impurities is preferably below 5% w/w (i.e., 0.0% w/w to 5.0% w/w), preferably below 2% w/w (i.e., 0.0% w/w to 2.0% w/w), and more preferably below 1% w/w (i.e., 0.0% w/w to 1.0% w/w). The disclosed precursors and inhibitors may be purified by recrystallisation, sublimation, distillation, and/or passing the gas liquid through a suitable adsorbent, such as a 4Å molecular sieve.

[0060] Purification of the disclosed precursors and inhibitors may also result in metal impurities at the 0 ppbw to 1 ppmw, preferably 0-500 ppbw (part per billion weight) level. These metal impurities may include, but are not limited to, Aluminum (Al), Arsenic (As), Barium (Ba), Beryllium (Be), Bismuth (Bi), Cadmium (Cd), Calcium (Ca), Chromium (Cr), Cobalt (Co), Copper (Cu), Gallium (Ga), Germanium (Ge), Hafnium (Hf), Zirconium (Zr), Iron (Fe), Lead (Pb), Lithium (Li), Magnesium (Mg), Manganese (Mn), Tungsten (W), Nickel (Ni), Potassium (K), Sodium (Na), Strontium (Sr), Thorium (Th), Tin (Sn), Titanium (Ti), Uranium (U), Zinc (Zn) and the like.

[0061] In addition to the disclosed precursors and inhibitors, a co-reactant may be used. The co-reactant may be O_3, O_2, H_2O, H_2O_2, D_2O, alcohols, NH_3, N_2, N_2H_2, H_2, radicals thereof. Preferably, the co-reactant is O_3 or NH_3. Preferably, the radicals are any radical forms of gases generated by plasma formed at room temperature or above. For an ALD process without plasma involved, the radical of the co-reactant may be formed prior to introducing the co-reactant into the reactor. Preferably, the co-reactant is a gas or in a vapor form. In case a liquid co-reactant is used, the vapor form of the co-reactant needs to be produced prior to introducing the co-reactant to a reactor. In some embodiments, a co-reactant and an inhibitor may be the same molecule such as ammonia. For example, ammonia may be used with a metalorganic precursor as a co-reactant for forming SiNx films, and then the ammonia may be used in a separate step in a deposition sequence as

an inhibitor.

[0062] Purity of the disclosed co-reactant is greater than 95% v/v or by volume (i.e., 95.0% v/v to 100.0% v/v), preferably greater than 98% v/v (i.e., 98.0% v/v to 100.0% v/v), and more preferably greater than 99% v/v (i.e., 99.0% v/v to 100.0% v/v). One of ordinary skill in the art will recognize that the purity may be determined by H NMR and gas liquid chromatography with mass spectrometry. The disclosed co-reactants may contain impurities of organic molecules. The total quantity of these impurities is preferably below 5% v/v (i.e., 0.0% v/v to 5.0% v/v), preferably below 2% v/v (i.e., 0.0% v/v to 2.0% v/v), and more preferably below 1% v/v (i.e., 0.0% v/v to 1.0% v/v). The disclosed co-reactants may be purified by distillation and/or passing the gas liquid through a suitable adsorbent, such as a 4Å molecular sieve.

[0063] The disclosed inhibitor deposition methods may be used to deposit films and to fill gaps on high aspect ratio structures using any deposition methods known to those of skill in the art. Examples of suitable vapor deposition methods include CVD and ALD. Exemplary CVD methods include thermal CVD, plasma enhanced CVD (PECVD), pulsed CVD (PCVD), low pressure CVD (LPCVD), sub-atmospheric CVD (SACVD) atmospheric pressure CVD (APCVD), hot-wire CVD (HWCVD, also known as cat-CVD, in which a hot wire serves as an energy source for the deposition process), radicals incorporated CVD, and combinations thereof. Exemplary ALD methods include thermal ALD, plasma enhanced ALD (PEALD), spatial ALD, hot-wire ALD (HWALD), radicals incorporated ALD, and combinations thereof, Super critical fluid deposition may also be used. The deposition method is preferably ALD, PE-ALD, spatial ALD in order to provide suitable step coverage and film thickness control.

[0064] The films deposited on the HAR structures using the disclosed inhibitor deposition methods may be metal films, metal oxide films, silicon-containing films, alloys, and so on. Exemplary film deposited on the HAR structures is ZrO_2 and HfO_2.

[0065] With the suitable vapor deposition methods, the disclosed precursors and inhibitors may be supplied either in neat form in a blend with a suitable solvent, such as ethyl benzene, xylene, mesitylene, decalin, decane, dodecane. The disclosed precursors and inhibitors may be present in varying concentrations in the solvent. A neat blended precursor and a neat blended inhibitor may be introduced into a reactor, respectively, in a vapor form by conventional means, such as tubing and/or flow meters. The vapor form may be produced by vaporizing the neat blended precursor and inhibitor through a conventional vaporization step such as direct vaporization, distillation, by bubbling, or by using a sublimator. The neat blended precursor and inhibitor may be fed in a liquid state to a

vaporizer where it is vaporized before it is introduced into the reactor. Alternatively, the neat blended precursor and inhibitor may be vaporized by passing a carrier gas into a container containing the composition by bubbling the carrier gas into the composition. The carrier gas may include, but is not limited to, Ar, He, N_2, and mixtures thereof. Bubbling with a carrier gas may also remove any dissolved oxygen present in the neat blended precursor and inhibitor. The carrier gas and precursor and the carrier gas and inhibitor are then introduced into the reactor as a vapor, respectively. Similarly, if a liquid co-reactant is used, the vapor form of the co-reactant will be produced in the same way as that of the precursor and inhibitor.

[0066] If necessary, the containers containing the disclosed precursor, inhibitor and co-reactant may be heated to a temperature that permits the precursor, inhibitor and co-reactant to be in their liquid phase and to have a sufficient vapor pressure. The container may be maintained at temperatures in the range of, for example, approximately 0°C to approximately 200°C. Those skilled in the art recognize that the temperature of the container may be adjusted in a known manner to control the amount of precursor vaporized.

[0067] The reactor or reaction chamber may be any enclosure chamber within a device in which deposition methods take place such as without limitation, a parallel-plate type reactor, a cold-wall type reactor, a hot-wall type reactor, a single-wafer reactor, a multi-wafer reactor, other types of deposition systems under conditions suitable to cause the compounds to react and form the layers. One of ordinary skill in the art will recognize that any of these reactors may be used for either ALD or CVD deposition processes.

[0068] The reactor contains one more substrates onto which the films will be deposited. A substrate is generally defined as the material on which a process is conducted. The substrates may be any suitable substrate used in semiconductor, photovoltaic, fiat panel, LCD-TFT device manufacturing. Examples of suitable substrates include wafers, such as silicon, silica, glass, GaAs wafers. The wafer may have one more layers of differing materials deposited on it from a previous manufacturing step. For example, the wafers may include a dielectric layer. Furthermore, the wafers may include silicon layers (crystalline, amorphous, porous, etc.), silicon oxide layers, silicon nitride layers, silicon oxy nitride layers, carbon doped silicon oxide (SiCOH) layers, metal, metal oxide metal nitride layers (Ti, Ru, Ta, etc.), and combinations thereof. Additionally, the wafers may include copper layers, noble metal layers (e.g., platinum, palladium, rhodium, gold). The wafers may include barrier layers, such as manganese, manganese oxide, etc. Plastic layers, such as poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate)[PEDOT:PSS] may also be used. The layers may be planar or patterned. The patterned layers may be alternating layers of two

specific layers such as In_2O_3 and ZrO_2 used in 3D NAND. The wafer may have one more apertures formed in it from a previous manufacturing step. The aperture may be a hole, via, trench, gap, etc. formed in the wafer or substrate. The aspect ratios of the aperture may range from approximately 5:1 to approximately 200:1. The disclosed methods may deposit a film directly on the aperture in the wafer. Furthermore, one of ordinary skill in the art will recognize that the terms "film" "layer" used herein refer to a thickness of some material laid on spread over a surface and that the surface may be a trench a line. Throughout the specification and claims, the wafer and any associated layers thereon are referred to as substrates.

[0069] The temperature and the pressure within the reactor or chamber are held at conditions suitable for vapor depositions, such as ALD and CVD. In other words, after introduction of the vaporized precursor, inhibitor and co-reactant into the reactor, conditions within the reactor are at least part of the precursor is deposited onto the substrate to form a layer. For instance, the pressure in the reactor or the deposition pressure may be held between about 10^{-3} Torr and about 100 Torr, more preferably between about 10^{-2} Torr and about 100 Torr, as required per the deposition parameters. The temperature of the reactor may be controlled by either controlling the temperature of the substrate holder controlling the temperature of the reactor wall. Devices used to heat the substrate are known in the art. The reactor wall is heated to a sufficient temperature to obtain the desired film at a sufficient growth rate and with desired physical state and composition. A non-limiting exemplary temperature range to which the reactor wall may be heated includes from room temperature to approximately 650°C. When a plasma deposition process is utilized, the reactor temperature may range from approximately 100°C to approximately 500°C. Alternatively, when a thermal process is performed, the reactor temperature may range from approximately 100°C to approximately 650°C.

[0070] Alternatively, the substrate may be heated to a sufficient temperature to obtain the desired film at a sufficient growth rate and with desired physical state and composition. A non-limiting exemplary temperature range to which the substrate may be heated includes from room temperature to approximately 650°C. Furthermore, one of ordinary skill in the art will recognize that the temperature of the reactor and the temperature of substrate will reach to an equilibrium temperature during the deposition process. Throughout the specification and claims, the reactor temperature and the substrate temperature refer to a deposition temperature. Thus, the deposition temperature of the disclosed methods ranges from room temperature to approximately 650°C. When a plasma deposition process is utilized, the deposition temperature may range from approximately 100°C to approximately

500°C. Alternatively, when a thermal process is performed, the deposition temperature may range from approximately 100°C to approximately 650°C.

[0071] The disclosed precursor, inhibitor and co-reactant may be introduced into the reactor either simultaneously (CVD) or sequentially (ALD) with various supplying orders of the inhibitor, the precursor and the co-reactant. The reactor may be purged with an inert gas (for example, N_2, Ar, Kr, Xe) between the introductions of the inhibitor, the precursor and the co-reactant. Alternatively, the inhibitor, the precursor and the co-reactant may be mixed together to form an inhibitor/precursor/co-reactant mixture, and then introduced to the reactor in a mixture form. Alternatively, the inhibitor and the precursor may be mixed together to form an inhibitor/precursor mixture introduced to the reactor in a mixture form and then a co-reactant is introduced to the reactor.

[0072] In the disclosed processes, the substrate exposure time may range from 0.1 second to 30 minutes, preferably, from 0.5 seconds to 10 minutes; the disclosed precursor exposure time may range from 0.1 second to 30 minutes, preferably, from 0.5 seconds to 10 minutes; the disclosed inhibitor exposure time may range from 0.1 second to 30 minutes, preferably, from 0.5 seconds to 10 minutes; the co-reactant exposure time may range from 0.1 second to 30 minutes, preferably, from 0.5 seconds to 10 minutes. In the disclosed processes, a dose of the inhibitor may be larger than a dose of the precursor and vice versa; a dose of the inhibitor may be larger than a dose of the co-reactant and vice versa.

[0073] Alternatively, the vaporized inhibitor, precursor and co-reactant may be simultaneously sprayed from different sectors of a shower head (without mixing of the inhibitor, precursor and the co-reactant) under which a susceptor holding several wafers is spun (spatial ALD).

[0074] Depending on particular process parameters, deposition may take place for a varying length of time. Generally, deposition may be allowed to continue as long as desired necessary to produce a film or to produce a gap fill with necessary properties. Typical film thicknesses may vary from several angstroms to several hundreds of microns, and typically from 2 to 100 nm, depending on the specific deposition process. Typical gap depth to be filled may vary from several hundreds of nanometers to several hundreds of micrometers, and typically from 100 nm to 100 um, depending on the specific deposition process. The deposition process may also be performed as many times (e.g., cycles of ALD) as necessary to obtain a desired film with an improved or a perfect step coverage (e.g., $\geq$ 100%) and a desired gap fill without voids and/or weakpoints formed in the deposited films and the gap fills. In some cases, by adding an inhibitor, the disclosed inhibitor deposition method may improve the step coverage and the gap fill over the cases that no inhibitors

are applied, even though the targeted step coverage does not reach to a perfect step coverage (e.g., ≥ 100%).

[0075] In a non-limiting exemplary ALD process of forming a metal oxide film, a three-step process may be performed. First, the vapor phase of the disclosed inhibitor, such as, dimethoxyethane (DME), is introduced into the reactor, where it is physisorbed on the surface. Excess inhibitor may then be removed from the reactor by purging and/or evacuating the reactor, that is, either by purging a reactor with an inert gas (for example, N_2, Ar, Kr, Xe), or passing the substrate in a sector under high vacuum and/or a carrier gas curtain. Secondly, a precursor, such as $ZrCp(NMe_2)_3$ or $HfCp(NMe_2)_3$, is introduced into the reactor where it is absorbed (chemisorbed and physisorbed as well) on the substrate. Excess precursor may then be removed from the reactor by purging the reactor using the inert gas and/or evacuating the reactor. Thirdly, a co-reactant (for example, O_3) is introduced into the reactor where it reacts with the adsorbed precursor to deposit a film on the surface in a self-limiting manner and reacts with the physisorbed inhibitor to remove it from the surface. After that, any excess co-reactant is removed from the reactor by purging and/or evacuating the reactor. If the desired film is an oxide, such as ZrO_2, this three-step process, i.e., inhibitor-precursor-co-reactant, may be repeated until a film having a necessary thickness and a desired step coverage has been obtained or a gap has been filled. Alternatively, the order of the inhibitor, the precursor and the co-reactant introduced to the reactor of this three-step process may vary. For example, the three-step process may be precursor-inhibitor-co-reactant sequentially; inhibitor-precursor-co-reactant sequentially; precursor-co-reactant-inhibitor sequentially; inhibitor-co-reactant-precursor sequentially, inhibitor and the precursor simultaneously and then co-reactant; and so on. This three-step process may provide a desired film thickness and film conformality and a desired gap fill.

[0076] In some embodiments, the disclosed method is related to a vapor deposition process, such as CVD or ALD, employing the disclosed inhibitors to improve step coverage of a deposited film in a substrate.

[0077] **FIG. 1** is a schematic diagram showing a poor step coverage of a HAR aperture. A substrate **102** has an aperture **104** therein. A film **106** is deposited using a vapor deposition process, such as ALD, on the top and sidewall of the aperture **104**. In this case, the film **106** is mainly deposited in the top part of the aperture and no film is deposited on the bottom of the aperture, because a deposition precursor could not access to the deep part of the aperture during a deposition process. The aperture **104** may be a hole, via, trench, gap, opening etc. formed in the substrate **102** from a previous manufacturing

process. The aspect ratios of the aperture **104** may range from approximately 5:1 to approximately 200:1. Without using an inhibitor, the film **106** deposited on the aperture is not conformal. Here, step coverage is defined as b/a x 100% (bottom thickness / top thickness x 100%); aspect ratio is defined as L/d. As shown, in this case, without using the inhibitor, b < a, therefore, the step coverage is less than 100%.

[0078] **FIG. 2** is a schematic diagram showing the inhibitor effect on step coverage of a HAR aperture with an inhibitor according to the disclosed methods. The aperture **204** may be a hole, via, trench, gap, etc. formed in the substrate **202** from a previous manufacturing process. The aspect ratios of the aperture **204** may range from approximately 5:1 to approximately 200:1. An inhibitor adsorption layer (not shown) may form a vertical gradient of physisorption along the aperture, which has a high adsorption near to the top entrance of the aperture, a low adsorption deep at the bottom. With the inhibitor physisorbed thereon (not shown), an incoming deposition precursor may be able to access to the deeper part of the aperture and adsorb thereon. The deposition precursor adsorption includes physisorption and chemisorption. The inhibitor adsorption layer may compete with the incoming deposition precursor for active binding sites of the surface of the aperture, resulting in the deposition precursor adsorbed in the deep part of the aperture. The concentration of the precursor in the bottom of the aperture **204** is higher than the concentration of the precursor in the top portion of the aperture **204**. An incoming co-reactant reacts with the adsorbed precursor, which forms a film **206** from the deep part of the aperture. Repeating this cycle more times, the film **206** is growing from the deep part of the aperture **204** to the top part of the aperture **204** and gradually reaches to the top entrance of the aperture. Eventually the film **206** is formed with a desired thickness and a perfect step coverage as shown in **FIG. 3a**, a schematic diagram showing a step coverage of 100% (b = a) of a HAR aperture with a conformal film, and **FIG. 3b**, a schematic diagram showing a step coverage of >100% (b > a) of a HAR aperture with a superconformal film. As shown, the aperture **304** may be a hole, via, trench, gap, etc. formed in the substrate **302** from a previous manufacturing process. An incoming co-reactant reacts with the adsorbed precursor, which forms a film **306** from the deep part of the aperture. Repeating this cycle more times, the film **306** is growing from the deep part of the aperture **304** to the top part of the aperture **304** and gradually reaches to the top entrance of the aperture. Here, prior to exposing the aperture to the deposition precursor, a purge step using an inert gas (e.g., N_2, Ar, Kr, etc.) is performed to remove excess inhibitor. Prior to exposing the aperture to the co-reactant, a purge step is performed to remove excess deposition precursor. For next cycle, prior to exposing the aperture to the inhibitor, a purge step is performed to

remove excess co-reactant. In this way, the disclosed inhibitor deposition methods are capable of producing a perfect conformal step coverage and superconformal step coverage, i.e., a step coverage of ≥100% film thickness on the apertures having an aspects ratio ranging from approximately 5:1 to approximately 200:1.

[0079] Continue to repeat the cycle even more times, the film **306** is growing from the deep bottom part of the aperture **304** to the top part of the aperture **304** and gradually the aperture **304** is filled up from the bottom of the aperture **304**, as shown in **FIG. 3c**, where the aperture **304** has been filled up to the middle part of the aperture **304**. Continue to repeat the cycle even more times, the film **306** keeps growing to the top part of the aperture **304** and gradually fills up the aperture **304** as shown in **FIG. 3d**, where the aperture **304** has been filled up to the top of the aperture **304** and the aperture **304** has been fully filled up. The cycles may be stopped until the aperture **304** is fully filled up.

[0080] **FIG. 4a** to **FIG. 4d** are various exemplary timing diagrams of a method and order of supplying an inhibitor, a precursor and a co-reactant according to the disclosed inhibitor deposition methods, in which each of feed materials, i.e., the inhibitor, the precursor and the co-reactant, may be pulse-supplied. Flow rate and supplying times of the respective feed materials may not be proportional to the heights and widths of pulses shown in **FIG. 4a** to **FIG. 4c**.

[0081] **FIG. 4a** refers to a three-step deposition process in a sequence of inhibitor-precursor-co-reactant. Although it described above in forming the metal oxide film, a more detailed description is described herein. When the inhibitor is introduced into a reactor, the inhibitor may be physisorbed on a surface of a substrate in the reactor. Then the reactor may be purged with a purge gas so that an excess amount of the inhibitor is removed and the physisorbed inhibitor may be left as a very thin layer, possibly one monolayer or less.

[0082] After that, a precursor is added. The precursor may be physisorbed and chemisorbed on the surface of apertures in the substrate while the chemisorption of the precursor on the substrate is being controlled by the physisorbed inhibitor layer. Since a substantial portion of the surface of apertures is covered with the inhibitor, the precursor may be physisorbed on the surface via the inhibitor. When the reactor is purged with the purge gas again, excess amount of the precursor is removed and an adsorption layer may be obtained by adsorbing the precursor on the surface. The adsorption layer may be in the level of a very thin layer, maybe one monolayer or less. More specifically, in this way, excessive adsorption of the precursor may be considerably controlled at an entrance and the top portion of the apertures. The precursor is able to access to the deep part of the

apertures.

[0083] Afterward, the co-reactant is introduced. The co-reactant may react with the adsorbed precursor to form a film, and react with the co-reactant to remove it. Then by purging, excessive amounts of the co-reactant and reaction byproducts may be removed from the reactor.

[0084] **FIG. 4b** refers to a three-step deposition process in a sequence of precursor-inhibitor-co-reactant. The precursor is first introduced into the reactor. The precursor may be adsorbed on the surface of the substrate. In this case, a considerable amount of precursor may be directly chemisorbed on the surface of the apertures in the substrate, while additional precursor may be physisorbed on the surface via the chemisorbed precursor. After that, by purging, the precursor physisorbed on the substrate may be partially removed, while some of the physisorbed precursor may still remain on the chemisorbed precursor. Since the physisorbed precursor is an excessively adsorbed source material, it may be necessary to remove the physisorbed precursor to form a conformal film. Thus, the inhibitor is added in the next step. The inhibitor may be combined with the precursor due to van der Waals attraction. More specifically, the inhibitor may be combined with the central atom of the precursor. The physisorbed precursor may be released due to this combination, and the excessively adsorbed precursor may be mostly removed. After that, by purging, the excessive inhibitor and the reaction byproducts may be removed from the reactor, and a layer at which the precursor is chemisorbed on the level of a very thin layer, one monolayer or less, may be obtained. The reaction byproducts may include a combination of the inhibitor with the precursor.

[0085] Subsequently, the co-reactant is introduced. The co-reactant may be reacted with the precursor that is chemisorbed in a monolayer state to form a film, and the inhibitor may be reacted with the co-reactant and removed. By purging, excessive amounts of co-reactant and the reaction byproducts may be removed from the reactor.

[0086] **FIG. 4c** refers to a three-step deposition process in a sequence of precursor- co-reactant-inhibitor. In this case, the precursor is added first and the precursor disposition on the surface of the apertures is the same as that in **FIG. 4b**. Next, after purging to remove excessive physisorbed precursor, the co-reactant is introduced. The co-reactant may be reacted with the precursor that is chemisorbed to form a film. Then, excessive amounts of the reaction byproducts may be removed from the reactor by purging. Subsequently, the inhibitor is introduced. The inhibitor may be adsorbed on the film and the chemisorbed precursor on the surface of the aperture. More specifically, the inhibitor may be combined with the central atom of the precursor. Since the inhibitor may form a vertical gradient

adsorption along the aperture, high adsorption near to the top entrance, low adsorption deep at the bottom, the chemisorbed precursor may be released near the top entrance of the aperture due to this combination, and the excessively adsorbed precursor may be mostly removed by purging, and a layer at which the precursor is chemisorbed on the level of one monolayer or less may be obtained. The reaction byproducts may include a combination of the inhibitor with the precursor.

[0087] **FIG. 4d** refers to a deposition process that the inhibitor and the precursor are introduced simultaneously and afterward the co-reactant is added. The precursor may be combined with each other and form a dimer or trimer when simultaneously introduced to the reactor first. The dimer or trimer is then adsorbed on the surface of the aperture, more layers of the precursor may be excessively adsorbed. When the inhibitor and the precursor are simultaneously added, the inhibitor may diminish the precursors' propensity to form the dimer or trimer. Thus, the excessive adsorption of the precursor may be alleviated, especially near the entrance of the aperture. By purging, the excessive amounts of the precursor, the inhibitor and unnecessary byproducts may be removed from the reactor. Afterward, the co-reactant is added. The co-reactant may be reacted with the adsorbed precursor to form a film, and the inhibitor in the reactor may be reacted with the co-reactant and removed. By purging, the excessive amounts of the co-reactant and the reaction byproducts may be removed from the reactor.

[0088] The processes described with reference to **FIG. 4a** to **FIG. 4d** may be dynamically performed to prevent excessive adsorption of the precursor. By purging with a purging gas, excessive amounts of the precursor, the inhibitor and co-reactant may be removed from the reactor, and unnecessary byproducts may also be removed from the reactor.

[0089] The combination of the order and timing of the inhibitor, the precursor and the co-reactant introduced into the reactor is not limited to those shown in **FIG. 4a** to **FIG. 4d**. The disclosed inhibitor deposition methods include all possible combinations of the orders and timings of the inhibitor, the precursor and the co-reactant introduced into the reactor.

[0090] In a non-limiting exemplary ALD process, the disclosed ALD processes include i) supplying an inhibitor into a reactor that contains a substrate having apertures to be deposited wherein the inhibitor molecules are physisorbed on the surface of the aperture; ii) purging the inhibitor and removing excess inhibitor by a purge gas; iii) supplying a precursor into the reactor wherein the precursor molecules are adsorbed on the surface of the aperture; iv) purging the precursor and removing excess precursor by the purge gas; v) supplying a co-reactant into the reactor wherein the co-reactant reacts with the adsorbed

precursor to form a film on the surface; vi) purging the co-reactant and removing byproducts and excess co-reactant by the purging gas; vii) repeating steps i) to vi) to achieve a desired thickness of the film deposited on the aperture or a desired gap fill in the substrate. The deposited film and the bottom up deposited gap fill produced by the disclosed inhibitor deposition methods have an improved step coverage and an improved gap fill comparing to the deposited film and the gap fill produced with an absence of the inhibitor and have no voids, no weakpoints and/or no seams as well.

[0091] In some embodiments, the disclosed method is related to a novel method of reducing growth rate or growth per cycle (GPC) or thickness in a vapor deposition process by inserting a step of so called "inhibitor", while maintaining CVD or ALD behavior without losing any benefits from it. The disclosed method may be applicable to adjusting growth rate or GPC for better thickness control of very thin layers and good quality of gap fills.

[0092] In some embodiments, the disclosed method is related to a novel method of gap filling by a vapor deposition method (e.g., ALD and CVD) without plasma through a bottom up superconformal thin film depositions with an additives or inhibitors. Referring to **FIG. 3c** and **FIG. 3d**, with an increase of the number of cycles of ALD, a gap in the substrate may be filled up from bottom up deposition. By adjusting the number of cycles, the disclosed inhibitor deposition method may improve the deposited film thickness control and step coverage and enhance the gap fill through bottom up deposition.

[0093] Upon obtaining a desired film thickness, an improved step coverage and a desired gap filling, the deposited film and the gap fill may be subject to further processing, such as thermal annealing, furnace-annealing, rapid thermal annealing, UV e-beam curing, and/or plasma gas exposure. Those skilled in the art recognize the systems and methods utilized to perform these additional processing steps. For example, the ZrO_2 film may be exposed to a temperature ranging from approximately 200°C and approximately 1000°C for a time ranging from approximately 0.1 second to approximately 7200 seconds under an inert atmosphere or an O-containing atmosphere, combinations thereof. Most preferably, the temperature is 400°C for 3600 seconds under an inert atmosphere or an O-containing atmosphere. The resulting film may contain fewer impurities and therefore may have an improved density resulting in improved leakage current. The annealing step may be performed in the same reaction chamber in which the deposition process is performed, or performed in a separate apparatus. Any of the above post-treatment methods, but especially thermal annealing, has been found effective to reduce carbon and nitrogen contamination of the ZrO_2 film. This in turn tends to improve the resistivity of the film.

Examples

[0094] The following non-limiting examples are provided to further illustrate embodiments of the invention. However, the examples are not intended to be all inclusive and are not intended to limit the scope of the inventions described herein.

Example 1: Step coverage without inhibitor in case of ALD of ZrO_2 by $ZrCp(NMe_2)_3$ with ozone.

[0095] The precursor vessel was heated at 80°C. O_3 was used as a co-oxidizing reactant and $ZrCp(NMe_2)_3$ was used as a precursor. A film of ZrO_2 was deposited on patterned wafers that have about 20:1 aspect ratio apertures through an ALD process. A reactor pressure was kept at around 1 Torr. Step coverage was tested with the same deposition conditions without the inhibitor in a temperature window of 200 - 400°C on the patterned wafers that have about 20:1 aspect ratio apertures. **FIG. 5** is a SEM image showing about 60% of step coverage of an aspect ratio 20:1 hole without an inhibitor.

Example 2: Step coverage with inhibitor DME in case of ALD of ZrO_2 by $ZrCp(NMe_2)_3$ with ozone.

[0096] The precursor vessel was heated at 80°C. O_3 was used as a co-oxidizing reactant, DME was used as an inhibitor and $ZrCp(NMe_2)_3$ was used as a precursor. A film of ZrO_2 was deposited on patterned wafers that have about 25:1 aspect ratio apertures through an ALD process. A reactor pressure was kept at around 1 Torr. Step coverage was tested with the same deposition conditions with the inhibitor in a temperature window of 200 - 400°C on patterned wafers, which have about 25:1 aspect ratio apertures. **FIG. 6** is a SEM image showing about 100% of step coverage of an aspect ratio 25:1 hole with the inhibitor DME.

Example 3: Step coverage with inhibitor TEA in case of ALD of ZrO_2 by $ZrCp(NMe_2)_3$ with ozone

[0097] The precursor vessel was heated at 80°C. O_3 was used as a co-oxidizing reactant, TEA as an inhibitor and $ZrCp(NMe_2)_3$ was used as a precursor. A film of ZrO_2 was deposited on patterned wafers that have about 25:1 aspect ratio apertures through an ALD process. A reactor pressure was kept at around 1 Torr. Step coverage was tested with the same deposition conditions with the inhibitor in a temperature window of 200 - 400°C on patterned wafers, which have about 25:1 aspect ratio apertures. **FIG. 7** is a SEM image showing about 100% of step coverage of an aspect ratio 25:1 hole with the inhibitor TEA.

Example 4: Step coverage with inhibitor THF in case of ALD of ZrO_2 by $ZrCp(NMe_2)_3$ with ozone

[0098] The precursor vessel was heated at 80°C. O_3 was used as a co-reactant, THF was used as an inhibitor and $ZrCp(NMe_2)_3$ was used as a precursor. A film of ZrO_2 was deposited on patterned wafers that have about 25:1 aspect ratio apertures through an ALD process. A reactor pressure fixed was kept at around 1 Torr. Step coverage was tested with the same deposition conditions with the inhibitor in a temperature window of 200 - 400°C on patterned wafers, which have about 20:1 aspect ratio apertures. **FIG. 8** is a SEM image showing about 100% of step coverage of an aspect ratio 20:1 hole with the inhibitor THF.

Example 5: ALD of Inhibitor Dose

[0099] The ALD process was done at 300°C. O_3 was used as a co-oxidizing reactant and tetrahydrofuran (THF) as an inhibitor. A reactor pressure was kept at around 1 Torr. The partial pressure of THF was 0.3 Torr. The aspect ratio of the apertures was 25:1 and the critical dimension (CD) was 100nm in a layer of SiO_2. The ALD process was performed with i) 5 second THF flow and 30 second purge; ii) 1 second precursor flow and 30 second purge; and iii) 1 second co-reactant flow and 30 second purge; repeatedly.

Example 6: Thickness control with inhibitor tetramethylethylenediamine (TMEDA) in case of ALD of HfO_2

[0100] ALD tests were performed using tris(dimethylamino)cyclopentadienyl hafnium $HfCp(NMe_2)_3$, ozone as a co-reactant and TMEDA as an inhibitor. In the inhibiting ALD, a reactor pressure was fixed at ~0.6 Torr. **FIG. 9** is a consistent decrease in the growth rate with precursor dose time at 300°C. Here the precursor dose time is shown as source induction time (sec).

Example 7: Thickness control with inhibitor dimethylethylenediamine (DMEDA) in case of ALD of HfO_2

[0101] ALD tests were performed using tris(dimethylamino)cyclopentadienyl hafnium, $HfCp(NMe_2)_3$, ozone as a co-reactant and DMEDA as an inhibitor. In the inhibiting ALD, a reactor pressure was fixed at ~0.6 Torr. **FIG. 10** is a comparison of GPC with and without inhibitor (DMEDA) within an ALD saturation regime, which shows a similar decrease in the growth rate with precursor dose time at 300°C. Here the precursor dose time is shown as source induction time (sec).

Example 8: Bottom up gap filling with an inhibitor tris(2-aminoethyl)amine in case of ALD of HfO_2 by cyclopentadienyl-tris(dimethylamido)hafnium(IV) $HfCp(NMe_2)_3$ with ozone

[0102] ALD tests were performed using cyclopentadienyl-tris(dimethylamido)hafnium(IV), where a precursor containing vessel was heated up to 80°C, O_3 used as an oxidizing reactant and tris(2-aminoethyl)amine used as an inhibitor. A reactor pressure was fixed at ~1 Torr. **FIG. 11** is a bottom up growth in 11:1 aspect ratio structure at 300°C. As the open CD was decreased, gap filling was progressed. **FIG. 12** is a full gap filling in 25:1 aspect ratio patterned structure, which shows the full gap filling without a seam in 25:1 aspect ratio structure at 300°C.

[0103] It will be understood that many additional changes in the details, materials, steps, and arrangement of parts, which have been herein described and illustrated in order to explain the nature of the invention, may be made by those skilled in the art within the principle and scope of the invention as expressed in the appended claims. Thus, the present invention is not intended to be limited to the specific embodiments in the examples given above and/or the attached drawings.

[0104] While embodiments of this invention have been shown and described, modifications thereof may be made by one skilled in the art without departing from the spirit or teaching of this invention. The embodiments described herein are exemplary only and not limiting. Many variations and modifications of the composition and method are possible and within the scope of the invention. Accordingly, the scope of protection is not limited to the embodiments described herein, but is only limited by the claims which follow, the scope of which shall include all equivalents of the subject matter of the claims.

What is claimed is:

1. A deposition method for improving thickness control of a film deposited on high aspect ratio (HAR) apertures in a substrate, the method comprising:

i) sequentially or simultaneously exposing the substrate to a vapor of an inhibitor, a vapor of a precursor and a vapor of a co-reactant; and

ii) depositing the film on the HAR apertures that has a desired thickness control through a vapor deposition process,

wherein the inhibitor contains O, N, S, P, B, C, F, Cl, Br, or I.

2. The deposition method of claim 1, further comprising maintaining a temperature of the substrate in a range of from room temperature to 650°C.

3. The deposition method of claim 1, wherein the inhibitor is selected from one or more of

a) oxygen based aliphatic and aromatic inhibitors including alcohols, diols, ethers, epoxides, aldehydes, ketones, carboxylic acids, enols, esters, anhydrides, phenols, substituted phenols;

b) nitrogen based aliphatic and aromatic inhibitors including amines, imines, imides, amides, azides, cyanates, nitrile, nitrate, nitrite, nitrogen containing heterocycles;

c) sulfur based aliphatic and aromatic inhibitors including thiols, sulfides, disulfide, sulfonxide, sulfone, thiocyanates, isothiocyanates, thioesters;

d) phosphorus based aliphatic and aromatic inhibitors including phosphines, phosphonic acid, phosphodiesters;

e) boron based aliphatic and aromatic inhibitors including boronic acid, boronic ester, borinic esters; carbon based aliphatic inhibitors including alkanes, alkenes, alkynes and benzene derivatives;

f) halide containing organic molecules and inorganic halides including I_2; or

g) H_2O vapor, H_2 gas, CO gas, CS gas and nitrogen oxide (NO_x) gases;

h) and combinations of a)-g).

4. The deposition method of claim 1, wherein the inhibitor is a radical form of a vapor or gas of the inhibitor at a temperature ranging from room temperature to approximately 650°C generated with or without plasma.

5. The deposition method of claim 1, wherein the inhibitor is selected from tetrahydrofuran (THF), dimethoxyethane (DME), triethylamine (TEA), tetramethylethylenediamine (TMEDA), dimethylethylenediamine (DMEDA) or tris(2-aminoethyl)amine.

6. The deposition method of claim 1, wherein the precursor is an organometallic precursor selected from alkylamino and cyclopendadiendyl derivatives of transition metals and main group elements that contain homoleptic or heteroleptic ligands selected from alkylamines, alkoxy, amidinates, or halides.

7. The deposition method of claim 6, wherein the transition metals and main group elements is selected from Hf, Zr, Nb, Ti, lanthanides, rare earths, Al or Si.

8. The deposition method of claim 1, wherein the precursor is $HfCp(NMe_2)_3$, $ZrCp(NMe_2)_3$, $Nb(=NtBu)Cp(NMe_2)_2$ or $TiCp^*(OMe)_3$.

9. The deposition method of claim 1, wherein a step coverage of the film is $\geq$ 100%.

10. The deposition method of claim 9, wherein the step coverage is larger than the step coverage with the absence of the inhibitor.

11. The deposition method of claim 1, wherein the film is a gap fill of the HAR aperture without a seam.

12. The deposition method of claim 1, wherein the gap fill is formed by a bottom up deposition.

13. The deposition method of claim 1, wherein the HAR ranges from 5:1 to 200:1.

14. The deposition method of claim 1, wherein the vapor deposition process is ALD, CVD or combination thereof.

15. The deposition method of claim 1, wherein the co-reactant is O_3, O_2, H_2O, H_2O_2, D_2O, alcohols, NH_3, N_2, N_2H_2, H_2, radicals or mixtures thereof generated by plasma.

16. The deposition method of claim 1, wherein the co-reactant is O_3 or O_3 radicals generated by plasma.

17. The deposition method of claim 1, wherein an order of exposing the substrate to the inhibitor, the precursor and the co-reactant includes

a) the inhibitor, the precursor and the co-reactant sequentially;

b) the precursor, the inhibitor and the co-reactant sequentially;

c) the precursor, the co-reactant and the inhibitor sequentially; or

d) the inhibitor and the precursor simultaneously and then the co-reactant,

wherein after each exposure, a purge gas is used to purge and remove one or more of an excess inhibitor, an excess precursor and an excess co-reactant,

wherein the purge gas is an inert gas selected from N_2, Ar, Kr or combinations thereof.

18. The deposition method of any one of claims 1 to 17, wherein a growth rate of the film decreases comparing to that with an absence of the inhibitor.

19. The deposition method of any one of claims 1 to 17, wherein the precursor, the inhibitor or both are plasma activated or not plasma activated.

20. A deposition method for improving thickness control of a ZrO_2, HfO_2, Nb_2O_5 or TiO_2 film deposited on apertures therein with an aspect ratio of about 5:1 to about 200:1 in a substrate, the method comprising:

i) exposing the substrate to a vapor of an inhibitor selected from the group consisting of tetrahydrofuran (THF), dimethoxyethane (DME) and triethylamine (TEA), tetramethylethylenediamine (TMEDA); dimethylethylenediamine (DMEDA) and tris(2-aminoethyl)amine;

ii) exposing the substrate to a vapor of a precursor selected from the group consisting of $ZrCp(NMe_2)_3$, $HfCp(NMe_2)_3$, $Nb(=NtBu)Cp(NMe_2)_2$ and $TiCp^*(OMe)_3$;

iii) exposing the substrate to a vapor of a co-reactant O_3; and

iv) repeating the steps of i) to iii) until a desired thickness control of the ZrO_2, HfO_2, Nb_2O_5 or TiO_2 film deposited on the apertures is formed through an ALD process in a temperature ranging from room temperature to 650°C,

wherein a step coverage of the ZrO_2, HfO_2, Nb_2O_5 or TiO_2 film is ≥ 100%;

wherein a growth per cycle (GPC) of the ZrO_2, HfO_2, Nb_2O_5 or TiO_2 film versus the

amount of a precursor decreases;

wherein the ZrO_2, HfO_2, Nb_2O_5 or TiO_2 film is a gap fill without a seam,

wherein, after each exposure, excess inhibitor, excess precursor and excess co-reactant is purged and removed using N_2, respectively.