SUMMARY

[0007] According to one aspect, a method of forming a metal-containing film by atomic layer deposition is provided. The method comprises delivering a metal-containing complex, a purge gas, and a co-reactant to a first substrate under conditions sufficient for the metal-containing complex to: (i) deposit metal and etch the metal-containing film; (ii) deposit metal, etch the metal-containing film and allow for desorption from the metal-containing film; or (iii) deposit metal and allow for desorption from the metal-containing film; such that the metal-containing film selectively grows on at least a portion of the first substrate.

[0007a] In yet another aspect, there is provided a method of forming a metal-containing film by atomic layer deposition, wherein the method comprises delivering a metal-containing complex, a purge gas, and a co-reactant to a first substrate under conditions sufficient for the metal-containing complex to (i) deposit metal and etch the metal-containing film; (ii) deposit metal, etch the metal-containing film and allow for desorption from the metal-containing film; or (iii) deposit metal and allow for desorption from the metal-containing film; such that the metal-containing film selectively grows on at least a portion of the first substrate; and wherein the conditions comprise a super-conformal growth cycle sufficient for the metal-containing film to selectively grow on a lower portion of a feature in the first substrate.

[0007b] In another aspect, there is provided a method of forming a metal-containing film by atomic layer deposition, wherein the method comprises delivering a metal-containing complex, a purge gas, and a co-reactant to a first substrate under conditions sufficient for the metal-containing complex to (i) deposit metal and etch the metal-containing film; (ii) deposit metal, etch the metal-containing film and allow for desorption from the metal-containing film; or (iii) deposit metal and allow for desorption from the metal-containing film; such that the metal-containing film selectively grows on at least a portion of the first substrate; and wherein the conditions comprise a super-conformal growth cycle sufficient for the metal-containing film to selectively grow on a lower portion of a feature in the first substrate, and wherein the co-reactant (i) deposits metal and etches the metal-containing film; (ii) deposits metal, etches the metal-containing film and allows for desorption from the metal-containing film; or (iii) deposits metal and allows for desorption from the metal-containing film.

[0008] Other embodiments, including particular aspects of the embodiments summarized above, will be evident from the detailed description that follows.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] Fig. 1a illustrates a feature having a non-uniform width (also known as a "re-entrant feature").

[00010] Fig. 1b illustrates a feature having substantially uniform width.

[00011] Figs. 2a and 2b illustrate an example of super-conformal growth.

[00012] Fig. 2c illustrates an example of bottom-up-fill.

[00013] Fig. 2d illustrates an example of conformal growth.

[00014] Fig. 3 provides a scanning electron microscopy (SEM) image of a top portion of feature A1, at 150 K magnification, tilted view, showing a thick molybdenum film was deposited both at an upper portion of feature A1 and outside the feature A1.

[00015] Fig. 4 provides an SEM image of a bottom portion of feature A2, at 150 K magnification, perpendicular view, showing that a thick molybdenum film was deposited at a lower portion of feature A2.

CLAIMS

1. A method of forming a metal-containing film by atomic layer deposition, wherein the method comprises delivering a metal-containing complex, a purge gas, and a co-reactant to a first substrate under conditions sufficient for the metal-containing complex to:

(i) deposit metal and etch the metal-containing film;

(ii) deposit metal, etch the metal-containing film and allow for desorption from the metal-containing film; or

(iii) deposit metal and allow for desorption from the metal-containing film;

such that the metal-containing film selectively grows on at least a portion of the first substrate; and

wherein the conditions comprise a super-conformal growth cycle sufficient for the metal-containing film to selectively grow on a lower portion of a feature in the first substrate.

2. The method of claim 1, wherein the co-reactant:

(i) deposits metal and etches the metal-containing film;

(ii) deposits metal, etches the metal-containing film and allows for desorption from the metal-containing film; or

(iii) deposits metal and allows for desorption from the metal-containing film.

3. The method of claim 1, wherein (i) a deposition rate of the metal-containing complex is higher in a lower portion of the feature than in an upper portion of the feature and/or (ii) an etching rate and/or a desorption rate of the metal-containing complex is higher in an upper portion of the feature than in a lower portion of the feature.

4. The method of claim 1, wherein the feature has one or more of:

i) a depth $\geq$ about 5 nm;

ii) a non-uniform width;

iii) a width $\leq$ about 1000 nm;

iv) about 5.0% to about 100% of the feature is filled; and

v) substantially no voids within the feature.

5. The method of claim 1, wherein the feature has one or more of:

i) a depth of about 5 nm to about 3000 nm;

ii) is wider at a lower portion compared to an upper portion of the feature; and

iii) a width of about 1 nm to about 1000 nm.

6. The method of claim 1, wherein the conditions further comprise one or more of:

a conformal growth cycle comprising delivering the metal-containing complex, the purge gas and the co-reactant to the substrate under conformal conditions, wherein the conformal growth cycle comprises a first series of one or more conformal growth cycles;

a sub-conformal growth cycle comprising delivering the metal-containing complex, the purge gas and the co-reactant to the substrate under sub-conformal conditions, wherein the sub-conformal growth cycle comprises a third series of one or more sub-conformal growth cycles; and

an etch cycle comprising delivering the metal-containing complex and the purge gas to the substrate under etching conditions, wherein the etch cycle comprises a fourth series of one or more etch cycles; and

wherein the super-conformal growth cycle comprises a second series of one or more super-conformal growth cycles.

7. The method of claim 6, wherein

the first series of conformal growth cycles comprises 1 to 10 cycles;

the third series of sub-conformal growth cycles comprises 1 to 10 cycles;

the fourth series of etch cycles comprises 1 to 10 cycles; and

the second series of super-conformal growth cycles comprises 1 to 10 cycles.

8. The method of claim 1, wherein the film selectively grows on at least a portion of the first substrate over a second substrate.

9. The method of claim 8, wherein the first substrate has a different deposition to etch/desorption ratio than the second substrate.

10. The method of claim 8, wherein the duration of delivery of the purge gas is varied between delivering the metal-containing complex and the co-reactant such that growth is promoted on the first substrate while growth is inhibited on the second substrate.

11. The method of claim 8, wherein the first substrate and the second substrate are each independently selected from the group consisting of silica, titanium nitride and molybdenum.

12. The method of claim 8, wherein the metal-containing film has a root mean square roughness of less than 1.5 nm, or less than 5% of the film's thickness; or wherein the metal-containing film has a root mean square roughness of less than 0.8 nm, or less than 2% of the film's thickness.

13. The method of claim 1, wherein the metal-containing complex comprises:

a metal selected from the group consisting of a transition metal, a lanthanide metal, an actinide metal, aluminum, gallium, indium, silicon, germanium, tin, lead, arsenic, antimony, bismuth, selenium, and tellurium; and

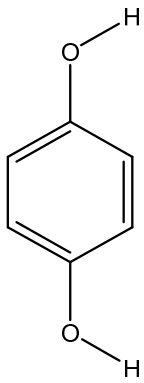
one or more ligands selected from the group consisting of a halogen, an alkoxy, an amidinate, a dialkyl-amide, an alkyl-sulfide, a dialkyl phosphide, an N,N'-dialkylamidinate, a cyclopentadienyl optionally substituted with at least one alkyl and/or at least one silyl, a carboxylate, an imide, an acetylacetonate, a hydride, a diketiminate, a mono-iminoketiminate, a trialkylsilyl, trihydrosilyl, a dialkylhydrosilyl, alkyldihydrosilyl, trialkylgermanyl, trihydrogermanyl, dialkylhydrogermanyl, alkyldihydrogermanyl, trialkylstannyl, trihydrostannyl, alkyldihydrostannyl, an amide optionally substituted with at least one silyl, a siloxy, a formamidinate optionally substituted with one or more hydride, alkyl and/or silyl, a acetamidinate optionally substituted with one or more hydride, alkyl and/or silyl, and a combination thereof.

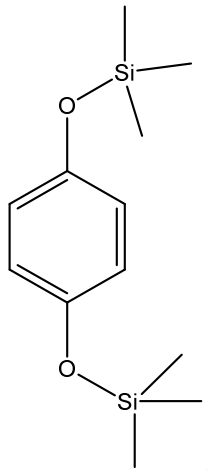
14. The method of claim 13, wherein the transition metal is selected from the group consisting of Mo, W, V, Nb, Fe, Ti, Ta, Co, and Ni; and/ or wherein the metal containing complex comprises one or more halogen ligands.

15. The method of claim 1, wherein the metal-containing complex is $MoCl_5$.

16. The method of claim 1, wherein the purge gas comprises an inert gas and/or hydrogen.

17. The method of claim 1, wherein the co-reactant is selected from the group consisting of:



or 

, 1,4-bis-trimethylsilyl-2-methyl-cyclohexa-2,5-diene, 1-trimethylsilylcyclohexa-2,5-diene, or 1,4-bis-trimethylsilyl-1,4-dihydropyrazine.

18. A method of forming a metal-containing film by atomic layer deposition, wherein the method comprises delivering a metal-containing complex, a purge gas, and a co-reactant to a first substrate under conditions sufficient for the metal-containing complex to:

(i) deposit metal and etch the metal-containing film;

(ii) deposit metal, etch the metal-containing film and allow for desorption from the metal-containing film; or

(iii) deposit metal and allow for desorption from the metal-containing film;

such that the metal-containing film selectively grows on at least a portion of the first substrate;

wherein the conditions comprise one or more of:

(i) a conformal growth cycle comprising delivering the metal-containing complex, the purge gas and the co-reactant to the substrate under conformal conditions;

(ii) a super-conformal growth cycle comprising delivering the metal-containing complex, the purge gas and the co-reactant to the substrate under super-conformal conditions; and

(iii) a sub-conformal growth cycle comprising delivering the metal-containing complex, the purge gas and the co-reactant to the substrate under sub-conformal conditions.

19. The method of claim 18, wherein the metal-containing film has a root mean square roughness of less than 1.5 nm, or less than 5% of the film's thickness; or wherein the metal-containing film has a root mean square roughness of less than 0.8 nm, or less than 2% of the film's thickness.

20. The method of claim 18, wherein the conditions further comprise: an etch cycle comprising delivering the metal-containing complex and the purge gas to the substrate under etching conditions.

21. A method of forming a metal-containing film by atomic layer deposition, wherein the method comprises delivering a metal-containing complex, a purge gas, and a co-reactant to a first substrate under conditions sufficient for the metal-containing complex to:

(i) deposit metal and etch the metal-containing film;

(ii) deposit metal, etch the metal-containing film and allow for desorption from the metal-containing film; or

(iii) deposit metal and allow for desorption from the metal-containing film;

such that the metal-containing film selectively grows on at least a portion of the first substrate;

wherein the conditions comprise a super-conformal growth cycle sufficient for the metal-containing film to selectively grow on a lower portion of a feature in the first substrate, and

wherein the co-reactant:

(i) deposits metal and etches the metal-containing film;

(ii) deposits metal, etches the metal-containing film and allows for desorption from the metal-containing film; or

(iii) deposits metal and allows for desorption from the metal-containing film.