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 or 2, wherein the purge gas is co-delivered with the metal-containing complex, the purge gas is co-delivered with the co-reactant, the purge gas is co-delivered with the metal-containing complex and the co-reactant, or the purge gas is delivered separately from the metal-containing complex and the co-reactant.

4. The method of any one of the previous claims, wherein the metal-containing complex and/or the purge gas are delivered to the substrate in an amount suitable to vary a deposition rate, an etching rate and/or a desorption rate.

5. The method of any one of the previous claims, 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.

6. The method of any one of the previous claims, wherein the feature has a depth ≥ about 5 nm.

7. The method of any one of the previous claims, wherein the feature has a depth of about 5 nm to about 3000 nm.

8. The method of any one of the previous claims, wherein the feature has a non-uniform width.

9. The method of any one of the previous claims, wherein the feature is wider at a lower portion compared to an upper portion of the feature.

10. The method of any one of the previous claims, wherein the feature has a width ≤ about 1000 nm.

11. The method of any one of the previous claims, wherein the feature has a width of about 1 nm to about 1000 nm.

12. The method of any one of the previous claims, wherein about 5.0% to about 100% of the feature is filled.

13. The method of any one of the previous claims, wherein the conditions further comprise a conformal growth cycle comprising delivering the metal-containing complex, the purge gas and the co-reactant to the substrate under conformal conditions.

14. The method of claim 13, wherein the conformal growth cycle comprises a first series of one or more conformal growth cycles.

15. The method of claim 14, wherein the first series of conformal growth cycles comprises 1 to 10 cycles.

16. The method of any one of claim 13 to 15, wherein there are substantially no voids within the feature.

17. The method of any one of the previous claims, wherein the film selectively grows on at least a portion of the first substrate over a second substrate.

18. The method of claim 17, wherein the first substrate has a different deposition to etch/desorption ratio than the second substrate.

19. The method of claim 17 or 18, 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.

20. The method of any one of claims 17 to 19, wherein the first substrate and the second substrate are each independently selected from the group consisting of silica, titanium nitride and molybdenum.

21. The method of claim 20, wherein the super-conformal growth cycle comprises a second series of one or more super-conformal growth cycles.

22. The method of claim 21, wherein the second series of super-conformal growth cycles comprises 1 to 10 cycles.

23. The method of any one of the previous claims, wherein the conditions further comprise 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.

24. The method of claim 23, wherein the sub-conformal growth cycle comprises a third series of one or more sub-conformal growth cycles.

25. The method of claim 24, wherein the third series of sub-conformal growth cycles comprises 1 to 10 cycles.

26. The method of any one of the previous claims, wherein the conditions further comprise an etch cycle comprising delivering the metal-containing complex and the purge gas to the substrate under etching conditions.

27. The method of claim 26, the etch cycle comprises a fourth series of one or more etch cycles.

28. The method of claim 27, wherein the fourth series of etch cycles comprises 1 to 10 cycles.

29. The method of any one of the previous claims, 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.

30. The method of any one of the previous claims, 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.

31. The method of any one of the previous claims, 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.

32. The method of claim 31, wherein the metal is a transition metal.

33. The method of claim 31 or 32, wherein the transition metal is selected from the group consisting of Mo, W, V, Nb, Fe, Ti, Ta, Co, and Ni.

34. The method of any one of claims 31 to 33, wherein the transition metal is selected from the group consisting of Mo, W, and Ta.

35. The method of any one of the previous claims, wherein the metal-containing complex comprises 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.

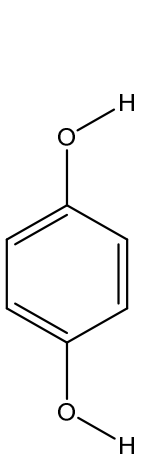
36. The method of any one of the previous claims, wherein the metal-containing complex comprises one or more halogen ligands.

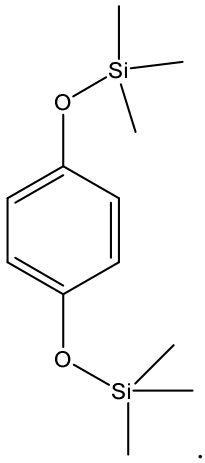
37. The method of any of one of the previous claims, wherein the metal-containing complex is $MoCl_5$.

38. The method of any one of the previous claims, wherein the purge gas comprises an inert gas and/or hydrogen.

39. The method of any one of the previous claims, wherein the co-reactant is a volatile reducing agent.

40. The method of any one of the previous claims, wherein the co-reactant is



or


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41. The method of any one of the previous claims, wherein the co-reactant is a non-aromatic compound which converts to an aromatic compound.

42. The method of claim 41, wherein the co-reactant is 1,4-bis-trimethylsilyl-2-methyl-cyclohexa-2,5-diene, 1-trimethylsilylcyclohexa-2,5-diene, or 1,4-bis-trimethylsilyl-1,4-dihydropyrazine.

43. The method of claim 41 or 42, wherein the co-reactant is 1,4-bis-trimethylsilyl-2-methyl-cyclohexa-2,5-diene.

44. 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.

45. The method of claim 44, 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.

46. The method of claim 44, 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.

47 The method of any one of claims 44 to 46, wherein the conditions further comprise:
iv) an etch cycle comprising delivering the metal-containing complex and the purge gas to the substrate under etching conditions.