

CLAIMS:

1. A chemical of the formula:

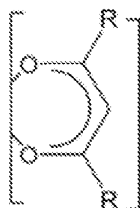


wherein M is a rare earth element, preferably selected from Yttrium, La, Ce, Sm, Tb, Yb,

wherein FAB is a Fluorinated Anionic Bidentate, preferably a β -diketonate, more preferably hfac, and

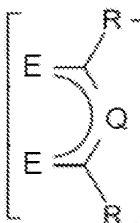
wherein D is a neutral ligand with $y = 0$ to 4, preferable $y = 1$ or 2 and preferably each D is independently selected from the group consisting of monoglyme (1,2-dimethoxyethane; dme), diglyme (bis(2-methoxyethyl) ether), dmp (1,2-dimethoxypropane), 1-(2-Methoxyethoxy)propane and Ethylene glycol ethyl methyl ether (2-Methoxyethanol).

2. The chemical of claim 1, wherein M is Yttrium.
 3. The chemical of claims 1 or 2, wherein the FAB is a β -diketonate.
 4. The chemical of claim 3, wherein the β -diketonate has a chemical formula I:



wherein each R may independently be CF_3 or a fluorocarbyl, preferably a fluorinated, linear or branched $\text{C}_1\text{-C}_4$ alkyl, more preferably each R is either CF_3 or C_2F_5 .

5. The chemical of claims 1 or 2, wherein the FAB has a chemical formula II:



wherein each E is independently O, S, or N-R' where R' is H, a linear or branched $\text{C}_1\text{-C}_6$ alkyl,

wherein each Q is independently N, P, CH, CF, CR' where R' is an a linear or branched $\text{C}_1\text{-C}_6$ alkyl,

wherein each R' may optionally be fluorinated with one or more F(s), and

wherein each R may independently be CF_3 or a fluorocarbyl, preferably a

fluorinated, linear or branched C₁-C₄ alkyl, more preferably each R is either CF₃ or C₂F₅.

6. The chemical of claims 1 or 2, wherein at least one FAB is selected from the group consisting of hexafluoroacetylacetone (hfac), trifluoroacetylacetone (tfac), 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione (fod), and combinations thereof.
7. The chemical of any one of claims 1 or 2, wherein at least one D is selected from the group consisting of monoglyme (1,2-dimethoxyethane; dme), diglyme (bis(2-methoxyethyl) ether), dmp (1,2-dimethoxypropane), 1-(2-Methoxyethoxy)propane and Ethylene glycol ethyl methyl ether (2-Methoxyethanol), and combinations thereof.
8. The chemical of any one of claims 1 or 2, wherein y = 1 or 2.
9. The chemical of any one of claims 1 or 2, wherein at least one D comprises a phosphorus.
10. The chemical of claim 9, wherein the at least one D is selected from the group consisting of TriMethyl Phosphate, Tri-n-ButylPhosphate, Tri-(2,2,2-TriFluoroethyl) Phosphate, Tri-(3,3,3,2,2-pentaFluoroPropyl) Phosphate, and combinations thereof.
11. The chemical of any one of claims 1 or 2, wherein the chemical is a liquid at 1 atmosphere pressure and 50 degrees C or less, preferably liquid at 25 degrees C or less, more preferably liquid at 20 degrees C or less.
12. The chemical of claim 1 selected from the group consisting of
 - a. Yttrium(III) hexafluoroacetylacetone 1,2-dimethoxyethane,
 - b. Yttrium(III) hexafluoroacetylacetone 1,2-dimethoxypropane,
 - c. Yttrium(III) hexafluoroacetylacetone 2-Methoxyethanol, and
 - d. Yttrium(III) hexafluoroacetylacetone 1-(2-Methoxyethoxy)propane.
13. The chemical of claim 1 selected from the group consisting of
 - a. Yttrium(III) hexafluoroacetylacetone 1,2-dimethoxypropane,
 - b. Yttrium(III) hexafluoroacetylacetone 2-Methoxyethanol, and
 - c. Yttrium(III) hexafluoroacetylacetone 1-(2-Methoxyethoxy)propane.
14. The chemical of claim 1 wherein the chemical is Yttrium(III) hexafluoroacetylacetone 1,2-Dimethoxyethane.
15. The chemical of claim 1 wherein the chemical is Yttrium(III) hexafluoroacetylacetone 1,2-dimethoxypropane.
16. The chemical of claim 1 wherein the chemical is Yttrium(III) hexafluoroacetylacetone 2-Methoxyethanol.
17. The chemical of claim 1 wherein the chemical is Yttrium(III) hexafluoroacetylacetone 1-(2-Methoxyethoxy)propane.
18. A chemical composition comprising a chemical according to any one of claims 1-17.

19. The chemical composition of claim 18, wherein the chemical according to any one of claims 1-17 is 95% or more of the chemical composition by weight, by molar percent, or both.
20. A chemical composition of claim 19, wherein the chemical according to any one of claims 1-17 is 99% or more of the chemical composition by weight, by molar percent, or both.
21. A chemical composition of claim 20, wherein the chemical according to any one of claims 1-17 is 99.9% or more of the chemical composition by weight, by molar percent, or both.
22. A chemical composition of claim 18, wherein the chemical composition has less than the following amounts of the following specified impurities:
 - a. Chlorine impurity lower than 1%, preferably lower than 0.1%.
23. A method of depositing a conformal and adherent MOF or MF_3 thin film on a surface of a chemically reactive material that forms all or part of an article of manufacture, the method comprising the steps of:
 - a. first exposing the surface to a vapor of a metal containing chemical composition according to claim 18,
 - b. second exposing the surface to an oxidant gas, preferably ozone, and
 - c. repeating steps a. and b., preferably sequentially a. then b., to form a desired thickness of the conformal and adherent MOF or MF_3 film on the surface.
24. The method of claim 23, wherein a temperature during step a. and/or step b. is from 200 degrees C to 350 degrees C, preferable from 250 degrees C to 300 degrees C, more preferably from 250 degrees C to 275 degrees C.
25. The method of claim 23 or 24, wherein the conformal and adherent MOF or MF_3 film comprises an atomic percentage of less than 15% for oxygen, preferably less than 10% oxygen, more preferably less than 5% for oxygen, and less than 3% for carbon, preferably less than 1.5% for carbon.
26. The method of any one of claims 23 or 24, wherein the surface of the chemically reactive material that is coated by the conformal and adherent MOF or MF_3 film, comprises structural features having an aspect ratio of 6.25:1 or greater, such as 10:1 or 20:1.
27. The method of any one of claims 23 or 24, wherein there is no purge of the vapor of a metal containing chemical composition according to any of claims 12-16 from step a., prior to step b.
28. The method of any one of claims 23 or 24, wherein a film growth per cycle of deposition is 0.11 angstroms or greater, preferably 0.14 angstroms or greater, more preferably 0.24 angstroms or greater, such as 0.24 to 0.30 angstroms.

29. The method of any one of claims 23 or 24, wherein the MOF or MF₃ film is from 5 nm to 1000 nm in thickness from the underlying surface, preferably 10 nm to 500 nm, more preferably 10 nm to 100 nm, such as 20 nm, 25 nm, or 30 nm.
30. The method of any one of claims 23 or 24, wherein the final MOF or MF₃ film is 20% to 100% conformal by scanning electron microscopy measurements, preferably 50% to 100%, more preferably 80% to 100%, such as 95% to 100%.
31. The method of any one of claims 23 or 24, wherein the MOF or MF₃ film is from 10 nm to 100 nm in thickness from the underlying surface and 95% to 100% conformal.
32. The method of claims 23 or 24, wherein the MOF or MF₃ film does not peel off the underlying surface using a peel test with adhesive tape having an adhesion to steel of 2.5 N/cm according to ASTM D3330 / D3330M-04(2018).
33. An article of manufacture comprising an chemically reactive material, the article of manufacture further comprising a conformal and adherent MOF or MF₃ layer coating the article of manufacture, wherein M is a rare earth element, and wherein the MOF or MF₃ coating layer covers more than 50% of a surface of the chemically reactive material, preferable more than 90% of the surface, even more preferably greater than 95% of the surface, such as 99% or 99.9 %.
34. The article of manufacture of claim 33, wherein M is Yttrium.
35. The article of manufacture of claim 33 or 34, wherein the conformal and adherent MOF or MF₃ layer coating the article of manufacture is 1000 nm or less in thickness, preferably 5 nm to 250 nm, more preferably 10 nm to 100 nm, such as 15 nm, 20 nm, 25 nm, or 30 nm.
36. The article of manufacture of any one of claims 33 or 34, wherein the conformal and adherent MOF or MF₃ layer coating the article of manufacture is 20% to 100% conformal by scanning electron microscopy measurements, preferably 50% to 100%, more preferably 80% to 100%, such as 95% to 100%.
37. The article of manufacture of any one of claims 33 or 34, wherein the conformal and adherent MOF or MF₃ layer coating the article of manufacture does not peel off the article of manufacture using a peel test with adhesive tape, where the adhesive tape has an adhesion to steel of 2.5 N/cm according to ASTM D3330 / D3330M-04(2018).
38. The article of manufacture of any one of claims 33 or 34, wherein the article of manufacture is designed for, and configured to operate in, an atomic layer deposition process in which a surface of the article both comprises the chemically reactive material and is to be exposed to a deposition process chemical used in the atomic layer deposition process, and wherein the deposition process chemical is capable of reacting with the chemically reactive material during the atomic layer deposition process.

39. The article of manufacture of any one of claims 33 or 34, wherein the article of manufacture is designed for, and configured to operate in, an etching gas environment in which a surface of the article both comprises the chemically reactive material and is to be exposed to an etching gas that is capable of chemically reacting with the chemically reactive material.
40. The article of manufacture of claim 39, wherein the etching gas environment is an etching process in a semiconductor manufacturing process.
41. The article of manufacture of claim 40, wherein the article of manufacture is a shower head designed and configured for introducing an etching gas into the etching process within an enclosure or chamber.
42. The article of manufacture of claim 40, wherein the enclosure or chamber is an etching chamber and the semiconductor manufacturing process is a dry etching process utilizing a fluorocarbon etching gas.
43. The article of manufacture of claim 42, wherein the article of manufacture is a shower head designed and configured for introducing an etching gas into the etching process within an enclosure or chamber.
44. The article of manufacture of claim 43, wherein the enclosure or chamber is a batch etching chamber and the semiconductor manufacturing process is a dry etching process utilizing a fluorocarbon etching gas.
45. The article of manufacture of any one of claims 33 or 34, wherein the etching gas environment is a NF_3 remote plasma.
46. The article of manufacture of any one of claims 33 or 34, wherein the surface of the chemically reactive material comprises structural features having an aspect ratio of 6.25:1 or greater, such as 10:1 or 20:1.
47. A method of delivering an etching gas to an etching process, comprising the step of:
 - a. introducing the etching gas into the etching process via an article of manufacture according to any one of claims 33 or 34.