- the oxophilic reagent having a purity ranging from approximately 99% w/w to approximately 99.999% w/w;
- the reducing agent having a purity ranging from approximately 93% w/w to approximately 100% w/w;
- the reducing agent having a purity ranging from approximately 99% w/w to approximately 99.999% w/w;
- the vapor deposition process being a thermal CVD;
- the vapor deposition process being a thermal ALD;
- the vapor deposition process being a plasma enhanced CVD;
- the vapor deposition process being a plasma enhanced ALD; and
- the vapor deposition process being a spatial ALD.

[0010a] In one aspect, there is provided a process for deposition of a metal or metal nitride film on a substrate, the process comprising

reacting a metal oxyhalide precursor with an oxophilic reagent in a reactor containing the substrate to deoxygenate the metal oxyhalide precursor;

after deoxygenation, exposing the substrate to a reducing agent sequentially; and

forming the metal or metal nitride film on the substrate through a vapor deposition process,

wherein

the metal oxyhalide precursor is $M^{(a)}X_cO_e$, wherein M is Mo, W, V, Nb, Ta, and Cr; X is a halogen selected from Cl, Br or I; a is the oxidation state of M and a is an integer ranging from 3 to 6; c is a number, $0 < c < 6$; e is a number, $0 < e < 3$; $c + 2e = a$; and

the oxophilic reagent is $N^{(b)}X_dO_f$, wherein N is a transition metal halide, a transition metal oxyhalide, or a Group 14 or 15 halide, oxyhalide or oxide; X is a halogen selected from Cl, Br or I; b is the oxidation state of N and b is an integer ranging from 3 to 6; d is a number, $0 \leq d < 6$; f is a number, $0 \leq f < 3$; $d + 2f = b$,

wherein oxophilicity of N is higher than oxophilicity of M,

wherein the oxophilic reagent and products of the oxophilic reagent are volatile.

[0011] Also disclosed is a method for removing oxygen from a metal oxyhalide precursor or an intermediate film deposited by the metal oxyhalide precursor to form a metal or metal nitride film on a surface, the process comprising

reacting the metal oxyhalide precursor or the intermediate film deposited by the metal oxyhalide precursor with an oxophilic reagent to form a metal intermediate; and

reducing the metal intermediate to a metal or metal nitride film on the surface by a reducing agent through a vapor deposition process,

wherein

the metal oxyhalide precursor is $M^{(a)}X_cO_e$, wherein M is Mo, W, V, Nb, Ta, and Cr; X is a halogen selected from Cl, Br or I; a is the oxidation state of M and a is an integer ranging from 3 to 6; c is a number, $0 < c < 6$; e is a number, $0 < e < 3$; $c + 2e = a$; and

the oxophilic reagent is $N^{(b)}X_dO_f$, wherein N is a transition metal halide or oxyhalide, or a Group 14 or 15 halide, oxyhalide or oxide; X is a halogen selected from Cl, Br or I; b is the oxidation state of N and b is an integer ranging from 3 to 6; d is a number, $0 \leq d < 6$; f is a number, $0 < f < 3$; $d + 2f = b$,

wherein oxophilicity of N is higher than oxophilicity of M,

wherein the oxophilic reagent and oxygenation products of the oxophilic reagent are volatile. The disclosed method may include one or more of the following aspects:

- the metal oxyhalide precursor being selected from MoO_2Cl_2, $MoOCl_4$, $WOCl_4$, WO_2Cl_2, $NbOCl_3$, $TaOCl_3$, and CrO_2Cl_2;
- the oxophilic reagent being selected from:

- the reducing agent being the oxophilic reagent selected from CO, $SiHCl_3$, $SiHBr_3$, or $SiHI_3$;
- an oxygen impurity in the metal or metal nitride film being less than approximately 1%;
- the vapor deposition process being a thermal CVD or ALD, or a plasma enhanced CVD or ALD;
- a deposition temperature ranging from 50°C to 500°C;
- a deposition temperature ranging from 100°C to 500°C;
- a deposition temperature ranging from 150°C to 485°C;
- a deposition temperature being less than 500°C; and
- a deposition temperature being less than 485°C.

[0011a] In another aspect, the present disclosure provides a process for removing oxygen from a metal oxyhalide precursor or an intermediate film deposited by the metal oxyhalide precursor to form a metal or metal nitride film on a surface, the process comprising

reacting the metal oxyhalide precursor or the intermediate film deposited by the metal oxyhalide precursor with an oxophilic reagent to form a metal intermediate; and

reducing the metal intermediate to a metal or metal nitride film on the surface by a reducing agent through a vapor deposition process,

wherein

the metal oxyhalide precursor is $M^{(a)}X_cO_e$, wherein M is Mo, W, V, Nb, Ta, and Cr; X is a halogen selected from Cl, Br or I; a is the oxidation state of M and a is an integer ranging from 3 to 6; c is a number, $0 < c < 6$; e is a number, $0 < e < 3$; $c + 2e = a$; and

the oxophilic reagent is $N^{(b)}X_dO_f$, wherein N is a transition metal halide, a transition metal oxyhalide, or a Group 14 or 15 halide, oxyhalide or oxide; X is a halogen selected from Cl, Br or I; b is the oxidation state of N and b is an integer ranging from 3 to 6; d is a number, $0 \leq d < 6$; f is a number, $0 < f < 3$; $d + 2f = b$, wherein oxophilicity of N is higher than oxophilicity of M,

wherein the oxophilic reagent and products of the oxophilic reagent are volatile.

[0012] Also disclosed is a reagent for deoxygenation of a metal oxyhalide precursor or an intermediate film deposited by the metal oxyhalide precursor to form a metal or metal nitride film in a vapor deposition process, the metal oxyhalide precursor having a general formula: $M^{(a)}X_cO_e$, wherein M is Mo, W, V, Nb, Ta, and Cr; X is a halogen selected from Cl,

Br or I; a is the oxidation state of M and a is an integer ranging from 3 to 6; c is a number, $0 < c < 6$; e is a number, $0 < e < 3$; $c + 2e = a$,

the reagent comprising:

an oxophilic reagent having a general formula: $N^{(b)}X_dO_f$, wherein N is a transition metal halide or oxyhalide, or a Group 14 or 15 halide, oxyhalide or oxide; X is a halogen selected from Cl, Br or I; b is the oxidation state of N and b is an integer ranging from 3 to 6; d is a number, $0 \leq d < 6$; f is a number, $0 < f < 3$; $d + 2f = b$,

wherein oxophilicity of N of the oxophilic reagent is higher than oxophilicity of M of the metal oxyhalide precursor,

wherein the oxophilic reagent and oxygenation products of the oxophilic reagent are volatile. The disclosed reagent may include one or more of the following aspects:

- the metal oxyhalide precursor being selected from MoO_2Cl_2, $MoOCl_4$, $WOCl_4$, WO_2Cl_2, $NbOCl_3$, $TaOCl_3$, and CrO_2Cl_2;
- the oxophilic reagent being selected from:
    a. Group 14-containing: CCl_4; CBr_4; $COCl_2$; CO; R-N=C=O, wherein R is H, or an alkyl group selected from Me, Et, iPr, nPr, iBu, tBu, sBu, nBu; or $Si_xR_yX_z$, wherein x = 1 to 5, y and z = 0 to 12, $y + z \leq 2x+2$, X is a halogen selected from Cl, Br, I, R is H, a saturated or unsaturated hydrocarbon group, amino group, alkoxy group, or silyl group;

We claim:

1. A process for deposition of a metal or metal nitride film on a substrate, the process comprising

reacting a metal oxyhalide precursor with an oxophilic reagent in a reactor containing the substrate to deoxygenate the metal oxyhalide precursor;

after deoxygenation, exposing the substrate to a reducing agent sequentially; and

forming the metal or metal nitride film on the substrate through a vapor deposition process,

wherein

the metal oxyhalide precursor is $M^{(a)}X_cO_e$, wherein M is Mo, W, V, Nb, Ta, and Cr; X is a halogen selected from Cl, Br or I; a is the oxidation state of M and a is an integer ranging from 3 to 6; c is a number, $0 < c < 6$; e is a number, $0 < e < 3$; $c + 2e = a$; and

the oxophilic reagent is $N^{(b)}X_dO_f$, wherein N is a transition metal halide, a transition metal oxyhalide, or a Group 14 or 15 halide, oxyhalide or oxide; X is a halogen selected from Cl, Br or I; b is the oxidation state of N and b is an integer ranging from 3 to 6; d is a number, $0 \leq d < 6$; f is a number, $0 \leq f < 3$; $d + 2f = b$,

wherein oxophilicity of N is higher than oxophilicity of M,

wherein the oxophilic reagent and products of the oxophilic reagent are volatile.

2. The process of claim 1, further comprising

exposing the substrate to the metal oxyhalide precursor and the oxophilic reagent simultaneously or sequentially.

3. The process of claim 1,

wherein the reducing agent is selected from H_2, HCl, B_2H_6, NH_3, CO, $SiHCl_3$, $SiHBr_3$, or $SiHl_3$.

4. The process of claim 1, wherein the metal oxyhalide precursor is selected from MoO_2Cl_2, $MoOCl_4$, $WOCl_4$, WO_2Cl_2, $NbOCl_3$, $TaOCl_3$, and CrO_2Cl_2.

5. The process of claim 1, wherein the oxophilic reagent is selected from:

a. Group 14-containing: CCl_4; CBr_4; $COCl_2$; CO; R-N=C=O, wherein R is H, or an alkyl group selected from Me, Et, iPr, nPr, iBu, tBu, sBu, nBu; or $Si_xR_yX_z$, wherein x = 1

to 5, y and z = 0 to 12, y + z ≤ 2x+2, X is a halogen selected from Cl, Br, I, R is H, a saturated or unsaturated hydrocarbon group, amino group, alkoxy group, or silyl group;

b. Group 15-containing: NO, N_2O, PCl_3, PBr_3, PI_3; or

c. Transition metal-containing: VCl_4, VCl_3, $NbCl_5$, $TaCl_5$, WCl_6, WCl_5, $WOCl_4$, or WCl_4.

6. The process of claim 1, wherein the oxophilic reagent is a Si-containing oxophilic reagent having a general formula: $Si_xR_yX_z$, wherein x = 1 to 5, y and z = 0 to 12, y + z ≤ 2x+2; X is a halogen selected from Cl, Br, I; R is H, a saturated or unsaturated hydrocarbon group, amino group, alkoxy group, or silyl group.

7. The process of claim 6, wherein the Si-containing oxophilic reagent is selected from Si_2Cl_6, Si_2Cl_5H, $Si_2Cl_4Me_2$, Si_2ClMe_5, $Si_2Cl_2Me_4$, Si_2Br_6, Si_2Br_5H, $Si_2Br_4Me_2$, Si_2BrMe_5, $Si_2Br_2Me_4$, Si_2Br_5H, Si_2Me_6, Si_2I_6, Si_2I_5H, $Si_2I_4(Me)_2$, $Si_2(OMe)_6$, $Si_2(NR_2)_6$ (wherein R=H, Me, Et), $Si_2(NMe_2)_5Cl$, Si_3Cl_8, Si_3Br_8, Si_3I_8, or $Si_4(Me)_9H$.

8. The process of any one of claims 1 to 7, wherein the oxophilic reagent is Si_2Cl_6.

9. The process of any one of claims 1 to 7, wherein the oxophilic reagent is R-N=C=O, wherein R is H, or an alkyl group selected from Me, Et, iPr, nPr, iBu, tBu, sBu, nBu or a metal halide or metal oxyhalide selected from VCl_4, VCl_3, $NbCl_5$, $TaCl_5$, WCl_6, WCl_5, $WOCl_4$, or WCl_4..

10. The process of any one of claims 1 to 7, wherein the vapor deposition process is a thermal CVD or ALD, or a plasma enhanced CVD or ALD at a deposition temperature less than 485°C.

11. A process for removing oxygen from a metal oxyhalide precursor or an intermediate film deposited by the metal oxyhalide precursor to form a metal or metal nitride film on a surface, the process comprising

reacting the metal oxyhalide precursor or the intermediate film deposited by the metal oxyhalide precursor with an oxophilic reagent to form a metal intermediate; and

reducing the metal intermediate to a metal or metal nitride film on the surface by a reducing agent through a vapor deposition process,

wherein

the metal oxyhalide precursor is $M^{(a)}X_cO_e$, wherein M is Mo, W, V, Nb, Ta, and Cr; X is a halogen selected from Cl, Br or I; a is the oxidation state of M and a is an integer ranging from 3 to 6; c is a number, $0 < c < 6$; e is a number, $0 < e < 3$; $c + 2e = a$; and

the oxophilic reagent is $N^{(b)}X_dO_f$, wherein N is a transition metal halide, a transition metal oxyhalide, or a Group 14 or 15 halide, oxyhalide or oxide; X is a halogen selected from Cl, Br or I; b is the oxidation state of N and b is an integer ranging from 3 to 6; d is a number, $0 \leq d < 6$; f is a number, $0 < f < 3$; $d + 2f = b$, wherein oxophilicity of N is higher than oxophilicity of M,

wherein the oxophilic reagent and products of the oxophilic reagent are volatile.

12. The process of claim 11, wherein

the metal oxyhalide precursor is selected from MoO_2Cl_2, $MoOCl_4$, $WOCl_4$, WO_2Cl_2, $NbOCl_3$, $TaOCl_3$, and CrO_2Cl_2; and

the oxophilic reagent is selected from:

a. Group 14-containing: CCl_4; CBr_4; $COCl_2$; CO; R-N=C=O, wherein R is H, or an alkyl group selected from Me, Et, iPr, nPr, iBu, tBu, sBu, nBu; or $Si_xR_yX_z$, wherein x = 1 to 5, y and z = 0 to 12, $y + z \leq 2x+2$, X is a halogen selected from Cl, Br, I, R is H, a saturated or unsaturated hydrocarbon group, amino group, alkoxy group, or silyl group;

b. Group 15-containing: NO, N_2O, PCl_3, PBr_3, PI_3; or

c. Transition metal-containing: VCl_4, VCl_3, $NbCl_5$, $TaCl_5$, WCl_6, WCl_5, $WOCl_4$, or WCl_4.

13. The process of any one of claims 11 to 12, wherein the vapor deposition process is a thermal CVD or ALD, or a plasma enhanced CVD or ALD at a deposition temperature less than 485°C.

14. A reagent for deoxygenation of a metal oxyhalide precursor or an intermediate film deposited by the metal oxyhalide precursor to form a metal or metal nitride film in a vapor deposition process, the metal oxyhalide precursor having a general formula: $M^{(a)}X_cO_e$, wherein M is Mo, W, V, Nb, Ta, and Cr; X is a halogen selected from Cl, Br or I; a is the oxidation state of M and a is an integer ranging from 3 to 6; c is a number, $0 < c < 6$; e is a number, $0 < e < 3$; $c + 2e = a$,

the reagent comprising:

an oxophilic reagent having a general formula: $N^{(b)}X_dO_f$, wherein N is a transition metal halide or oxyhalide, or a Group 14 or 15 halide, oxyhalide or oxide; X is a halogen selected from Cl, Br or I; b is the oxidation state of N and b is an integer ranging from 3 to 6; d is a number, $0 \leq d < 6$; f is a number, $0 < f < 3$; $d + 2f = b$,

wherein oxophilicity of N of the oxophilic reagent is higher than oxophilicity of M of the metal oxyhalide precursor,

wherein the oxophilic reagent and oxygenation products of the oxophilic reagent are volatile.