CLAIMS

What is claimed is:

1. A selective plasma enhanced atomic layer deposition (ALD) process, comprising:

(a) loading a substrate comprising a dielectric material, and a metal into a reactor;

(b) reacting the substrate with a non-plasma based oxidant, thereby forming an oxidized metal surface on the metal;

(c) heating the substrate to a temperature less than, or equal to, 150°C;

(d) exposing the substrate to a passivation agent that preferentially adsorbs more onto the oxidized metal surface than the dielectric material, thereby forming a passivation layer on the oxidized metal surface;

(e) exposing the substrate to a silicon precursor that preferentially adsorbs more onto the dielectric material than the passivation layer on the oxidized metal surface, thereby forming a chemi-adsorbed silicon-containing layer on the dielectric material; and

(f) exposing the substrate to a plasma based oxidant that simultaneously (1) partially oxidizes the passivation layer, thereby forming a partially oxidized passivation layer on the oxidized metal surface, and (2) oxidizes the chemi-adsorbed silicon-containing layer on the dielectric material, thereby forming a silicon-containing dielectric film on the dielectric material.

2. The selective plasma enhanced ALD process according to claim 1, wherein the dielectric material is selected from the group consisting of silicon oxide, carbon doped silicon oxide, silicon oxynitride, carbon doped oxynitride, silicon nitride, and metal oxide such as zirconium oxide, hafnium oxide, silicon doped zirconium oxide, silicon doped hafnium oxide, or any other high k materials.

3. The selective plasma enhanced ALD process according to claim 1, wherein the metal is selected from the group consisting of cobalt, aluminum, copper, tantalum, ruthenium, molybdenum, tungsten, platinum, iridium, nickel, titanium, silver, gold or combination thereof.

4. The selective plasma enhanced ALD process according to claim 1, wherein the non-plasma based oxidant is selected from the group consisting of hydrogen peroxide, oxygen, and ozone.

5. The selective plasma enhanced ALD process according to claim 1, wherein step (b), the reacting the substrate with a non-plasma based oxidant, thereby forming an oxidized metal surface on the metal step, occurs at a temperature less than, or equal to, 500°C.

6. The selective plasma enhanced ALD process according to claim 5, wherein step (b), the reacting the substrate with a non-plasma based oxidant, thereby forming an oxidized metal surface on the metal step, occurs at a temperature less than, or equal to, 150°C.

7. The selective plasma enhanced ALD process according to claim 1, wherein the passivation agent is selected from the group consisting of methanethiol, ethanethiol, propanethiol, butanethiol, pentanethiol, hexanethiol, heptanethiol, octanethiol, nonanethiol, decanethiol, undecanethiol, dodecanethiol, tridecanethiol, tetradecanethiol, pentadecanethiol, hexadecanethiol, heptadecanethiol, octadecanethiol, nonadecanethiol, tetrahydro-2H-pyran-4-thiol, 2-Propene-1-thiol, tetrahydro-2H-pyran-4-thiol, thiophenol, 4-methyl-1-thiophenol, 3-methyl-1-thiophenol, 2-Methyl-1-thiophenol, and para-xylene-alpha-thiol.

8. The selective plasma enhanced ALD process according to claim 1, wherein the passivation agent is selected from the group consisting of di-tert-butyl disulfide, and di-heptane disulfide.

9. The selective plasma enhanced ALD process according to claim 1, wherein the passivation agent is selected from the group consisting of 1H,1H,2H,2H-perfluorodecanethiol, 2,2,2-trifluoroethanethiol, 4-methyl-6-trifluoromethyl-pyrimidine-2-thiol, 4-trifluoromethylbenzyl mercaptan, 4-(trifluoromethoxy)benzyl mercaptan, 4-fluorobenzyl mercaptan, 3,5-bis(trifluoromethyl)benzenethiol, 2-(trifluoromethyl)benzenethiol, 4-trifluoromethyl-2,3,5,6-tetrafluorothiophenol, 3,5-difluorobenzyl mercaptan, 4-trifluoromethyl-2,3,5,6-tetrafluorothiophenol, and para-trifluoromethylbenzenethiol.

10. The selective plasma enhanced ALD process according to claim 1, wherein the passivation layer comprises a monolayer of the passivation agent chemi-adsorbed to the oxidized metal surface.

11. A selective plasma enhanced atomic layer deposition (ALD) process, comprising:

(g) loading a substrate comprising a dielectric material, and metal having a native metal oxide surface into a reactor;

(h) heating the substrate to a temperature less than, or equal to, 150°C;

(i) exposing the substrate to a passivation agent that preferentially adsorbs more onto the native metal oxide surface than the dielectric material, thereby forming a passivation layer on the native metal oxide surface;

(j) exposing the substrate to a silicon precursor that preferentially adsorbs more onto the dielectric material than the passivation layer on the native metal oxide surface, thereby forming a chemi-adsorbed silicon-containing layer on the dielectric material; and

(k) exposing the substrate to a plasma based oxidant that simultaneously (1) partially oxidizes the passivation layer on the native metal oxide surface, thereby forming a partially oxidized passivation layer on the native metal oxide surface, and (2) oxidizes the chemi-adsorbed silicon-containing layer on the dielectric material, thereby forming a silicon-containing dielectric film on the dielectric material.

12. The selective plasma enhanced ALD process according to claim 11, wherein the dielectric material is selected from the group consisting of silicon oxide, carbon doped silicon oxide, silicon oxynitride, carbon doped oxynitride, silicon nitride, and metal oxide such as zirconium oxide, hafnium oxide, silicon doped zirconium oxide, silicon doped hafnium oxide, or any other high k materials.

13. The selective plasma enhanced ALD process according to claim 11, wherein the metal is selected from the group consisting of cobalt, aluminum, copper, tantalum, ruthenium, molybdenum, tungsten, platinum, iridium, nickel, titanium, silver, gold, or combination thereof.

14. The selective plasma enhanced ALD process according to claim 11, wherein the plasma based oxidant is selected from the group consisting of oxygen plasma, nitrous oxide plasma, and carbon dioxide plasma.

15. The selective plasma enhanced ALD process according to claim 11, wherein the passivation agent is selected from the group consisting of methanethiol, ethanethiol, propanethiol, butanethiol, pentanethiol, hexanethiol, heptanethiol, octanethiol, nonanethiol, decanethiol, undecanethiol, dodecanethiol, tridecanethiol, tetradecanethiol, pentadecanethiol, hexadecanethiol, heptadecanethiol, octadecanethiol, nonadecanethiol, tetrahydro-2H-pyran-4-thiol, 2-Propene-1-thiol, tetrahydro-2H-pyran-4-thiol, thiophenol, 4-methyl-1-thiophenol, 3-methyl-1-thiophenol, 2-Methyl-1-thiophenol, and para-xylene-alpha-thiol.

16. The selective plasma enhanced ALD process according to claim 11, wherein the passivation agent is selected from the group consisting of di-tert-butyl disulfide, and di-heptane disulfide.

17. The selective plasma enhanced ALD process according to claim 11, wherein the passivation agent is selected from the group consisting of 1H,1H,2H,2H-perfluorodecanethiol, 2,2,2-trifluoroethanethiol, 4-methyl-6-trifluoromethyl-pyrimidine-2-thiol, 4-trifluoromethylbenzyl mercaptan, 4-(trifluoromethoxy)benzyl mercaptan, 4-fluorobenzyl mercaptan, 3,5-bis(trifluoromethyl)benzenethiol, 2-(Trifluoromethyl)benzenethiol, 4-trifluoromethyl-2,3,5,6-tetrafluorothiophenol, 3,5-difluorobenzyl mercaptan, 4-trifluoromethyl-2,3,5,6-tetrafluorothiophenol, and para-trifluoromethylbenzenethiol.

18. The selective plasma enhanced ALD process according to claim 11, wherein the passivation layer comprises a monolayer of the passivation agent chemi-adsorbed to the native metal oxide surface.

19. The selective plasma enhanced ALD process according to claim 18, wherein the passivation layer further comprises a second layer of the passivation agent physi-adsorbed to the monolayer of the passivation agent chemi-adsorbed to the native metal oxide surface.

20. The selective plasma enhanced ALD process according to claim 11, wherein the silicon precursor is an organoaminomonsilane selected from the group consisting of di-iso-propylaminosilane, di-sec-butylaminosilane, bis(diethylamino)silane, bis(dimethylamino)silane, bis(ethylmethylamino)silane, bis(tert-butylamino)silane, di-iso-propylaminomethylsilane, di-sec-butylaminomethylsilane, dimethylaminodimethylsilane, dimethylaminotrimethylsilane, bis(dimethylamino)methylsilane, tetrakis(dimethylamino)silane, tris(dimethylamino)silane, diethylaminodimethylsilane, dimethylaminodimethylsilane, di-iso-propylaminodimethylsilane, piperidinodimethylsilane, 2,6-dimethylpiperidinodimethylsilane, di-sec-butylaminodimethylsilane, iso-propyl-sec-butylaminodimethylsilane, tert-butylaminodimethylsilane, Iso-propylaminodimethylsilane, tert-pentylaminodimethylaminosilane, dimethylaminomethylsilane, di-iso-propylaminomethylsilane, iso-propyl-sec-butylaminomethylsilane, 2,6-dimethylpiperidinomethylsilane, di-sec-butylaminomethylsilane, bis(dimethylamino)methylsilane, bis(diethylamino)methylsilane, bis(di-iso-propylamino)methylsilane, bis(iso-propyl-sec-butylamino)methylsilane, bis(2,6-dimethylpiperidino)methylsilane, bis(iso-propylamino)methylsilane, bis(tert-butylamino)methylsilane, bis(sec-butylamino)methylsilane, bis(tert-pentylamino)methylsilane, bis(cyclohexylamino)methylsilane, bis(iso-propylamino)dimethylsilane, bis(iso-butylamino)dimethylsilane, bis(sec-butylamino)dimethylsilane, bis(tert-butylamino)dimethylsilane, bis(tert-pentylamino)dimethylsilane, bis(cyclohexylamino)dimethylsilane, and combinations thereof.