Claims

What is claimed is

1. A thermal ALE process for etching a surface of a metal oxide substrate comprising performing the steps of:

(i) a first surface modification comprising exposing the surface of the metal oxide substrate to one or more fluorinating agent to produce a fluorinated surface;

(ii) a first purge;

(iii) a ligand-exchange comprising exposing the fluorinated surface to one or more chlorine ligand-supplying agent to produce a volatile chlorinated species;

(iv) a second purge;

(v) a second surface modification comprising exposing the surface of the metal oxide substrate to one or more oxidants to oxidize metal byproducts; and

(vi) a third purge.

2. The process of claim 1, wherein the metal oxide comprises one or more of ZrO_2, HfO_2, $Hf_xZr_{1-x}O_2$ where x is a value between 0 and 1, TiO_2, Al_2O_3 and combinations thereof.

3. The process of claim 1, wherein the step (i) one or more fluorinating agent comprises one or more metal fluorides.

4. The process of claim 1, wherein the step (i) one or more fluorinating agent comprises one or more of VF_5, NbF_5, TaF_5, MoF_6, WF_6, ReF_6, ReF_7, AsF_5, SbF_5, and TeF_6.

5. The process of claim 1, wherein the step (i) exposure time of the one or more fluorinating agent to the surface of the metal oxide is from 0.5 seconds to 30 seconds.

6. The process of claim 1, wherein step (i) is carried out at a pressure from 0.5 torr to 100 torr.

7. The process of claim 1, wherein the step (iii) one or more chlorine ligand-supplying agent comprises one or more of dimethylaluminum chloride (DMAC; $Al(CH_3)_2Cl$), diethylaluminum chloride (DEAC; $Al(C_2H_5)_2Cl$), titanium tetrachloride ($TiCl_4$), boron trichloride (BCl_3) and combinations thereof.

8. The process of claim 1, wherein the step (iii) exposure time of the one or more chlorine ligand-supplying agent to the surface of the metal oxide is from 0.5 seconds to 30 seconds.

9. The process of claim 1, wherein step (iii) is carried out at a pressure from 0.5 torr to 100 torr.

10. The process of claim 1, wherein the step (v) one or more oxidants comprises one or more of oxygen (O_2), ozone (O_3), nitric oxide (NO), water (H_2O) vapor, hydrogen peroxide (H_2O_2), oxygen plasma (O*), and combinations thereof.

11. The process of claim 1, wherein the step (v) exposure time of the one or more oxidants is from 1 second to 60 seconds.

12. The process of claim 1, wherein step (v) is carried out at a pressure from 0.5 torr to 100 torr.

13. A metal-containing film etched by the process of claim 1, wherein the film comprises topographical features having an aspect ratio of 0 to 60.

14. A metal-containing film etched by the process of claim 1, wherein the film comprises topographical features having an aspect ratio of 10 to 100.

15. A metal-containing film etched by the process of claim 1, wherein the film has a dielectric constant of between 1.5 to 80.

16. A metal-containing film etched by the process of claim 1, wherein a majority of the film has a cubic crystal structure.

17. A metal-containing film etched by the process of claim 1, wherein a majority of the film has a tetragonal crystal structure.

18. A metal-containing film etched by the process of claim 1, wherein a majority of the film has an orthorhombic crystal structure.

19. A metal-containing film etched by the process of claim 1, wherein a majority of the film has a noncentrosymmetric crystal structure.

20. A metal-insulator-metal capacitor device comprising a first electrode, a dielectric layer and a second electrode, where the dielectric layer is made by the process of claim 1.

21. The metal-insulator-metal capacitor device of claim 20, wherein the dielectric layer has a thickness of between 5 nm and 10 nm before etching and a thickness of between 1 nm and 6 nm after etching.

22. The use of a metal-containing film etched by the process of claim 1 as a dielectric layer in a metal-insulator-metal capacitor.