Claims

What is claimed is:

1. A vapor-phase etch process comprising the steps of:

(i) a surface modification comprising exposing a metal oxide-containing surface to one or more fluorinating surface modifying agent to produce one or more fluorinated metal compound at the surface;

(ii) a purge;

(iii) a volatilization comprising exposing the fluorinated metal compound to one or more chlorine-supplying volatilizing agent to produce one or more chlorine-containing volatile byproduct containing one or more metals of the fluorinated metal compound;

(iv) a purge;

(v) a surface cleaning comprising exposing the surface to one or more oxidants to remove contaminants and convert at least a portion of the surface to a metal oxide; and

(vi) a purge.

2. The process of claim 1, further comprising step (vii) an oxidizing post-treatment to remove impurities remaining on the surface.

3. The process of claim 1, wherein the metal oxide-containing surface comprises one or more of zirconium (Zr), hafnium (Hf), aluminum (Al), titanium (Ti), cobalt (Co), nickel (Ni), molybdenum (Mo), ruthenium (Ru), tungsten (W) and combinations thereof.

4. The process of claim 1, wherein the metal oxide-containing surface comprises zirconium (Zr).

5. The process of claim 1, wherein the metal oxide-containing surface comprises hafnium (Hf).

6. The process of claim 1, wherein the metal oxide-containing surface comprises one or more of molybdenum (Mo), titanium (Ti) and tungsten (W).

7. The process of claim 1, wherein the metal oxide-containing surface comprises one or more of aluminum (Al) and nickel (Ni).

8. 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.

9. The process of claim 1, wherein the step (i) one or more fluorinating surface modifying agent comprises one or more metal-free fluorides.

10. The process of claim 1, wherein the step (i) one or more fluorinating surface modifying agent comprises one or more of *N,N*-diethyl-1,1,2,3,3,3-hexafluoropropylamine (Ishikawa's reagent), ammonium bifluoride, sodium bifluoride, potassium bifluoride, hydrogen fluoride pyridine,

triethylamine trishydrofluoride, hydrogen fluoride and combinations thereof.

11. The process of claim 1, wherein step (i) is carried out at a pressure from about 0.5 torr to about 100 torr, the exposure time of the one or more fluorinating surface modifying agent to the metal oxide-containing surface is from about 0.5 seconds to about 30 seconds and the one or more fluorinating surface modifying agent is flowed at from about 0.5 sccm to about 500 sccm.

12. The process of claim 1, wherein the step (iii) one or more chlorine-supplying volatilizing 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), thionyl chloride ($SOCl_2$), chlorine (Cl_2) and combinations thereof.

13. The process of claim 1, wherein the step (iii) one or more chlorine-supplying volatilizing agent comprises dimethylaluminum chloride (DMAC; $Al(CH_3)_2Cl$).

14. The process of claim 1, wherein the step (iii) one or more chlorine-supplying volatilizing agent comprises diethylaluminum chloride (DEAC; $Al(C_2H_5)_2Cl$).

15. The process of claim 1, wherein the step (iii) one or more chlorine-supplying volatilizing agent comprises titanium tetrachloride ($TiCl_4$).

16. The process of claim 1, wherein the step (iii) one or more chlorine-supplying volatilizing agent comprises boron trichloride (BCl_3).

17. The process of claim 1, wherein the step (iii) one or more chlorine-supplying volatilizing agent comprises thionyl chloride ($SOCl_2$).

18. The process of claim 1, wherein the step (iii) one or more chlorine-supplying volatilizing agent comprises chlorine (Cl_2).

19. The process of claim 1, wherein step (iii) is carried out at a pressure from about 0.5 torr to about 100 torr, the exposure time of the one or more chlorine-supplying volatilizing agent to the fluorinated metal compound is from about 0.5 seconds to about 30 seconds and the one or more chlorine-supplying volatilizing agent is flowed at from about 1 sccm to about 500 sccm.

20. The process of claim 1, wherein the step (v) one or more oxidants comprises one or more of oxygen (O_2), ozone (O_3), water (H_2O) vapor, hydrogen peroxide (H_2O_2), oxygen plasma (O*), N_xO_y wherein x = 1 or 2 and y = 1, 2, 3 or 4, nitric oxide (NO), and combinations thereof.

21. The process of claim 1, wherein step (v) is carried out at a pressure from about 0.5 torr to about 100 torr, the exposure time of the one or more oxidants is from about 1 second to about 60 seconds, the one or more oxidants is flowed at from about 10 sccm to about 1000 sccm and the substrate is heated to a temperature from about 100 °C to about 450 °C.

22. The process of claim 1, wherein the process comprises about 5 to about 250 cycles.