Claims

What is claimed is

1. A thermal atomic layer etching process performed in a reactor for selectively etching a metal substrate comprising the steps of:

Step 1 comprising sequentially performing:

Step 1A comprising exposing a metal surface to an oxidizing vapor comprising one or more of water vapor, oxygen, ozone, nitrous oxide, nitric oxide, hydrogen peroxide, oxygen plasma, and combinations thereof, and

Step 1B comprising purging the oxidizing vapor with an inert gas; and

Step 2 comprising sequentially performing:

Step 2A comprising exposing the metal surface to one or more halogen-free organic acid volatizer, and

Step 2B comprising purging the one or more halogen-free organic acid volatizer with an inert gas;

wherein one cycle of the process is determined by the formula $(\text{Step 1})_n + (\text{Step 2})_m$, wherein n and m are each independently = 1-20.

2. The process of claim 1, wherein the process comprises 20 to 2200 cycles.

3. The process of claim 1 or 2, wherein the process comprises selectively etching one or more of copper, cobalt, molybdenum and tungsten.

4. The process of any one of claims 1 to 3, wherein the process comprises selectively etching copper, cobalt, molybdenum and/or tungsten preferentially instead of one or more of nickel, platinum, ruthenium, zirconium oxide and SiO_2.

5. The process of any one of claims 1 to 4, wherein the reactor chamber comprises an outer heater heated to a temperature of 100 °C to 300 °C and an inner heater heated to a temperature of 100 °C to 350 °C.

6. The process of any one of claims 1 to 5, wherein the Step 1A oxidizing vapor comprises one or more of water vapor, oxygen, ozone and hydrogen peroxide.

7. The process of any one of claims 1 to 6, wherein the Step 1A oxidizing vapor comprises water vapor and one or more of oxygen and ozone.

8. The process of any one of claims 1 to 6, wherein the Step 2A one or more halogen-free organic acid volatizer comprises one or more of propionic acid, isobutyric acid, pivalic acid, acetic acid, butanoic acid, acrylic acid, methacrylic acid, 2-methylbutanoic acid, 3-methylbutanoic acid, 3-butenoic acid, cyclopropanecarboxylic acid, pentanoic acid, (2*E*)-but-2-enoic acid, (*Z*)-2-butenoic acid and combinations thereof, preferably one or more of propionic acid, isobutyric acid, pivalic acid and combinations thereof, more preferably, propionic acid, isobutyric acid, or pivalic acid.

9. The process of any one of claims 1 to 8, wherein the Step 2A one or more halogen-free organic acid volatizer comprises two or more of propionic acid, isobutyric acid and pivalic acid.

10. The process of any one of claims 1 to 8, wherein the Step 2A one or more halogen-free organic acid volatizer comprises a mixture of halogen-free organic acids comprising one or more of propionic acid, isobutyric acid and pivalic acid.

11. The process of any one of claims 1 to 10, wherein the Step 2A one or more halogen-free organic acid volatizer is heated to and held at from 50 ^{O}C to 100 ^{O}C.

12. A metal-containing film etched by the process of any of claims 1-11, wherein the film comprises topographical features having an aspect ratio of 1 to 60.

13. A metal-containing film etched by the process of any of claims 1-11, wherein the film has a resistivity of between 1 μΩ.cm to 250 μΩ.cm.

14. The metal-containing film etched by the process of any of claims 1-11, wherein the metal comprises one or more of copper, cobalt, molybdenum and tungsten.

15. The use of one or more of propionic acid, isobutyric acid, pivalic acid, acetic acid, butanoic acid, acrylic acid, methacrylic acid, 2-methylbutanoic acid, 3-methylbutanoic acid, 3-butenoic acid, cyclopropanecarboxylic acid, pentanoic acid, (2*E*)-but-2-enoic acid, (*Z*)-2-butenoic acid and

combinations thereof as halogen-free organic volatilizer together with one or more of water vapor, oxygen, ozone, nitrous oxide, hydrogen peroxide, and oxygen plasma and combinations thereof as oxidizing vapor in selective thermal atomic layer etching of a metal substrate comprising one or more of copper, cobalt, molybdenum and tungsten.