

CLAIMS

1. A method of processing a substrate in a chamber, the method comprising:
 - (a) exposing the substrate to a boron-containing halide gas and an additive selected from the group consisting of hydrogen-containing and halogen-containing gases for a duration sufficient to selectively deposit a first layer of boron-containing halide material on a surface of a mask on the substrate, and the duration sufficient to selectively deposit a second layer of boron-containing halide material on a surface of a non-volatile metal of the substrate, wherein the first layer is thicker than the second layer; and
 - (b) exposing the substrate to an activation gas and an activation source that ionizes the activation gas to form an activated activation gas reactive with the first and second layers of boron-containing halide material on the mask and the non-volatile metal to form etch products; andwherein (a) and (b) are conducted for a first set of cycles, followed by (a) and (b) conducted for a second set of cycles, in which the duration of (a) is longer in the first set of cycles than the duration of (a) in the second set of cycles resulting in a net deposition process, and in which the duration of (b) in the second set of cycles is longer than the duration of (b) in the first set of cycles, resulting in a net etch process.
2. The method of claim 1, wherein the first layer is thicker than the second layer due at least in part to chemical selectivity.
3. The method of claim 1, wherein the second set of cycles is greater in number than the first set of cycles.
4. The method of claim 3, wherein the first set of cycles numbers between 1 and 10, and the second set of cycles numbers between 20 and 30.
5. The method of claim 1, wherein the non-volatile metal of the substrate selected from the group consisting of cobalt, iron, manganese, nickel, platinum, palladium, and ruthenium.

6. The method of claim 5, wherein the mask comprising a material consisting of elements selected from the group consisting of nitrogen, oxygen, carbon, and titanium atoms.
7. The method of claim 1, wherein (b) results in a self-limiting etch of the substrate.
8. The method of claim 1, wherein a bias is applied during (b).
9. The method of claim 4, wherein a bias is applied during (b) at a first bias power during the first set of cycles and a second bias power during the second set of cycles.
10. The method of claim 9, wherein the second bias power is between about 30 V and about 150 V.
11. The method of claim 1, wherein the additive is selected from the group consisting of H₂, CH₄, CF₄, NF₃, Cl₂, and combinations thereof.
12. The method of claim 1, wherein the activation gas is selected from the group consisting of Ar, H₂, CH₄, CF₄, He, Ne, Xe, NF₃, and combinations thereof.
13. The method of claim 1, wherein the boron-containing halide gas is selected from the group consisting of BCl₃, BBr₃, BF₃, and BI₃.
14. The method of claim 1, wherein the non-volatile metal is cobalt.
15. The method of claim 1, wherein the activation source is a plasma.
16. The method of claim 1, wherein roughness of the surface of the metal is less than about 5 nm RMS.
17. The method of claim 1, wherein (a) and (b) are performed without breaking vacuum.

18. The method of claim 1, wherein (a) comprises a self-limiting reaction.
19. The method of claim 1, wherein the metal is cobalt and the mask is TiN.
20. The method of claim 1, wherein the metal is cobalt and the mask is an ashable hard mask made primarily of carbon material.
21. An apparatus for processing a substrate, the apparatus comprising:
- (a) one or more process chambers, each process chamber comprising a chuck;
 - (b) one or more gas inlets into the process chambers and associated flow-control hardware;
- and
- (c) a controller having at least one processor and a memory, wherein
 - the at least one processor and the memory are communicatively connected with one another,
 - the at least one processor is at least operatively connected with the flow-control hardware,
 - and
 - the memory stores computer-executable instructions for controlling the at least one processor to at least control the flow-control hardware by:
 - (i) flowing a boron-containing halide gas and an additive to at least one of the one or more process chambers, for a duration sufficient to selectively deposit a first layer of boron-containing halide material on a surface of a mask on the substrate, and the duration sufficient to selectively deposit a second layer of boron-containing halide material on a surface of a non-volatile metal of the substrate, wherein the first layer is thicker than the second layer; and
 - (ii) flowing an activation gas to the one of the one or more process chambers and igniting an activation source that ionizes the activation gas to form an activated activation gas reactive with the first and second layers of boron-containing halide material on the mask and the non-volatile metal to form etch products; and
- wherein (i) and (ii) are conducted for a first set of cycles, followed by (i) and (ii) conducted for a second set of cycles, in which the duration of (i) is longer in the first set of cycles than the duration of (i) in the second set of cycles resulting in a net

deposition process, and in which the duration of (ii) in the second set of cycles is longer than the duration of (ii) in the first set of cycles, resulting in a net etch process.