~~What is claimed is:~~CLAIMS

1. A method of forming a protective coating on a substrate, comprising:

exposing the substrate to a chromium precursor and a first oxidizing agent to form a chromium oxide layer comprising amorphous chromium oxide on a surface of the substrate during a first atomic layer deposition (ALD) process or a first chemical vapor deposition (CVD) process;

heating the substrate containing the chromium oxide layer comprising the amorphous chromium oxide to convert at least a portion of the amorphous chromium oxide to crystalline chromium oxide during a first annealing process;

exposing the substrate to an aluminum precursor and a second oxidizing agent to form an aluminum oxide layer comprising amorphous aluminum oxide on the chromium oxide layer during a second ALD process or a second CVD process; and

heating the substrate containing the aluminum oxide layer disposed on the chromium oxide layer to convert at least a portion of the amorphous aluminum oxide to crystalline aluminum oxide during a second annealing process.

2. The method of claim 1, wherein the first annealing process comprises heating the substrate to a temperature of ~~about~~ 400°C to less than 1,000°C for ~~about~~ 0.5 hours to ~~about~~ 48 hours.

3. The method of claim 1, wherein the chromium oxide layer is deposited to a thickness of ~~about~~ 10 nm to ~~about~~ 10,000 nm.

4. The method of claim 1, wherein the substrate is exposed to an annealing gas during the first annealing process, and wherein the annealing gas comprises nitrogen (N_2), oxygen (O_2), a mixture of nitrogen and oxygen, nitrous oxide, nitric oxide, air, argon, helium, or any mixture thereof.

5. The method of claim 1, wherein the aluminum oxide layer is deposited to a thickness of ~~about~~ 10 nm to ~~about~~ 10,000 nm.

6. The method of claim 1, wherein the aluminum oxide layer comprises a dopant aluminum oxide containing hafnium, zirconium, yttrium, or any combination thereof.

7. The method of claim 6, wherein the aluminum oxide layer comprises a combination of aluminum oxide and one or more of hafnium oxide, a hafnium-doped aluminum oxide, hafnium aluminate, a combination of aluminum oxide and zirconium oxide, a zirconium-doped aluminum oxide, zirconium aluminate, a combination of aluminum oxide and yttrium oxide, a yttrium-doped aluminum oxide, yttrium aluminate, dopants thereof, or any combination thereof.

8. The method of claim 6, wherein the aluminum oxide layer has a dopant concentration of ~~about~~ 0.01 at% to ~~about~~ 8 at%.

9. The method of claim 1, wherein the second annealing process comprises heating the substrate to a temperature of ~~about~~ 400°C to less than 1,000°C for ~~about~~ 0.5 hours to ~~about~~ 48 hours.

10. The method of claim 1, wherein the second annealing process comprises heating the substrate to a temperature of ~~about~~ 450°C to ~~about~~ 950°C for ~~about~~ 0.8 hours to ~~about~~ 30 hours.

11. The method of claim 1, wherein the substrate is exposed to an annealing gas during the second annealing process, and wherein the annealing gas comprises nitrogen (N_2), oxygen (O_2), a mixture of nitrogen and oxygen, nitrous oxide, nitric oxide, air, argon, helium, or any mixture thereof.

12. The method of claim 1, wherein the chromium oxide layer comprising the amorphous chromium oxide is deposited by the first ALD process and the aluminum oxide layer comprising the amorphous aluminum oxide is deposited by the second ALD process.

13. The method of claim 12, wherein each of the first oxidizing agent and the second oxidizing agent independently comprises water, ozone, oxygen (O_2), atomic oxygen, nitrous oxide, a peroxide, an alcohol, plasmas thereof, or any combination thereof.

14. The method of claim 1, wherein the substrate comprises a silicon substrate, a silicon oxide substrate, a polymeric or plastic substrate, a nanostructured device, a surface or component within a processing chamber, a surface or component of a tool, or any combination thereof.

15. The method of claim 1, wherein the substrate comprises an aerospace component.

16. The method of claim 15, wherein the aerospace component is a turbine blade, a turbine vane, a support member, a frame, a rib, a fin, a pin fin, a fuel nozzle, a combustor liner, a combustor shield, a heat exchanger, a fuel line, a fuel valve, an internal cooling channel, or any combination thereof.

17. The method of claim 15, wherein the surface of the substrate is an interior surface of the aerospace component, and wherein the interior surface has an aspect ratio of ~~about~~ 5 to ~~about~~ 1,000.

18. The method of claim 15, wherein the aerospace component comprises nickel, nickel superalloy, nickel-aluminum alloy, aluminum, iron, stainless steel, cobalt, chromium, molybdenum, titanium, alloys thereof, or any combination thereof.

19. A method of forming a protective coating on a substrate, comprising:

exposing the substrate to a chromium precursor and a first oxidizing agent to form a chromium oxide layer on a surface of the substrate during a first atomic layer deposition (ALD) process or a first chemical vapor deposition (CVD) process;

exposing the substrate to an aluminum precursor and a second oxidizing agent to form an aluminum oxide layer comprising amorphous aluminum oxide on the chromium oxide layer during a second ALD process or a second CVD process; and

heating the substrate containing the aluminum oxide layer disposed on the chromium oxide layer to convert the amorphous aluminum oxide to crystalline aluminum oxide.

20. A method of forming a protective coating on a substrate, comprising:

depositing a chromium oxide layer comprising amorphous chromium oxide on a surface of the substrate during a first atomic layer deposition (ALD) process or a

first chemical vapor deposition (CVD) process, wherein the substrate comprises a nickel-aluminum alloy;

depositing an upper aluminum oxide layer comprising amorphous aluminum oxide on the chromium oxide layer during a second ALD process or a second CVD process;

heating the substrate containing the upper aluminum oxide layer disposed on the chromium oxide layer to diffuse aluminum from the nickel-aluminum alloy in the substrate to an interface between the substrate and the chromium oxide layer during a first annealing process, wherein the interface comprises a greater concentration of aluminum after the first annealing process than before the first annealing process; and

heating the substrate containing the upper aluminum oxide layer disposed on the chromium oxide layer during a second annealing process, further comprising:

converting the aluminum in the interface between the substrate and the chromium oxide layer to a lower aluminum oxide layer comprising crystalline aluminum oxide;

converting at least a portion of the amorphous chromium oxide in the chromium oxide layer to crystalline chromium oxide; and

converting at least a portion of the amorphous aluminum oxide in the upper aluminum oxide layer to crystalline aluminum oxide.