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(54) **CORROSION-RESISTANT COMPONENTS AND METHODS OF MAKING**

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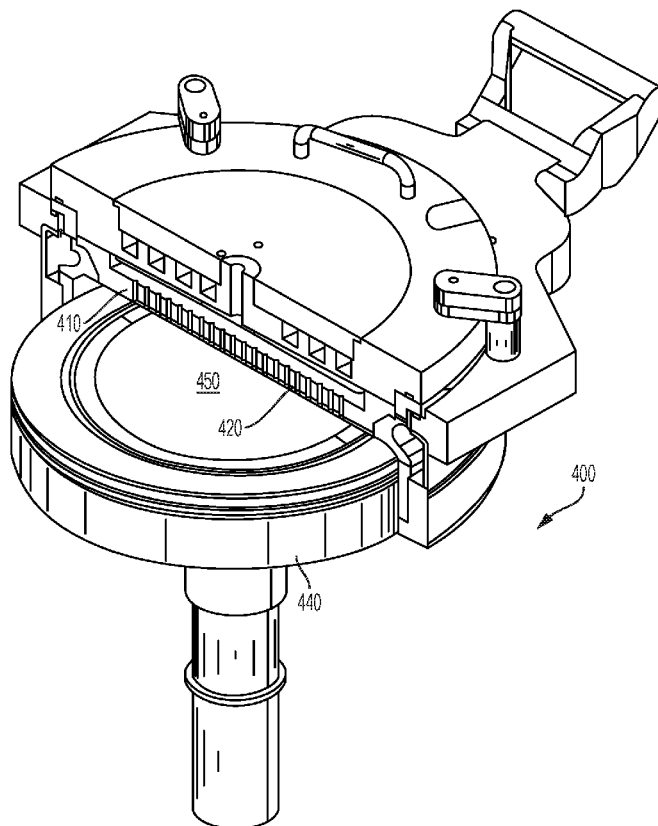
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(57)

ABSTRACT

A corrosion-resistant component configured for use with a semiconductor processing reactor, the corrosion-resistant component comprising: a) a ceramic insulating substrate; and, b) a corrosion-resistant non-porous layer associated with the ceramic insulating substrate, the corrosion-resistant non-porous layer having a composition comprising at least 15% by weight of a rare earth compound based on total weight of the corrosion-resistant non-porous layer; and, the corrosion-resistant non-porous layer characterized by a microstructure substantially devoid of microcracks and fissures, and having an average grain size of at least about 100 nm and at most about 100 μm. Assemblies including corrosion-resistant components and methods of making are also disclosed.



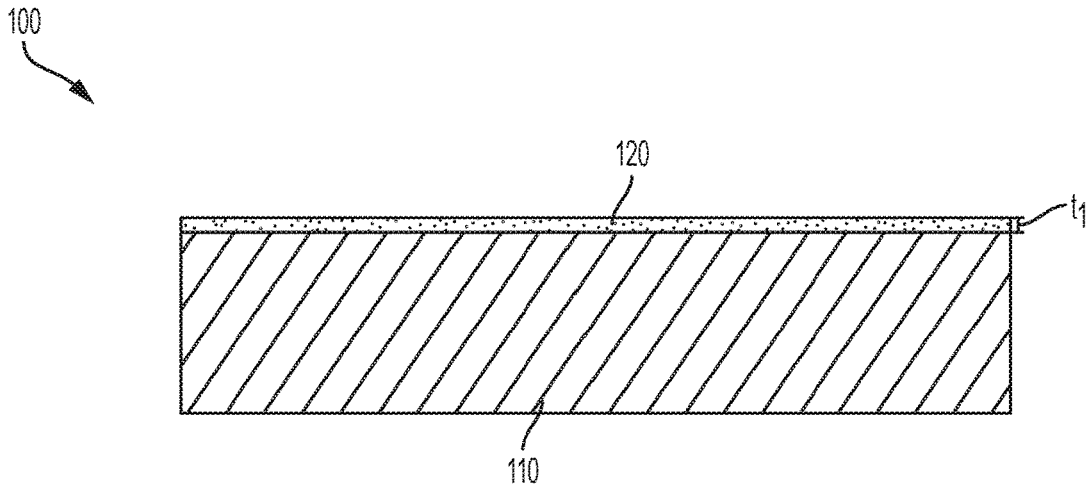


FIG. 1A

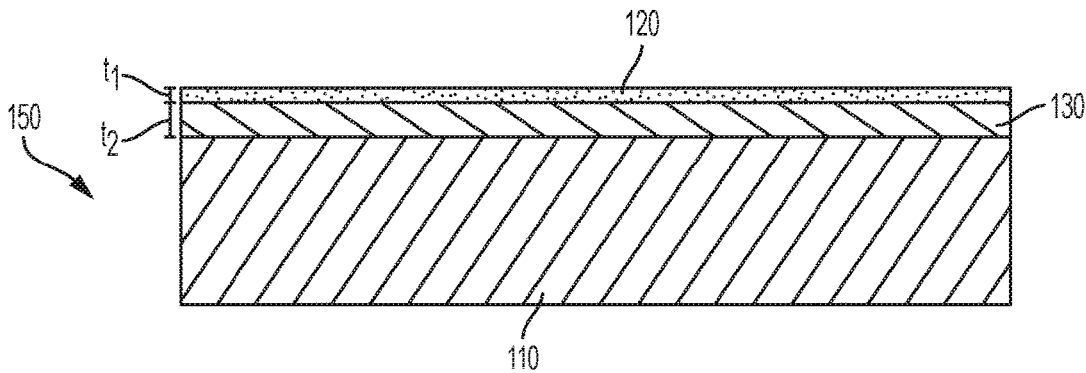


FIG. 1B

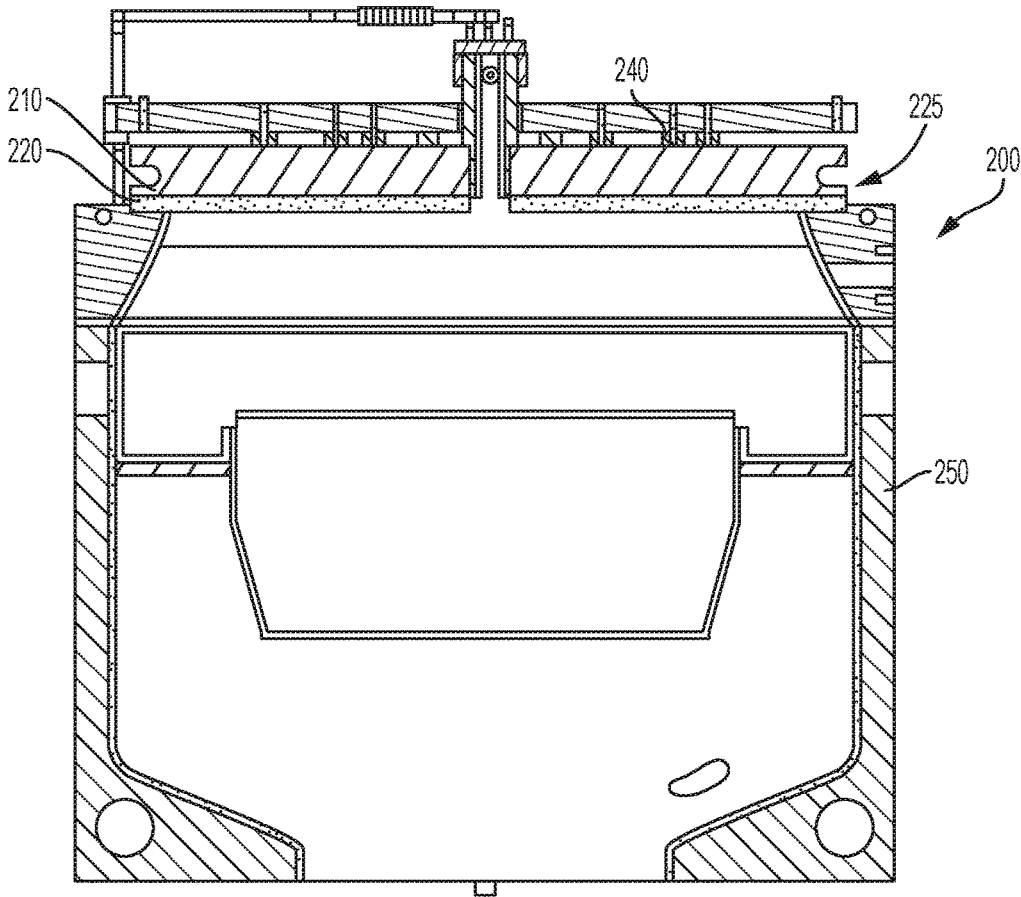


FIG. 2

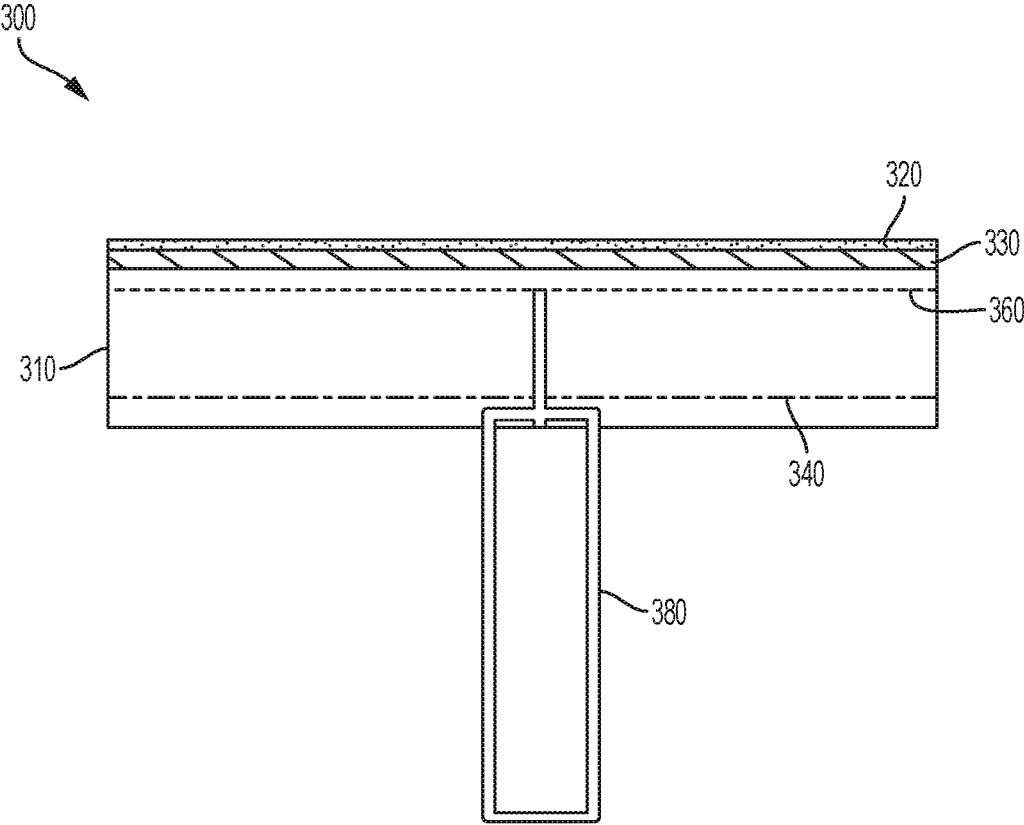


FIG. 3

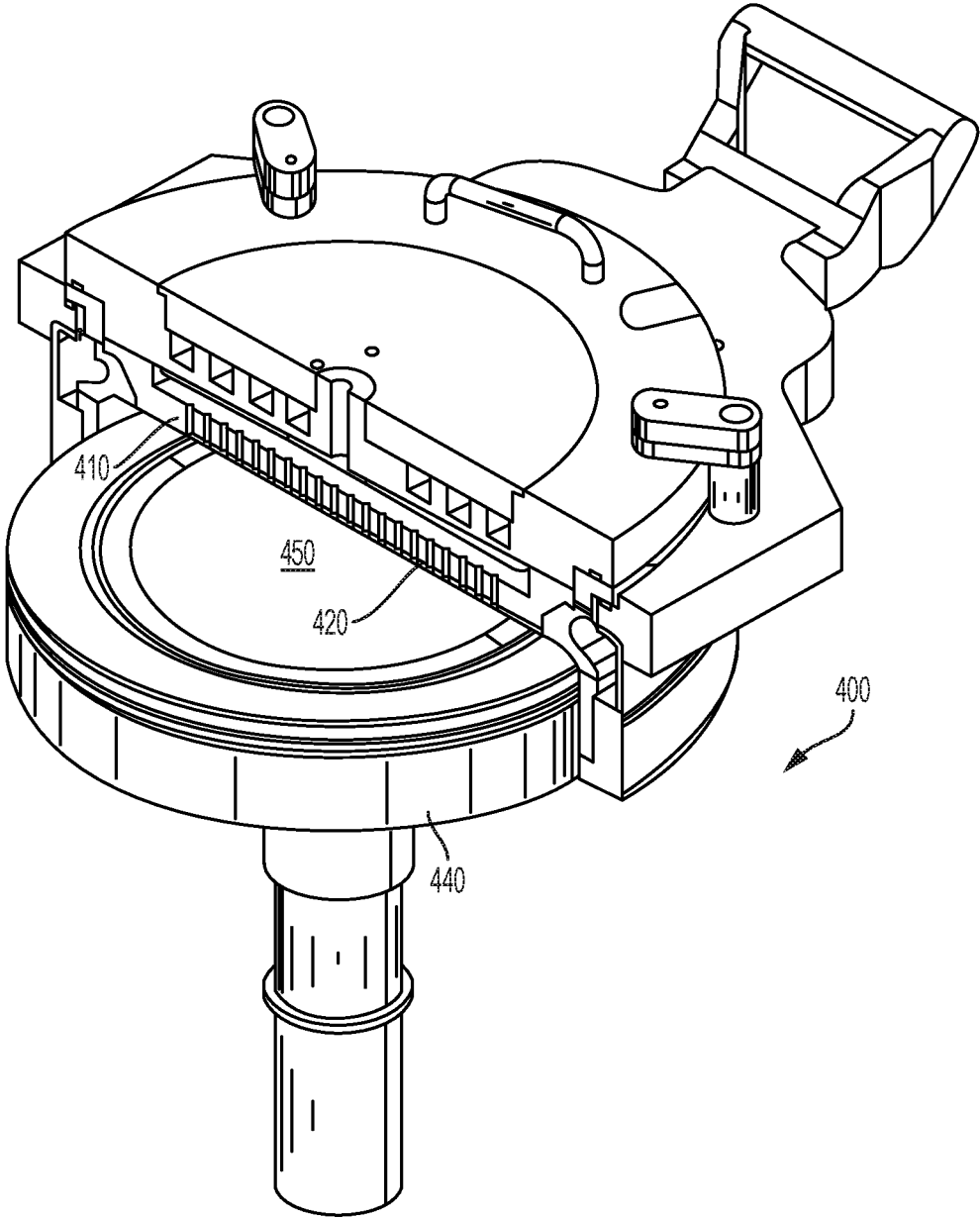


FIG. 4

**CORROSION-RESISTANT COMPONENTS
AND METHODS OF MAKING****CROSS-REFERENCE TO RELATED
APPLICATION**

[0001] This non-provisional patent application claims priority to and the benefit of U.S. Provisional Patent Application Ser. No. 62/255,769 filed Nov. 16, 2015. The foregoing provisional patent application is incorporated herein by reference in its entirety for all purposes.

FIELD

[0002] The present disclosure relates generally to corrosion-resistant components for the processing of equipment, such as semiconductors, and to methods of making such corrosion-resistant components.

BACKGROUND

[0003] The processing of semiconductors frequently involves corrosive gases such as halogens in association with strong electric and magnetic fields. This combination of a corrosive environment and strong electric/magnetic fields generates a need for corrosion-resistant insulators. It is generally accepted that the most corrosion-resistant insulating materials for such applications are rare earth compounds, such as yttrium oxide (also known as “yttria”). Unfortunately, rare earth compounds tend to be both expensive and mechanically weak. The industry therefore tends to use coatings of rare earth compounds on less expensive insulators like aluminum oxide.

[0004] Several different coating methods have been used for the insulators. Physical vapor deposition (PVD) coatings have been used. These have the drawback that they are costly to apply for thicknesses of more than 10 μm . Thick, dense layers tend to spall due to internal stresses in the as-deposited coatings. Strain-tolerant thick PVD coatings made are known to contain fissures between crystallites that create the potential for shedding particles. Chemical vapor deposition (CVD) for coating application has been used, but it suffers the similar drawbacks. High rate deposition tends to produce fissures between grains. Denser coatings made by CVD are characterized by a grain size that tends to be small, typically less than 100 nm. Aerosol deposition has been used and it also suffers from cost limitations and an inability to make thick coatings that do not spall. Thermal plasma spray is the most widely used coating technology in the semiconductor equipment industry, but it cannot produce rare-earth coatings with porosity less than 1%, and therefore is prone to the shedding of particles. Furthermore, plasma spray coatings commonly contain a high density of microcracks (typically more than 100/mm²), and this, together with the porosity, leads to the shedding of particles.

[0005] Ceramic lids are commonly interposed between induction coils and induction plasma used for etching in the semiconductor industry. Insulating rings surrounding the wafer chuck and other chamber parts in etch and deposition equipment need to be corrosion-resistant as well as stable, for the reasons outlined above.

[0006] Another need in the semiconductor equipment industry is for high temperature corrosion-resistant wafer heaters. These needs are addressed by the corrosion-resistant components and assemblies of the invention.

BRIEF SUMMARY

[0007] These and other needs are addressed by the various aspects, embodiments, and configurations of the present disclosure.

[0008] Embodiments of the present disclosure include a corrosion-resistant component configured for use with a semiconductor processing reactor, the corrosion-resistant component comprising: a) a ceramic insulating substrate; and, b) a corrosion-resistant non-porous layer associated with the ceramic insulating substrate, the corrosion-resistant non-porous layer having a composition comprising at least 15% by weight of a rare earth compound based on total weight of the corrosion-resistant non-porous layer; and, the corrosion-resistant non-porous layer characterized by a microstructure substantially devoid of microcracks and fissures, and having an average grain size of at least about 100 nm and at most about 100 μm .

[0009] The corrosion-resistant component according to paragraph [0008], wherein the ceramic insulating substrate is selected from the group consisting of aluminum oxide, aluminum nitride, silicon nitride, silicate-based materials and mixtures of two or more thereof.

[0010] The corrosion-resistant component according to either paragraph [0008] or [0009], wherein the rare earth compound is selected from the group consisting of yttrium oxide (Y₂O₃), yttrium silicates, yttrium fluorides, yttrium oxyfluorides, yttrium aluminates, nitrides, complex nitride compounds, and combinations of two or more thereof.

[0011] The corrosion-resistant component according to any of paragraphs [0008]-[0010], wherein the corrosion-resistant non-porous layer is adhered to the ceramic insulating substrate, and the corrosion-resistant non-porous layer has: a porosity of at most 1%; an adhesion strength of at least 20 MPa; and, a thickness of at least 50 μm .

[0012] The corrosion-resistant component according to any of paragraphs [0008]-[0011], wherein the corrosion-resistant non-porous layer has: a porosity of at most 0.5%; an adhesion strength of at least 30 MPa; a thickness of at least 100 μm ; and, an average grain size of at least about 300 nm and at most about 30 μm .

[0013] The corrosion-resistant component according to any of paragraphs [0008]-[0012], wherein the ceramic insulating substrate is aluminum oxide and the rare earth compound is a trivalent rare earth oxide.

[0014] The corrosion-resistant component according to any of paragraphs [0008]-[0013], wherein the ceramic insulating substrate is aluminum nitride and the corrosion-resistant non-porous layer is a rare earth silicate.

[0015] The corrosion-resistant component according to any of paragraphs [0008]-[0014], wherein the corrosion-resistant component is a lid configured for releasable engagement with a plasma etch reactor and has a loss tangent of less than 1×10^{-4} .

[0016] The corrosion-resistant component according to any of paragraphs [0008]-[0015], further comprising at least one interposing layer embedded in the ceramic insulating substrate, or layered between the ceramic insulating substrate and the corrosion-resistant non-porous layer.

[0017] The corrosion-resistant component according to any of paragraphs [0008]-[0016], wherein the at least one interposing layer is selected from the group consisting of rare earth oxides, rare earth silicates, rare earth aluminates, and mixtures of two or more thereof.

[0018] The corrosion-resistant component according to any of paragraphs [0008]-[0017], wherein the at least one interposing layer is ytterbium oxide (Yb_2O_3).

[0019] The corrosion-resistant component according to any of paragraphs [0008]-[0018], wherein the at least one interposing layer comprises conducting materials.

[0020] The corrosion-resistant component according to any of paragraphs [0008]-[0019], wherein the at least one interposing layer further comprises insulating materials.

[0021] The corrosion-resistant component according to any of paragraphs [0008]-[0020], wherein the at least one interposing layer is adhered to both the corrosion-resistant non-porous layer and to the ceramic insulating substrate, and the corrosion-resistant non-porous layer has: a porosity of at most 1%; an adhesion strength of at least 20 MPa; and, a thickness of at least 50 μm .

[0022] Embodiments of the present disclosure also include a green laminate configured for use with a semiconductor processing reactor, the green laminate comprising: a first layer of green sinterable material selected from the group consisting of aluminum oxide, aluminum nitride, silicon nitride, silicate-based materials, and mixtures of two or more thereof; a second layer of green sinterable material selected from the group consisting of yttrium oxide (Y_2O_3), yttrium silicates, yttrium fluorides, yttrium oxyfluorides, yttrium aluminates, nitrides, complex nitride compounds, and combinations of two or more thereof; and, wherein upon heat treatment of the green laminate, the second layer has a porosity of at most 1% and an average grain size of at least about 100 nm and at most about 100 μm .

[0023] The green laminate according to paragraph [0022], wherein upon heat treatment of the green laminate, the second layer has a porosity of at most 0.5% and an average grain size of at least about 300 nm and at most about 30 μm .

[0024] The green laminate according to either paragraph [0022] or [0023], further comprising at least one interposing layer between the first and second layers, wherein the at least one interposing layer comprises green sinterable material selected from the group consisting of rare earth oxides, rare earth silicates, rare earth aluminates, and mixtures of two or more thereof.

[0025] The green laminate according to any of paragraphs [0022]-[0024], wherein the heat treatment is selected from the group consisting of hot pressing and hot isostatic pressing.

[0026] Embodiments of the present disclosure also include an assembly configured for use in fabricating semiconductor chips, the assembly comprising: a reactor; and, a corrosion-resistant component including: a ceramic insulating substrate; and, a corrosion-resistant non-porous layer associated with the ceramic insulating substrate, the corrosion-resistant non-porous layer of a composition comprising at least 15% by weight of a rare earth compound based on total weight of the corrosion-resistant non-porous layer and is characterized by a microstructure substantially devoid of microcracks and fissures, and having: a thickness of at least 50 μm ; a porosity of at most 1%; and, an average grain size of at least 100 nm and at most 100 μm .

[0027] The assembly according to paragraph [0026], wherein the ceramic insulating substrate is selected from the group consisting of aluminum oxide, aluminum nitride, silicon nitride, silicate-based materials and mixtures of two or more thereof.

[0028] The assembly according to either paragraph [0026] or [0027], wherein the rare earth compound is selected from the group consisting of yttrium oxide (Y_2O_3), yttrium silicates, yttrium fluorides, yttrium oxyfluorides, yttrium aluminates, nitrides, complex nitride compounds, and combinations of two or more thereof.

[0029] The assembly according to any of paragraphs [0026]-[0028], wherein the corrosion-resistant non-porous layer is adhered to the ceramic insulating substrate and has an adhesion strength of at least 20 MPa.

[0030] The assembly according to any of paragraphs [0026]-[0029], wherein the corrosion-resistant non-porous layer has: a thickness of at least 100 μm ; a porosity of at most 0.5%; an adhesion strength of at least 30 MPa; and, an average grain size of at least about 300 nm and at most about 30 μm .

[0031] The assembly according to any of paragraphs [0026]-[0030], further comprising at least one interposing layer embedded in the ceramic insulating substrate, or layered between the ceramic insulating substrate and the corrosion-resistant non-porous layer.

[0032] The assembly according to any of paragraphs [0026]-[0031], wherein the at least one interposing layer is selected from the group consisting of rare earth oxides, rare earth silicates, rare earth aluminates, and mixtures of two or more thereof.

[0033] The assembly according to any of paragraphs [0026]-[0032], wherein the at least one interposing layer is ytterbium oxide (Yb_2O_3).

[0034] The assembly according to any of paragraphs [0026]-[0033], wherein the at least one interposing layer comprises conducting materials.

[0035] The assembly according to any of paragraphs [0026]-[0034], wherein the at least one interposing layer further comprises insulating materials.

[0036] The assembly according to any of paragraphs [0026]-[0035], wherein the at least one interposing layer is selected from the group consisting of ytterbium oxide (Yb_2O_3), molybdenum (Mo), tungsten (W), molybdenum disilicide (MoSi_2), tungsten carbide (WC), tungsten disilicide (WSi_2), and mixtures of two or more thereof.

[0037] The assembly according to any of paragraphs [0026]-[0036], wherein the reactor is a plasma etch reactor configured for plasma etching and the corrosion-resistant component is a lid configured for releasable engagement with the plasma etch reactor; and, wherein the lid has a loss tangent of less than 1×10^{-4} .

[0038] The assembly according to any of paragraphs [0026]-[0037], wherein the reactor is a deposition reactor configured for in-situ cleaning with halogen gases and the corrosion-resistant component is a heater.

[0039] The assembly according to any of paragraphs [0026]-[0038], wherein the reactor is a deposition reactor configured for in-situ cleaning with halogen gases and the corrosion-resistant component is a showerhead.

[0040] The assembly according to any of paragraphs [0026]-[0039], wherein the substrate further includes at least one interposing conductive layer embedded therein, the conductive layer having a sheet resistivity of at most 10 Megaohm-cm and a coefficient thermal expansion difference of at most $4 \times 10^{-6}/\text{K}$ relative to the coefficients of thermal expansion for the ceramic insulating substrate and the corrosion-resistant non-porous layer.

[0041] Embodiments of the present disclosure also include a corrosion-resistant component configured for use with a semiconductor processing reactor, the corrosion-resistant component comprising: a) a ceramic insulating substrate; and, b) a corrosion-resistant non-porous layer associated with the ceramic insulating substrate, the corrosion-resistant non-porous layer having a composition comprising at least 15% by weight of a rare earth compound based on total weight of the corrosion-resistant non-porous layer; and, the corrosion-resistant non-porous layer characterized by a microstructure devoid of microcracks and fissures, and having an average grain size of at least 100 nm and at most 100 μm .

[0042] The corrosion-resistant component according to paragraph [0041], wherein the ceramic insulating substrate is selected from the group consisting of aluminum oxide, aluminum nitride, silicon nitride, silicate-based materials and mixtures of two or more thereof.

[0043] The corrosion-resistant component according to either paragraph [0041] or [0042], wherein the rare earth compound is selected from the group consisting of yttrium oxide (Y_2O_3), yttrium silicates, yttrium fluorides, yttrium oxyfluorides, yttrium aluminates, nitrides, complex nitride compounds, and combinations of two or more thereof.

[0044] The corrosion-resistant component according to any of paragraphs [0041]-[0043], wherein the corrosion-resistant non-porous layer is adhered to the ceramic insulating substrate, and the corrosion-resistant non-porous layer has: a porosity of at most 1%; an adhesion strength of at least 20 MPa; and, a thickness of at least 50 μm .

[0045] The corrosion-resistant component according to any of paragraphs [0041]-[0044], wherein the corrosion-resistant non-porous layer has: a porosity of at most 0.5%; an adhesion strength of at least 30 MPa; a thickness of at least 100 μm ; and, an average grain size of at least 300 nm and at most 30 μm .

[0046] The corrosion-resistant component according to any of paragraphs [0041]-[0045], wherein the ceramic insulating substrate is aluminum oxide and the rare earth compound is a trivalent rare earth oxide.

[0047] The corrosion-resistant component according to any of paragraphs [0041]-[0046], wherein the ceramic insulating substrate is aluminum nitride and the corrosion-resistant non-porous layer is a rare earth silicate.

[0048] The corrosion-resistant component according to any of paragraphs [0041]-[0047], wherein the corrosion-resistant component is a lid configured for releasable engagement with a plasma etch reactor and has a loss tangent of less than 1×10^{-4} .

[0049] The corrosion-resistant component according to any of paragraphs [0041]-[0048], further comprising at least one interposing layer embedded in the ceramic insulating substrate, or layered between the ceramic insulating substrate and the corrosion-resistant non-porous layer.

[0050] The corrosion-resistant component according to any of paragraphs [0041]-[0049], wherein the at least one interposing layer is selected from the group consisting of rare earth oxides, rare earth silicates, rare earth aluminates, and mixtures of two or more thereof.

[0051] The corrosion-resistant component according to any of paragraphs [0041]-[0050], wherein the at least one interposing layer is ytterbium oxide (Yb_2O_3).

[0052] The corrosion-resistant component according to any of paragraphs [0041]-[0051], wherein the at least one interposing layer comprises conducting materials.

[0053] The corrosion-resistant component according to any of paragraphs [0041]-[0052], wherein the at least one interposing layer further comprises insulating materials.

[0054] The corrosion-resistant component according to any of paragraphs [0041]-[0053], wherein the at least one interposing layer is adhered to both the corrosion-resistant non-porous layer and to the ceramic insulating substrate, and the corrosion-resistant non-porous layer has: a porosity of at most 1%; an adhesion strength of at least 20 MPa; and, a thickness of at least 50 μm .

[0055] Embodiments of the present disclosure also include a green laminate configured for use with a semiconductor processing reactor, the green laminate comprising: a first layer of green sinterable material selected from the group consisting of aluminum oxide, aluminum nitride, silicon nitride, silicate-based materials, and mixtures of two or more thereof; a second layer of green sinterable material selected from the group consisting of yttrium oxide (Y_2O_3), yttrium silicates, yttrium fluorides, yttrium oxyfluorides, yttrium aluminates, nitrides, complex nitride compounds, and combinations of two or more thereof; and, wherein upon heat treatment of the green laminate, the second layer has a porosity of at most 1% and an average grain size of at least 100 nm and at most 100 μm .

[0056] The green laminate according to paragraph [0055], wherein upon heat treatment of the green laminate, the second layer has a porosity of at most 0.5% and an average grain size of at least 300 nm and at most 30 μm .

[0057] The green laminate according to either paragraph [0055] or [0056], further comprising at least one interposing layer between the first and second layers, wherein the at least one interposing layer comprises green sinterable material selected from the group consisting of rare earth oxides, rare earth silicates, rare earth aluminates, and mixtures of two or more thereof.

[0058] The green laminate according to any of paragraphs [0055]-[0057], wherein the heat treatment is selected from the group consisting of hot pressing and hot isostatic pressing.

[0059] Embodiments of the present disclosure also include an assembly configured for use in fabricating semiconductor chips, the assembly comprising: a reactor; and, a corrosion-resistant component including: a ceramic insulating substrate; and, a corrosion-resistant non-porous layer associated with the ceramic insulating substrate, the corrosion-resistant non-porous layer of a composition comprising at least 15% by weight of a rare earth compound based on total weight of the corrosion-resistant non-porous layer and is characterized by a microstructure devoid of microcracks and fissures, and having: a thickness of at least 50 μm ; a porosity of at most 1%; and, an average grain size of at least 100 nm and at most 100 μm .

[0060] The assembly according to paragraph [0059], wherein the ceramic insulating substrate is selected from the group consisting of aluminum oxide, aluminum nitride, silicon nitride, silicate-based materials and mixtures of two or more thereof.

[0061] The assembly according to either paragraph [0059] or [0060], wherein the rare earth compound is selected from the group consisting of yttrium oxide (Y_2O_3), yttrium silicates, yttrium fluorides, yttrium oxyfluorides, yttrium alu-

minates, nitrides, complex nitride compounds, and combinations of two or more thereof.

[0062] The assembly according to any of paragraphs [0059]-[0061], wherein the corrosion-resistant non-porous layer is adhered to the ceramic insulating substrate and has an adhesion strength of at least 20 MPa.

[0063] The assembly according to any of paragraphs [0059]-[0062], wherein the corrosion-resistant non-porous layer has: a thickness of at least 100 μm ; a porosity of at most 0.5%; an adhesion strength of at least 30 MPa; and, an average grain size of at least 300 nm and at most 30 μm .

[0064] The assembly according to any of paragraphs [0059]-[0063], further comprising at least one interposing layer embedded in the ceramic insulating substrate, or layered between the ceramic insulating substrate and the corrosion-resistant non-porous layer.

[0065] The assembly according to any of paragraphs [0059]-[0064], wherein the at least one interposing layer is selected from the group consisting of rare earth oxides, rare earth silicates, rare earth aluminates, and mixtures of two or more thereof.

[0066] The assembly according to any of paragraphs [0059]-[0065], wherein the at least one interposing layer is ytterbium oxide (Yb_2O_3).

[0067] The assembly according to any of paragraphs [0059]-[0066], wherein the at least one interposing layer comprises conducting materials.

[0068] The assembly according to any of paragraphs [0059]-[0067], wherein the at least one interposing layer further comprises insulating materials.

[0069] The assembly according to any of paragraphs [0059]-[0068], wherein the at least one interposing layer is selected from the group consisting of ytterbium oxide (Yb_2O_3), molybdenum (Mo), tungsten (W), molybdenum disilicide (MoSi_2), tungsten carbide (WC), tungsten disilicide (WSi_2), and mixtures of two or more thereof.

[0070] The assembly according to any of paragraphs [0059]-[0069], wherein the reactor is a plasma etch reactor configured for plasma etching and the corrosion-resistant component is a lid configured for releasable engagement with the plasma etch reactor; and, wherein the lid has a loss tangent of less than 1×10^{-4} .

[0071] The assembly according to any of paragraphs [0059]-[0070], wherein the reactor is a deposition reactor configured for in-situ cleaning with halogen gases and the corrosion-resistant component is a heater.

[0072] The assembly according to any of paragraphs [0059]-[0071], wherein the reactor is a deposition reactor configured for in-situ cleaning with halogen gases and the corrosion-resistant component is a showerhead.

[0073] The assembly according to any of paragraphs [0059]-[0072], wherein the substrate further includes at least one interposing conductive layer embedded therein, the conductive layer having a sheet resistivity of at most 10 Megaohm-cm and a coefficient thermal expansion difference of at most $4 \times 10^{-6}/\text{K}$ relative to the coefficients of thermal expansion for the ceramic insulating substrate and the corrosion-resistant non-porous layer.

[0074] Embodiments of the present disclosure include a method for preparing a corrosion-resistant component for use with a semiconductor processing reactor, comprising: laying up a thinner layer of a sinterable powder composition comprising at least 15% by weight based on total weight of the thinner layer of a rare earth compound, and a thicker

layer of sinterable substrate material to form a pre-laminate; and, heat treating the pre-laminate to form a corrosion-resistant component including a corrosion-resistant non-porous outermost layer characterized by a microstructure devoid of microcracks and fissures, and having an average grain size of at least 100 nm and at most 100 μm .

[0075] The method according to paragraph [0074], wherein heat treating is selected from the group consisting of hot pressing and hot isostatic pressing.

[0076] The method according to either paragraph [0074] or [0075], wherein the sinterable substrate material is selected from the group consisting of aluminum oxide, aluminum nitride, silicate-based materials, and mixtures of two or more thereof.

[0077] The method according to any of paragraphs [0074]-[0076], wherein the rare earth compound is selected from the group consisting of yttrium oxide (Y_2O_3), yttrium silicates, yttrium fluorides, yttrium oxyfluorides, yttrium aluminates, nitrides, complex nitride compounds and combinations of two or more thereof.

[0078] The method according to any of paragraphs [0074]-[0077], wherein the sinterable substrate material is aluminum oxide and the rare earth compound is a trivalent rare earth oxide.

[0079] The method according to any of paragraphs [0074]-[0078], wherein the sinterable substrate material is aluminum nitride and the rare earth compound is a rare earth silicate.

[0080] The method according to any of paragraphs [0074]-[0079], wherein the corrosion-resistant component is a lid configured for releasable engagement with a plasma etch reactor.

[0081] The method according to any of paragraphs [0074]-[0080], wherein the lid has a loss tangent of less than 1×10^{-3} .

[0082] The method according to any of paragraphs [0074]-[0081], wherein the lid has a loss tangent of less than 1×10^{-4} .

[0083] The method according to any of paragraphs [0074]-[0082], further comprising laying up at least one additional sinterable powder composition layer interposed between the rare earth compound thinner layer and the substrate material thicker layer, prior to heat treating.

[0084] The method according to any of paragraphs [0074]-[0083], wherein the at least one additional sinterable powder composition comprises a compound or metal having a coefficient thermal expansion difference of at most $4 \times 10^{-6}/\text{K}$ relative to the coefficients of thermal expansion for the ceramic insulating substrate and the corrosion-resistant non-porous outermost layer.

[0085] The method according to any of paragraphs [0074]-[0084], wherein the at least one additional sinterable powder composition comprises a compound or metal selected from the group consisting of ytterbium oxide (Yb_2O_3), molybdenum (Mo), tungsten (W), niobium (Nb), molybdenum disilicide (MoSi_2), tungsten carbide (WC), tungsten disilicide (WSi_2), titanium carbide (TiC), titanium nitride (TiN), and mixtures of two or more thereof.

[0086] The method according to any of paragraphs [0074]-[0085], wherein the at least one additional sinterable powder composition further comprises an insulating material selected from the group consisting of alumina, aluminum nitride, aluminates, silicates and mixtures of two or more thereof.

[0087] The method according to any of paragraphs [0074]-[0086], wherein the at least one additional sinterable powder composition is ytterbium oxide (Yb_2O_3).

[0088] The method according to any of paragraphs [0074]-[0087], wherein the at least one additional sinterable powder composition comprises conducting materials.

[0089] The method according to any of paragraphs [0074]-[0088], wherein the at least one additional sinterable powder composition further comprises insulating materials.

[0090] The method according to any of paragraphs [0074]-[0089], wherein the semiconductor processing reactor is a deposition reactor configured for in-situ cleaning with halogen gases and the corrosion-resistant component is a heater.

[0091] The method according to any of paragraphs [0074]-[0090], wherein the semiconductor processing reactor is a deposition reactor configured for in-situ cleaning with halogen gases and the corrosion-resistant component is a showerhead.

[0092] The method according to any of paragraphs [0074]-[0091], wherein the sinterable substrate material further includes at least one interposing conductive layer embedded therein, the conductive layer having a sheet resistivity of at most 10 Megaohm-cm and a coefficient thermal expansion difference of at most $4 \times 10^{-6}/\text{K}$ relative to the coefficients of thermal expansion for the ceramic insulating substrate and the corrosion-resistant non-porous outermost layer.

BRIEF DESCRIPTION OF THE DRAWINGS

[0093] FIG. 1A illustrates a cross-sectional view of an embodiment, such as a lid, including a corrosion-resistant component according to an example aspect of the invention;

[0094] FIG. 1B illustrates a cross-sectional view of an embodiment, such as a lid, including a corrosion-resistant component according to another example aspect of the invention;

[0095] FIG. 2 illustrates an assembly for plasma etching of semiconductor chips, including a corrosion-resistant lid according to an example aspect of the invention;

[0096] FIG. 3 illustrates a cross-sectional view of a corrosion-resistant wafer heater according to an example aspect of the invention; and,

[0097] FIG. 4 illustrates a chemical vapor deposition reactor assembly including a wafer heater and a showerhead, each including a corrosion-resistant non-porous layer, according to an example aspect of the invention.

DETAILED DESCRIPTION

[0098] A ceramic substrate and a corrosion-resistant layer comprising a rare earth compound are sintered together to form a dense corrosion-resistant laminate or corrosion-resistant component. This is to solve the problem of coatings (via plasma spray coating operation, for example) being applied to previously sintered substrates, wherein the coating subsequently suffers from problems such as spalling or shedding particles during use. In an example aspect, the heat treating of a thin rare earth compound layer on a suitable substrate material provides a corrosion-resistant component. In another example aspect, the rare earth compound is yttrium oxide and the substrate material is a ceramic, such as aluminum oxide. In yet another example aspect, the rare earth compound comprises a rare earth silicate such as yttrium silicate on an aluminum nitride substrate. In an example aspect, a corrosion-resistant layer including a rare

earth compound is co-sintered with insulating substrate materials to form corrosion-resistant ceramic lids, for example, that are commonly interposed between induction coils and induction plasma used for etching. In other example aspects, corrosion-resistant components useful as insulating rings surrounding the wafer chuck and other chamber parts in etch and deposition reactors, such as wafer heaters and deposition showerheads, also benefit from this technology. Components, assemblies and methods of the present disclosure provide a way to meet the need for physically and chemically stable, corrosion-resistant layers and parts such as ceramic lids integral to the plasma reactors used in the semiconductor industry.

[0099] As used herein, various terms are defined as follows. "Alumina" is commonly understood to be aluminum oxide, substantially comprising Al_2O_3 . "Yttria" is commonly understood to be yttrium oxide, substantially comprising Y_2O_3 . "Ytterbia" is commonly understood to be ytterbium oxide, substantially comprising Yb_2O_3 . The term "substantially" generally refers a purity of 90 wt %, preferably 91 wt % or 92 wt % or 93 wt % or 94 wt % or 95 wt % or 96 wt % or 97 wt % or 98 wt % or 99 wt % or about 100 wt %. The term "about" generally refers to plus or minus 10% of the indicated number. For example, "about 10%" may indicate a range of 9% to 11%, and "about 20" may mean from 18-22. Other meanings of "about" may be apparent from the context, such as rounding off; so, for example "about 1" may also mean from 0.5 to 1.4. The term "soak" (see Tables in the Examples) refers to the holding time at a particular temperature or pressure in a hot pressing cycle.

[0100] Other definitions include the following. "Adhesion strength" is measured by the ASTM C633 method. "Loss tangent" is the ratio of the imaginary part of the dielectric constant to the real part; it is directly proportional to the power absorbed by the component. "Color" is described using the 1976 CIELAB color space: this reduces colors to a lightness/darkness variable L^* , for which absolute black is 0 and complete white is 100, and other parameters a^* and b^* which describe the hue of the object. "Porosity" is measured by image analysis of a polished section, polished according to the following scheme (polishing supplies provided by Struers, Inc.): (i) 60 μm diamond: as needed to flatten the surface; (ii) 15 μm diamond, fixed abrasive pad: 2 min; (iii) 9 μm diamond, Largo (plastic) pad: 8 min; (iv) 3 μm diamond, DAC (nylon) pad: 6 min; and, (v) 1 μm diamond, napped cloth: 3 min. "Grain size" is measured by the by ASTM-E112 method. "Green" or "unsintered" ceramics as referred to herein include ceramic materials or powders which have not been densified via a high temperature thermal process. "Sintered" or "Cosintered" refers to one or more ceramic materials that have been exposed to a high temperature thermal process to promote sintering. "Sintering" is a thermal or heat treatment process to promote material transport and densification through the gradual elimination of porosity. The sintering process is used to produce materials with controlled microstructure and porosity. "Coating" is a layer applied to a substrate, for example, a sintered substrate. "Laminate" or "composite laminate" is an assembly of layers that are joined via a process such as sintering, for example. "Component" is a part or product.

[0101] A reactor for semiconductor fabrication or semiconductor processing is useful for etching or deposition or both. A reactor is referred to interchangeably herein as a

semiconductor processing reactor, a semiconductor fabrication reactor, or simply as reactor. Reactors are useful for plasma etching or deposition or both. In an example aspect, both the ceramic insulating substrate and the corrosion-resistant non-porous layer are resistant to a plasma etching treatment employed in semiconductor processing. In an example aspect, the corrosion-resistant component is a lid for a plasma etch reactor. Reactors used for deposition periodically run an etching process for cleaning of the reactor. In an example aspect, the reactor is a deposition reactor configured for in-situ cleaning with halogen gases and the corrosion-resistant component is a heater. In another example aspect, the reactor is a deposition reactor configured for in-situ cleaning with halogen gases and the corrosion-resistant component is a showerhead.

[0102] Ceramics are inorganic, non-metallic materials known for their ability to withstand high temperatures. Ceramics include oxides, non-oxides and composites (combinations of oxides and non-oxides). Oxides include, in non-limiting examples, alumina, glass-ceramics, beryllia, mullite, ceria, and zirconia. In a preferred embodiment the ceramic oxide is alumina (Al_2O_3). Non-oxides include carbides, borides, nitrides, and silicides. In another preferred embodiment, the non-oxide is a nitride, such as aluminum nitride (AlN). Ceramic oxides, non-oxides, and composites are useful as substrates.

[0103] A corrosion-resistant layer including a rare-earth element or compound is advantageously joined with a ceramic substrate and/or other layers to provide a laminate, wherein the outermost layer is corrosion-resistant and non-porous. Examples of rare-earth compounds include, but are not limited to trivalent rare earth oxides such as in an example embodiment, yttrium oxide (Y_2O_3). In other example embodiments, the rare earth compound is selected from the group consisting of yttrium oxide, yttrium silicates, yttrium fluorides, yttrium oxyfluorides, yttrium aluminates, nitrides, complex nitride compounds, and combinations of two or more thereof. In an example aspect, the rare earth compound is $\text{Y}_3\text{Si}_3\text{O}_{10}\text{F}$. In other example aspects, the rare earth compound is a complex nitride compound such as $\text{YN.Si}_3\text{N}_4$ or $\text{YN.AIN.Y}_2\text{O}_3.2\text{SiO}_2$, for example.

[0104] Sintering aids, as known to one of skill in the art, are useful for example to minimize porosity, reduce grain size, and/or to enable less extreme processing conditions to be employed (for example, lower pressures in hot pressing) for sintering. In an example aspect, a sintering aid is added to the rare-earth compound. In an example aspect, the sintering aid added to the rare-earth compound is an oxide of tetravalent elements (e.g. Zr, Hf, Ce). In an example aspect, the amount of sintering aid added to the rare-earth compound is in the range from about 300 ppm to about 20% by weight based upon total weight of the rare-earth compound; in another example aspect from about 0.5% by weight to about 15% by weight based upon total weight of the rare-earth compound. In an example aspect, the amount of sintering aid added to the rare-earth compound is about 1% by weight, or about 2% by weight, or about 5% by weight, or about 10% by weight, or about 15% by weight. In an example aspect, the sintering aid added to the rare-earth compound is ZrO_2 or HfO_2 . In an example aspect, where the rare-earth compound is yttria, for example, ZrO_2 is used as a sintering aid in the amount of about 1% by weight based upon total weight of the rare-earth compound. In another example aspect, ZrO_2 is used as a sintering aid in

the amount of about 15% by weight based upon total weight of the rare-earth compound. In an example aspect for processing large parts such as a lid, for which maintaining pressure levels is challenging, about 1% by weight sintering aid is added to the rare-earth compound based upon total weight of the rare-earth compound.

[0105] Interposer layers can be placed between the substrate and the rare-earth compound containing corrosion-resistant layer in assembling the laminate. In an example aspect, at least one interposer layer between a yttria layer and an alumina substrate is useful in order to detect wear of the outermost corrosion-resistant layer. Interposer layers may also advantageously include a rare-earth element or compound. In one embodiment, ytterbium oxide (Yb_2O_3) is used as an interposer layer since its fluorescence at infrared (IR) wavelengths can be used to detect corrosion-resistant layer wear without producing a cosmetic color change of the material. As owners of semiconductor equipment frequently care about cosmetic issues, Yb_2O_3 layers offer the advantage of not being visible to the human eye (in other words colorless) while allowing detection of wear by irradiating with appropriate IR wavelengths and observing the fluorescence. The thickness of interposer layer(s) depends on function; typically interposer layers are at most about 2 mm in thickness. In an example aspect, interposer layers such as conductive layers or bonding layers function acceptably at thicknesses of less than 10 μm .

[0106] Optionally, it may also be advantageous to include metal layers in the ceramic lid, insulating rings and other chamber parts that are commonly found in etching and deposition equipment. As noted above, ceramic lids, which are also referred to as ceramic windows or simply as lids or windows interchangeably herein, are commonly interposed between induction coils and induction plasma used for etching. The electrical resistance of a metal layer could also serve to monitor the temperature of the lid, thus enabling feedback control over its temperature. Embedding or interposing the layers within the lid or component simplifies the assembly of the system and also improves shielding and the coupling of the heat to the lid.

[0107] It is important to choose the materials of the embedded layers to match the thermal expansion coefficient of the bulk composite as well as to the individual layer(s) of the composite as mismatches tend to lead to delayed delamination within the component. Thermal expansion mismatches can be considered close or acceptable if the difference in thermal expansion coefficients is at most $4 \times 10^{-6}/\text{K}$ relative to the coefficients for the ceramic insulating substrate and the corrosion-resistant non-porous layer. In an example aspect, the at least one interposing layer is chosen to be a material having a thermal expansion coefficient difference of at most at most $4 \times 10^{-6}/\text{K}$ relative to the coefficients for the ceramic insulating substrate and the corrosion-resistant non-porous layer. Thermal expansion mismatches can often be helped by making the layer a composite of several different materials, whose combined thermal expansion matches the expansion of the bulk of the part. In an example aspect, MoSi_2 is a particularly suitable conductive metal, because its thermal expansion is close to that of alumina, and it does not react with alumina at the high processing temperatures.

[0108] Since the components of the invention may operate in strong electromagnetic fields, minimizing the loss tangent is an important consideration. In an example aspect, the

corrosion-resistant component has a loss tangent of the component of at most 1×10^{-3} , preferably at most 1×10^{-4} . A component having a loss tangent of at most 1×10^{-4} is substantially transparent to radio-frequency (RF) energy. Excessive carbon content in the parts tends to promote high loss tangent and therefore carbon content should be minimized. Free carbon contents in excess of 2000 ppm are undesirable. In one embodiment the carbon content is at most 1500 ppm. In another embodiment the carbon content is at most 1000 ppm. In a further embodiment the carbon content is at most 500 ppm. In yet another embodiment the carbon content is at most 100 ppm.

[0109] The presence or exposure to certain elements during the semiconductor processing, for example, can be undesirable. In applications for which light-colored ceramic components are desired, due to industry users being sensitive to the color of the components or parts as with semiconductor processing, undesired elements are to be avoided. Metal contamination in the parts (which affects the properties of transistors in the wafers processed in the equipment) can be visible as dark spots on the parts. Thus lighter colors for the parts are preferred as the spots show up more clearly. This enables problem or unacceptable parts to be identified and discarded before use. In an example aspect, the corrosion-resistant component has a CIE Lab color L^* parameter of at least 50. In another example aspect, the corrosion-resistant component has a CIE Lab color L^* parameter of at least 80.

[0110] First row transition elements such as V, Cr, Mn, Fe, Co, Ni, Cu, and Zn, for example, diffuse relatively quickly through silicon and can alter the electrical properties of devices. The presence of Au and Ag can cause similar problems. In addition, elements such as Li, Na, and K diffuse quickly through silica and can affect the charge density on device gates. The corrosion-resistant component of the invention is substantially contaminant free. Total concentration of undesirable elements in the raw materials for making corrosion-resistant components is to be minimized. The total concentration of these undesirable elements should be substantially less than 1 at %. In an example aspect, the total concentration of undesirable elements in raw materials used in making of the corrosion-resistant components is at most 1 at %.

[0111] Layer thickness for the outermost layer may be tailored to the component and its application for use. The outermost layer is the corrosion-resistant non-porous layer. Depending upon use, the outermost layer may be oriented toward the inside of a chamber or reactor, for example. For lids or windows, which are typically larger than 500 mm in diameter, relatively thick layers are desired. The as-fired profile of such a large component may depart by a millimeter or more from the desired profile; therefore, it is desirable for the as-fired thickness of the outermost layer to be substantially more than one millimeter thick, in order to ensure the presence of enough outermost material even after grinding. Thinner layers are more appropriately used on smaller parts, because departures from the true form are typically less.

[0112] One example aspect of the invention is directed to a corrosion-resistant component configured for use with a semiconductor processing reactor, the corrosion-resistant component comprising: a) a ceramic insulating substrate; and, b) a corrosion-resistant non-porous layer associated with the ceramic insulating substrate, the corrosion-resistant non-porous layer having a composition comprising at least

15% by weight of a rare earth compound based on total weight of the corrosion-resistant non-porous layer; and, the corrosion-resistant non-porous layer characterized by a microstructure substantially devoid of microcracks and fissures, and having an average grain size of at least about 100 nm and at most about 100 μm . In an example aspect, the corrosion-resistant non-porous layer associated with the ceramic insulating substrate is adhered to the substrate. In an example aspect, the corrosion-resistant non-porous layer is adhered directly to the substrate. In another example aspect, the corrosion-resistant non-porous layer is adhered indirectly to the substrate, for example with interposing layers therebetween.

[0113] The microstructure of the corrosion-resistant non-porous layer is important to the durability and performance of the component. A component or laminate including a non-porous layer free of microcracks and fissures does not suffer deleterious effects such as particle shedding. In an example aspect, the corrosion-resistant non-porous layer is characterized by a microstructure devoid of microcracks and fissures. In another example aspect, the corrosion-resistant non-porous layer is characterized by a microstructure substantially devoid of microcracks and fissures. In an example aspect, the corrosion-resistant non-porous layer has microcracks and fissures of less than 50 per mm^2 , in an example aspect less than 10 per mm^2 , in another example aspect less than 5 per mm^2 , and in yet another example aspect less than 1 per mm^2 . In an example aspect, the corrosion-resistant non-porous layer is characterized by a microstructure having microcracks and fissures of at most 1 per mm^2 , as quantified by image analysis, for example, or other methods as known in the art. Whereas microcracks and fissures are deleterious to the microstructural integrity of the corrosion-resistant non-porous layer, second phases in the microstructure may conversely increase strength of the layer (refer to Example 10).

[0114] In an example aspect, grain size of the corrosion-resistant non-porous layer is important to the performance of the component. Generally, corrosion occurs fastest at grain boundaries, thus materials with larger grain sizes corrode more slowly. In addition, if corrosion on boundaries is relatively rapid, entire grains can be dislodged by grain boundary corrosion. This is also referred to herein as particle loss or shedding. In an example aspect, the corrosion-resistant component includes a corrosion-resistant non-porous layer having an average grain size as measured by ASTM-E112 of at least 100 nm. In an example aspect, the corrosion-resistant non-porous layer is characterized as having an average grain size of at least 100 nm, or at least 150 nm, or at least 200 nm, or at least 300 nm, or at least 500 nm. However, problems may develop with overly large grain sizes, for example, the size of flaws weakening the material scales as the grain size; therefore, grain sizes larger than 100 μm are also undesirable. In an example aspect, the corrosion-resistant non-porous layer is characterized as having an average grain size of at most 100 μm , or at most 30 μm , or at most 10 μm , or at most 1 μm , or at most 750 nm. Alternatively, the average grain size of the corrosion-resistant non-porous layer is in the range of about 100 nm to about 100 μm , preferably about 200 nm to about 50 μm , more preferably about 300 nm to about 30 μm . In another example aspect, the average grain size of the corrosion-resistant non-porous layer is at least 300 nm and at most 30 μm .

[0115] In an example aspect, the corrosion-resistant component includes a corrosion-resistant non-porous layer having: a) a porosity of $\leq 2\%$, preferably $\leq 1\%$ or $\leq 0.9\%$ or $\leq 0.8\%$ or $\leq 0.7\%$ or $\leq 0.6\%$ or $\leq 0.5\%$ or $\leq 0.4\%$ or $\leq 0.3\%$ or $\leq 0.2\%$ or $\leq 0.1\%$; and b) an adhesion strength of ≥ 15 MPa, preferably ≥ 20 MPa or ≥ 25 MPa or ≥ 30 MPa or ≥ 35 MPa or ≥ 40 MPa; and c) a layer thickness of ≥ 50 μm , preferably ≥ 100 μm or ≥ 150 μm or ≥ 200 μm or ≥ 250 μm or ≥ 300 μm . Layer thickness, as mentioned previously, may be tailored to the application of use or component specifications desired. Alternatively, the layer thickness can be in the range of about 50 to about 500 μm , preferably about 100 to about 400 μm , more preferably about 150 to about 300 μm . In an example aspect, the corrosion-resistant non-porous layer has: a porosity of at most 1%; an adhesion strength of at least 20 MPa; and, a layer thickness of at least 50 μm . In another example aspect, the corrosion-resistant non-porous layer has: a porosity of at most 0.5%; an adhesion strength of at least 30 MPa; and, a layer thickness of at least 100 μm .

[0116] FIGS. 1A and 1B illustrate cross-sectional schematic views of example aspects of corrosion-resistant components. In FIG. 1A, corrosion-resistant component 100 includes substrate 110 having corrosion-resistant non-porous layer 120 adjacent to the substrate 110 where layer 120 provides an outermost layer for the component. Layer 120 has thickness t_1 . In FIG. 1B, corrosion-resistant component 150 includes substrate 110 having interposing layer 130 situated between substrate 110 and corrosion-resistant non-porous layer 120. Layer 130 has thickness t_2 . In one embodiment of the corrosion-resistant component both the substrate and the corrosion-resistant non-porous layer are resistant to the plasma etching conditions employed in semiconductor processing.

[0117] In an example aspect, as shown in FIG. 1A, corrosion-resistant component 100 includes non-porous corrosion-resistant layer 120 comprising a rare earth compound. In an example aspect, layer 120 comprises a trivalent rare earth oxide. In another example aspect, the rare earth compound is selected from the group consisting of yttrium oxide (Y_2O_3), yttrium silicates, yttrium fluorides, yttrium oxyfluorides, yttrium aluminates, nitrides, complex nitride compounds, and combinations of two or more thereof. In another example aspect, the rare earth compound is a complex nitride compound such as, for example, $\text{YN.Si}_3\text{N}_4$ or $\text{YN.AIN.Y}_2\text{O}_3.2\text{SiO}_2$.

[0118] In an example aspect, the corrosion-resistant component includes ceramic insulating substrate 110, as shown also in FIG. 1A, selected from the group consisting of aluminum oxide ("alumina", also Al_2O_3), aluminum nitride, silicon nitride, silicate-based materials and mixtures of two or more thereof. In an example aspect, for applications requiring high strength, for example, the substrate may further include zirconia (ZrO_2). In an example aspect, the ceramic insulating substrate is aluminum oxide. In an example aspect, the ceramic insulating substrate consists essentially of aluminum oxide. In an example aspect, the ceramic insulating substrate is aluminum oxide and the rare earth compound is a trivalent rare earth oxide. In another example aspect, the ceramic insulating substrate is aluminum nitride and the corrosion-resistant non-porous layer is a rare earth silicate.

[0119] In an example aspect, the corrosion-resistant non-porous layer is adhered to the ceramic insulating substrate, and the corrosion-resistant non-porous layer has: a porosity

of at most 1%; an adhesion strength of at least 20 MPa; and, a thickness of at least 50 μm . In another example aspect, the corrosion-resistant non-porous layer is adhered to the ceramic insulating substrate, and the corrosion-resistant non-porous layer has: a porosity of at most 0.5%; an adhesion strength of at least 30 MPa; a thickness of at least 100 μm ; and, an average grain size of at least about 300 nm and at most about 30 μm .

[0120] In an example aspect, corrosion-resistant component 100 is a lid configured for releasable engagement with a plasma etch reactor. In an example aspect, the corrosion-resistant component or lid has a loss tangent of less than 1×10^{-4} . In an example aspect, ceramic insulating substrate 110 and corrosion-resistant non-porous layer 120 are substantially transparent to radio-frequency (RF) energy. In an example aspect, ceramic insulating substrate 110 and corrosion-resistant non-porous layer 120 are transparent to radio-frequency (RF) energy.

[0121] In an example aspect, corrosion-resistant component 150, as shown in FIG. 1B, includes at least one interposing layer 130 selected from the group consisting of rare earth oxides, rare earth silicates, rare earth aluminates, and mixtures of two or more thereof. In an example aspect, the at least one interposing layer 130 is ytterbium oxide (Yb_2O_3). In an example aspect, the at least one interposing layer comprises conducting materials. In an example aspect, the at least one interposing layer further comprises insulating materials.

[0122] In an example aspect, the at least one interposing layer is adhered to both the corrosion-resistant non-porous layer and to the ceramic insulating substrate, and the corrosion-resistant non-porous layer has: a porosity of at most 1%; an adhesion strength of at least 20 MPa; and, a thickness of at least 50 μm . In another example aspect, the at least one interposing layer is adhered to both the corrosion-resistant non-porous layer and to the ceramic insulating substrate, and the corrosion-resistant non-porous layer has: a porosity of at most 0.5%; an adhesion strength of at least 30 MPa; a thickness of at least 100 μm ; and, an average grain size of at least about 300 nm and at most about 30 μm .

[0123] In an example aspect, at least one interposing layer is either embedded in the ceramic insulating substrate 110 (see FIG. 3, layers 340, 360), or between and adhered to both the substrate and the corrosion-resistant non-porous layer 120 (see FIG. 1B). In an example aspect, the interposing layer is selected from the group consisting of rare earth oxides, rare earth silicates, rare earth aluminates and mixtures of two or more thereof. A rare earth oxide suitable as an at least one interposing layer is ytterbium oxide (Yb_2O_3). In another example aspect, the interposing layer comprises conducting materials, which can optionally further comprise insulating materials. With regard to the conducting materials, for most applications direct current (DC) or low frequency, for example less than 100 MHz, conductivity is required. Conducting metal layers are useful as actively driven electrodes or as a passive RF shield. The insulating materials are generally selected from the group consisting of alumina, aluminum nitride, silicon nitride, aluminates, silicates, and mixtures of two or more thereof, although any material compatible with the processing of the part and the metals in the layer could be also used; the reasons to add materials to the conducting layer can include obtaining better thermal expansion match to the rest of the part and improving the adhesion between the layer and the rest of the

part. In the case where conducting materials are used, the layer will usually have large openings in it to allow RF energy to pass through. In other words, in an example aspect, an interposing layer such as a conductive layer is non-continuous. In one embodiment of the corrosion-resistant component the substrate and the corrosion-resistant non-porous layer are substantially transparent to radio-frequency (RF) energy.

[0124] In an example aspect, and prior to heat treatment, a green laminate configured for use with a semiconductor processing reactor comprises a first layer of green sinterable material and a second layer of green sinterable material including a rare earth compound. In an example aspect, the first layer of green sinterable material is selected from the group consisting of aluminum oxide, aluminum nitride, silicon nitride, silicate-based materials, and mixtures of two or more thereof. In an example aspect, the second layer of green sinterable material comprises a trivalent rare earth oxide. In another example aspect, the second layer comprises a rare earth compound selected from the group consisting of yttrium oxide (Y_2O_3), yttrium silicates, yttrium fluorides, yttrium oxyfluorides, yttrium aluminates, nitrides, complex nitride compounds, and combinations of two or more thereof. In an example aspect, upon heat treatment of the laminate, the second layer has a porosity of at most 1% and an average grain size of at least 100 nm and at most 100 μm . In another example aspect, upon heat treatment of the laminate, the second layer has a porosity of at most 0.5%. In an example aspect, upon heat treatment of the laminate, the average grain size of the second layer is at least 300 nm and at most 30 μm .

[0125] In an example aspect, the green laminate further includes at least one interposing layer between the first and second layers, wherein the interposing layer comprises green sinterable material selected from the group consisting of rare earth oxides, rare earth silicates, rare earth aluminates, and mixtures of two or more thereof. In an example aspect, the green laminate further includes at least one interposing layer wherein the at least one interposing layer comprises conducting materials. In an example aspect, the green laminate further includes at least one interposing layer wherein the at least one interposing layer comprises insulating materials. In an example aspect, the heat treatment for the green laminate is selected from the group consisting of hot pressing and hot isostatic pressing. After heat treatment, the heat treated or sintered laminate including interposing layer(s) has an adhesion strength of at least 15 MPa, or at least 20 MPa, or at least 25 MPa, or at least 30 MPa, or at least 35 MPa, or at least 40 MPa.

[0126] FIG. 2 illustrates an example aspect of an assembly configured for use in plasma etching semiconductor wafers. Plasma etch reactor assembly 200 includes plasma etch reactor 250. Alternating magnetic fields generated by induction coils 240 extend through lid 225, creating electric fields inside reactor 250 directly under lid 225, which in turn create the etch plasma. Corrosion-resistant lid 225 is configured for releasable engagement with plasma etch reactor 250. Lid 225 includes a corrosion-resistant ceramic insulating substrate 210 having an inner surface and an outer surface; and, further includes corrosion-resistant non-porous layer 220, which is adjacent to the inner surface of substrate 210. Corrosion-resistant non-porous layer 220, having inner and outer planar surfaces, is positioned so that the inner planar surface of layer 220 faces the interior of reactor 250.

Optionally, interposing layer(s) (example layer 130 as shown in FIG. 1B) are situated between substrate 210 and corrosion-resistant non-porous layer 220. In an example aspect, layer 220 comprising a rare earth compound, wherein the non-porous layer is adhered to the corrosion-resistant substrate and has 1) an adhesion strength of ≥ 15 MPa, preferably ≥ 20 MPa or ≥ 25 MPa or ≥ 30 MPa or ≥ 35 MPa or ≥ 40 MPa, 2) a thickness of ≥ 50 μm , preferably ≥ 100 μm or ≥ 150 μm or ≥ 200 μm or ≥ 250 μm or ≥ 300 μm ; alternately a thickness in the range of about 50 to about 500 μm , preferably about 100 to about 400 μm , more preferably about 150 to about 300 μm , and 3) a porosity of preferably $\leq 1\%$ or $\leq 0.9\%$ or $\leq 0.8\%$ or $\leq 0.7\%$ or $\leq 0.6\%$ or $\leq 0.5\%$ or $\leq 0.4\%$ or $\leq 0.3\%$ or $\leq 0.2\%$ or $\leq 0.1\%$. In an example aspect, layer 220 includes at least 15% by weight based on total weight of layer of a rare earth compound. In example aspect, layer 220 includes an adhesion strength of at least 20 MPa; a porosity of at most 1%; a microstructure substantially devoid of microcracks and fissures and an average grain size of at least 100 nm and at most 100 μm ; and, a layer thickness of at least 50 μm . In another example aspect, the grain size is at least 300 nm and at most 30 μm .

[0127] In an example aspect, lid 225 of the assembly includes layer 220, wherein the rare earth compound is selected from the group consisting of yttrium oxide (Y_2O_3), yttrium silicates, yttrium fluorides, yttrium oxyfluorides, yttrium aluminates, nitrides, complex nitride compounds and combinations of two or more thereof. In another example aspect, the assembly includes the corrosion-resistant ceramic insulating substrate 210, wherein the substrate is selected from the group consisting of aluminum oxide, aluminum nitride, silicon nitride, silicate-based materials and mixtures of two or more thereof.

[0128] Another embodiment of the assembly further comprises an interposing layer embedded in the substrate, or an interposing layer between and adhered to both the corrosion-resistant substrate and the non-porous layer. In an example aspect, the interposing layer may serve one or more functions, for example, to promote adhesion between the non-porous layer and the substrate, to prevent an adverse reaction between the non-porous layer and the substrate, and/or to provide some electrical function for the assembly. In other example aspects, for applications involving very high electric fields as required for particular lids, high electrical resistivity is desirable to prevent losses affecting processing, and therefore, an interposing layer such as ytterbium oxide (Yb_2O_3) can be beneficial.

[0129] In an example aspect, the interposing layer is selected from the group consisting of ytterbium oxide (Yb_2O_3), $MoSi_2$, radio-frequency (RF) conducting materials and mixtures of two or more thereof. Preferably the corrosion-resistant lid of the assembly is substantially transparent to radio-frequency (RF) energy. The assembly, including the corrosion-resistant lid, is preferably resistant to the plasma etching treatment employed in semiconductor processing. Thus, the corrosion-resistant substrate and the corrosion-resistant non-porous layer of corrosion-resistant lid of the assembly are resistant to the plasma etching treatment employed in semiconductor processing.

[0130] Another aspect of the invention is directed to a high temperature corrosion-resistant wafer heater. FIG. 3 illustrates a cross-sectional schematic view of wafer heater apparatus 300 as in an example aspect. The wafer (not shown) sits on the outermost layer (320) of insulating

ceramic disk **310** having heating elements **340** embedded therein and also, optionally, metal RF shield **360**. In an example aspect insulating ceramic **310**, from which these heaters are made, is aluminum nitride. In other example aspects, alumina or silicon nitride are useful as ceramic insulating substrate **310**. During operation, the heater is sometimes cleaned with fluorine-containing gas. If the temperature of the heater exceeds about 500° C., then the heater itself may be attacked by the fluorine thus making a corrosion-resistant protective layer included onto the 'hot' parts necessary. In an example aspect, insulating ceramic **310** includes corrosion-resistant non-porous layer **320** and optional interposing layer **330** therebetween. Corrosion-resistant non-porous layer **320** includes an outer surface for holding the wafer (not shown). Of particular importance is that the region of the rare earth compound containing layer directly under the wafer, in other words corrosion-resistant non-porous layer **320**, be dense. Otherwise particles from the heater would tend to be shed onto the underside of the wafer. These shed particles could migrate to the top side of the wafer in a subsequent step, which would in turn result in defects in the patterns on the wafer. The sides, bottom and coverage on the stalk or supporting disk **380** of the wafer heater are less critical, as there is no direct path for particles to migrate to the wafer. A plasma spray coating suffices to prevent against contamination for these other regions.

[0131] FIG. 4 illustrates a chemical vapor deposition reactor assembly including a wafer heater according to an example aspect of the invention. Chemical vapor deposition (CVD) reactor assembly **400** includes showerhead **410** and heater **440**. Reactive gases flow through showerhead **410**, which is protected by corrosion-resistant non-porous layer **420**, onto wafer **450**, where a deposit is formed. The temperature of the wafer is maintained and kept uniform by heater **440**, which may also have a non-porous corrosion-resistant layer on it (as shown in FIG. 3) to protect it during cleaning. Showerhead **410** may further include interposing or embedded layers, such as an electrode, within to assist the generation of a plasma to promote chemical reactions.

[0132] In an example aspect, assembly **400** is configured for use in fabricating semiconductor chips. Assembly **400** includes corrosion-resistant components (i) wafer heater **440**, shown in FIG. 3 as wafer heater **300** in more detail), and/or (ii) showerhead **410**. In an example aspect, the deposition reactor is configured for in-situ cleaning with halogen gases and a corrosion-resistant component. Each corrosion-resistant component includes a ceramic insulating substrate; and, a corrosion-resistant non-porous layer of a composition comprising at least 15% by weight of a rare earth compound based on total weight of layer. In an example aspect, the rare earth compound is a trivalent oxide. In another example aspect, the rare earth compound is selected from the group consisting of yttrium oxide (Y_2O_3), yttrium silicates, yttrium fluorides, yttrium oxyfluorides, yttrium aluminates, nitrides, complex nitride compounds and combinations of two or more thereof. In an example aspect, the rare earth compound is yttrium oxide (Y_2O_3). In an example aspect, the ceramic insulating substrate is selected from the group consisting of aluminum oxide, aluminum nitride, silicon nitride, silicate-based materials, and mixtures of two or more thereof. In an example aspect the corrosion-resistant component further includes at least interposing layer between the substrate and the corrosion-resistant non-porous layer. In an example aspect, the inter-

posing layer is selected from the group consisting of ytterbium oxide (Yb_2O_3), $MoSi_2$, radio-frequency (RF) conducting materials and mixtures of two or more thereof. In an example aspect, the substrate further includes at least one additional interposing conductive layer embedded therein, the conductive layer having a sheet resistivity of at most 10 Megaohm-cm, which may also be written as 10 megohm-cm interchangeably herein.

[0133] In an example aspect, an assembly configured for use in fabricating semiconductor chips, the assembly comprising a reactor and a corrosion-resistant component. The corrosion-resistant component includes a ceramic insulating substrate and a corrosion-resistant non-porous layer associated with the ceramic insulating substrate. In an example aspect, the corrosion-resistant non-porous layer has a composition comprising at least 15% by weight of a rare earth compound based on total weight of the corrosion-resistant non-porous layer. In an example aspect, the corrosion-resistant non-porous layer is characterized by a microstructure substantially devoid of microcracks and fissures, and having: a thickness of at least 50 μm ; a porosity of at most 1%; and, an average grain size of at least 100 nm and at most 100 μm .

[0134] In an example aspect, the ceramic insulating substrate of the assembly is selected from the group consisting of aluminum oxide, aluminum nitride, silicon nitride, silicate-based materials and mixtures of two or more thereof. In an example aspect, the rare earth compound of the assembly is selected from the group consisting of yttrium oxide (Y_2O_3), yttrium silicates, yttrium fluorides, yttrium oxyfluorides, yttrium aluminates, nitrides, complex nitride compounds, and combinations of two or more thereof. In an example aspect, the corrosion-resistant non-porous layer of the assembly is adhered to the ceramic insulating substrate and has an adhesion strength of at least 20 MPa. In another example aspect, the corrosion-resistant non-porous layer has a thickness of at least 100 μm ; a porosity of at most 0.5%; an adhesion strength of at least 30 MPa; and, an average grain size of at least about 300 nm and at most about 30 μm .

[0135] In an example aspect, the assembly further comprises at least one interposing layer embedded in the ceramic insulating substrate, or layered between the ceramic insulating substrate and the corrosion-resistant non-porous layer. In an example aspect, the at least one interposing layer is selected from the group consisting of rare earth oxides, rare earth silicates, rare earth aluminates, and mixtures of two or more thereof. In an example aspect, the at least one interposing layer is ytterbium oxide (Yb_2O_3). In an example aspect, the at least one interposing layer comprises conducting materials that have a good coefficient of thermal expansion match with the ceramic insulating substrate and the corrosion-resistant non-porous layer. Thermal expansion mismatches can be considered close if the difference in thermal expansion coefficients is at most $4 \times 10^{-6}/K$ relative to the coefficients for the ceramic insulating substrate and the corrosion-resistant non-porous layer. In an example aspect, the at least one interposing layer is chosen to be a material having a thermal expansion coefficient difference of at most at most $4 \times 10^{-6}/K$ relative to the coefficients for the ceramic insulating substrate and the corrosion-resistant non-porous layer. In an example aspect, the at least one interposing layer further comprises insulating materials. In an example aspect, the at least one interposing layer is selected from the group consisting of ytterbium oxide (Yb_2O_3),

molybdenum (Mo), tungsten (W), molybdenum disilicide (MoSi_2), tungsten carbide (WC), tungsten disilicide (WSi_2), and mixtures of two or more thereof.

[0136] In an example aspect, the reactor is a plasma etch reactor configured for plasma etching and the corrosion-resistant component is a lid configured for releasable engagement with the plasma etch reactor; and, wherein the lid has a loss tangent of less than 1×10^{-4} and is substantially transparent to radio-frequency (RF) energy. In an example aspect, the reactor is a deposition reactor configured for in-situ cleaning with halogen gases and the corrosion-resistant component is a heater. In an example aspect, the ceramic insulating substrate further includes at least one interposing conductive layer embedded therein, the conductive layer having a sheet resistivity of at most 10 Megaohm-cm. In another example aspect, the reactor is a deposition reactor configured for in-situ cleaning with halogen gases and the corrosion-resistant component is a showerhead.

[0137] Another aspect is directed to a method for preparing a corrosion-resistant component for use with a reactor. The method includes the steps as follows: a) laying up a thinner layer of a sinterable powder composition comprising at least 15% by weight based on total weight of the thinner layer of a rare earth compound, and a thicker layer of sinterable substrate material to form a pre-laminate (also referred to herein as 'green laminate'); and, b) heat treating the pre-laminate to form a corrosion-resistant laminate. The terms "thinner" versus "thicker" indicate that the thinner powder layer is less than 50% of the thicker powder layer in the pressing direction. Heat treating is selected from the group consisting of hot pressing and hot isostatic pressing.

[0138] In an example aspect of the method, the sinterable substrate material is selected from the group consisting of aluminum oxide, aluminum nitride, silicon nitride, silicate-based materials, and mixtures of two or more thereof. In an example aspect of the method, the rare earth compound is a tri-valent rare earth oxide. In an example aspect of the method, the rare earth compound is selected from the group consisting of yttrium oxide (Y_2O_3), yttrium silicates, yttrium fluorides, yttrium oxyfluorides, yttrium aluminates, nitrides, complex nitride compounds and combinations of two or more thereof. In an example aspect of the method, the amount of rare earth compound is about 15 to 100 wt %, or about 20 to about 90 wt %, or about 25 to about 80 wt %. In an example aspect, the rare earth compound is $\text{Y}_3\text{Si}_3\text{O}_{10}\text{F}$. In an example aspect of the method, the sinterable substrate material is aluminum oxide and the rare earth compound is a trivalent rare earth oxide. In another example aspect of the method, the sinterable substrate material is aluminum nitride and the corrosion-resistant non-porous layer is a rare earth silicate. In an example aspect of the method, the corrosion-resistant component is a lid configured for releasable engagement with a plasma etch reactor. In an example aspect of the method, the lid has a loss tangent of less than 1×10^{-3} . In another example aspect of the method, the lid has a loss tangent of less than 1×10^{-4} . In an example aspect of the method, the corrosion-resistant component is substantially transparent to radio-frequency (RF) energy.

[0139] In an example aspect the method further comprises laying up at least one additional sinterable powder composition layer interposed between the rare earth compound thinner layer and the substrate material thicker layer, prior to heat treatment. In another example aspect of the method, the at least one additional sinterable powder composition com-

prises a compound or metal selected from the group consisting of ytterbium oxide (Yb_2O_3), molybdenum (Mo), tungsten (W), niobium (Nb), and compounds like molybdenum disilicide (MoSi_2), tungsten carbide (WC), tungsten disilicide (WSi_2), titanium carbide (TiC), titanium nitride (TiN), and other such conducting materials and compounds that show metallic behavior and have a good coefficient of thermal expansion match to the ceramic insulating substrate and the corrosion-resistant non-porous layer, and mixtures of two or more thereof. In an example aspect of the method, the at least one additional sinterable powder composition is ytterbium oxide (Yb_2O_3). In an example aspect, the method includes at least one additional sinterable powder composition comprising conducting materials. In an example aspect, the method includes at least one additional sinterable powder composition comprising conducting metals. In an example aspect, the method includes the at least one additional sinterable powder composition further comprises insulating materials. In another example aspect, the method includes the at least one additional sinterable powder composition further comprises an insulating material selected from the group consisting of alumina, aluminum nitride, silicon nitride, silicates, and mixtures of two or more thereof.

[0140] In an example aspect of the method, the semiconductor processing reactor is a deposition reactor configured for in-situ cleaning with halogen gases and the corrosion-resistant component is a heater. In an example aspect of the method, the sinterable substrate material further includes at least one interposing conductive layer embedded therein, the conductive layer having a sheet resistivity of at most 10 Megaohm-cm. In another example aspect of the method, the semiconductor processing reactor is a deposition reactor configured for in-situ cleaning with halogen gases and the corrosion-resistant component is a showerhead.

EXAMPLES

[0141] For all examples, and in view of the need to minimize contamination, a total concentration of undesirable elements in raw materials used is at most 1 at %.

Example 1

[0142] Two disks (S1 and S12) made from an alumina-ytria laminate were manufactured as follows. High purity chemically precipitated yttrium oxide powder from AMR Corp. was attrition milled in water to particle size $d_{90} < 1 \mu\text{m}$. The slurry was then freeze dried and sieved through a 150 μm mesh.

[0143] Spray dried alumina powder of approximate composition 0.25 wt % SiO_2 , 0.05 wt % Na_2O , 0.12 wt % MgO , 0.12 wt % CaO , balance Al_2O_3 was heated in air at 800°C . for 8 hours to remove binder from the spray dried powder. This powder is referred to as CoorsTek 99512.

[0144] The alumina powder was cold pressed in a 6-inch diameter die to a pressure of 440 psi and a total thickness of about 1 inch. A layer of the yttria powder described above was then added on top of the alumina and cold pressed to 440 psi again. The yttria layer was about 2000 μm thick at this point.

[0145] For the second laminate (S12), the process was repeated except that a layer of ytterbium oxide (Yb_2O_3) powder about 1000 μm was interposed between the yttria layer and the alumina layer.

[0146] The cold pressed laminate was transferred to a hot press mold assembly, consisting of the stack arrangement depicted below in Table 1.

TABLE 1

Stack arrangement for Example 1 Hot Pressing.	
TOP	
1-inch Graphite Spacer	
1 Part	
1-inch Graphite Spacer	
3-inch Graphite Spacer	
BOTTOM	

[0147] All spacers and parts were 6 inches in diameter. The Die Barrel was 7 inches inside diameter (ID) and 15 inches outside diameter (OD). The assembly was hot pressed according to the temperature schedule shown in Table 2.

TABLE 2

Temperature Cycle during Hot Pressing.				
Temperature, ° C.				
Time (min)	Ramp (° C./min)	Setpoint, ° C.	Soak (min)	Atmos.
0.0		20	1	Ar
1.0	5	1050		Ar
207.0		1050	10	Ar
217.0	5	1400		Ar
287.0		1400	60	Ar
347.0	3	1550		Ar
397.0		1550	60	Ar
457.0	5	1050		Ar
557.0		1050	10	Ar
567.0	5	300		Ar
717.0	5	20		Ar
773.0		20	1	Ar

Ar = under argon atmosphere

[0148] Pressure was applied according to the cycle shown in Table 3.

TABLE 3

Pressure Cycle during Hot Pressing.					
Pressure	Ramp	Soak	total	Time	
				segment	
Psi	(min)	(min)	min	h	m
6000	0		0	0	0
6000		287	287	4	47
7500	60		347	1	0
7500		102	449	1	42
6000	105		554	1	45
6000		208	762	3	28

[0149] Gray dense yttria-alumina laminates emerged from the hot press operation. The grain size of the alumina as measured by the ASTM-E112 method was 1.7 μm. The carbon content was 640 ppm. The loss tangent of Si measured at 5 GHz was 9.1×10⁻⁵. Porosity was measured by image analysis of a polished section, polished according to the following scheme (polishing supplies provided by Struers, Inc.):

- [0150] 60 μm diamond: as needed to flatten the surface
- [0151] 15 μm diamond, fixed abrasive pad: 2 min
- [0152] 9 μm diamond, Largo (plastic) pad: 8 min
- [0153] 3 μm diamond, DAC (nylon) pad: 6 min
- [0154] 1 μm diamond, napped cloth: 3 min.

[0155] The porosity of S1 and S12 were found to be 0.24% and 0.72% respectively. The corrosion-resistant non-porous yttria layer was observed to substantially have no microcracks or fissures. Measuring from the sections, S1 and S12 had yttria layer thickness of 910 μm and 940 μm respectively. The yttrium oxide layer thickness measured from the section was 520 μm. Adhesion strength as measured by a variant of ASTM C633 was found to be 30 MPa. As measured herein, adhesion strength is the force required to cause failure when tension is applied between the outermost layer and the substrate, irrespective of the presence or absence of interposing layers or of the location of the failure, provided that the failure is not confined exclusively to the substrate. The outermost layer being adhered to the substrate may include instances wherein at least one interposing layer is included and/or a reaction layer inherently resulting from sintering exists between the outermost layer and the substrate. For sample S1, a reaction layer having composition Y₃Al₅O₁₂ between the yttria layer and the alumina substrate was present. Darkness L* of the sample, measured on the yttria side with a Hunterlab MiniScan XE colorimeter using the CIE L*a*b* color scale, was 53.9.

Example 2

[0156] Two yttria-aluminate laminates were cold pressed as described for sample S1 in Example 1, except that one laminate (S4) used Grade APA alumina powder from Sasol and the other laminate (S5) used Grade AHPA alumina powder also from Sasol. The cold-pressed disks were hot pressed with the same stackup as shown in Table 4.

TABLE 4

Stack arrangement for Example 2 Hot Pressing.	
TOP	
1-inch Graphite Spacer	
1 Part	
1-inch Graphite Spacer	
3-inch Graphite Spacer	
1 Part	
1-inch Graphite Spacer	
3-inch Graphite Spacer	
BOTTOM	

[0157] The temperature and pressure cycles are shown in Tables 5 and 6.

TABLE 5

Temperature Cycle during Example 2 Hot Pressing.				
Temperature, ° C.				
Time (min)	Ramp (/min)	Setpoint, ° C.	Soak (min)	Atmos.
0.0		20	1	Ar
1.0	5	1050		Ar
207.0		1050	10	Ar
217.0	5	1200		Ar
247.0		1200	60	Ar
307.0	3	1400		Ar
373.7		1400	60	Ar

TABLE 5-continued

Temperature Cycle during Example 2 Hot Pressing.				
Temperature, ° C.				
Time (min)	Ramp (/min)	Setpoint, ° C.	Soak (min)	Atmos.
433.7	5	1050		Ar
503.7		1050	10	Ar
513.7	5	300		Ar
663.7	5	20		Ar
719.7		20	1	Ar

Ar = under argon atmosphere

TABLE 6

Pressure Cycle during Example 2 Hot Pressing.					
Pressure Psi	Ramp (min)	Soak (min)	Time		
			total min	segment	
				h	m
6000	0		0	0	0
6000		247	247	4	7
7500	60		307	1	0
7500		127	434	2	7
6000	80		514	1	20
6000		208	722	3	28

[0158] The grain sizes of the alumina as measured by the ASTM-E112 method were 0.76 μm (S4) and 0.92 μm (S5). The grain size of the yttria measured in the same way was found to be 0.4 μm. The loss tangent of S4 at 5 GHz was found to be 11×10⁻⁵, and that of S5 to be 15.7×10⁻⁵.

[0159] The porosity of both samples was measured by the method described in Example 1. S4 had a porosity of 0.50% and S5 of 0.69%. Substantially no microcracks or fissures were observed in the corrosion-resistant non-porous yttria layer. Adhesion strength as measured by ASTM C633 was found to be 20 MPa for S4 and 26 MPa for S5. As with sample S1, a reaction layer between the yttria layer and alumina substrate was present. Darkness L* of the sample, measured on the yttria side with a Hunterlab MiniScan XE colorimeter using the CIE L*a*b* color scale, was 49.7 for S4 and 66.1 for S5.

Example 3

[0160] Two yttria-alumina laminates were cold pressed as described in Example 2. One laminate (S6) used AHPA alumina powder from Sasol, and the other laminate (S7) used Baikowski TCPLS DBM alumina powder from Baikowski-Malakoff. Each laminate was placed between sheets of Mo foil.

[0161] The cold-pressed disks were hot pressed with the same stack configuration as in Example 2. The temperature and pressure cycles are shown in Tables 7 and 8.

TABLE 7

Temperature Cycle during Example 3 Hot Pressing.				
Temperature, ° C.				
Time (min)	Ramp (/min)	Setpoint, ° C.	Soak (min)	Atmos.
0.0		20	1	Ar
1.0	5	1050		Ar
207.0		1050	10	Ar
217.0	3	1200		Ar
267.0		1200	1	Ar
268.0	3	1400		Ar
334.7		1400	60	Ar
394.7	5	1050		Ar
464.7		1050	10	Ar
474.7	5	300		Ar
624.7	5	20		Ar
680.7		20	1	Ar

Ar = under argon atmosphere

TABLE 8

Pressure cycle during Example 3 Hot Pressing.					
Pressure Psi	Ramp (min)	Soak (min)	Time		
			total min	segment	
				h	m
6000	0		0	0	0
6000		217	217	3	37
7500	30		247	0	30
7500		148	395	2	28
6000	80		475	1	20
6000		208	683	3	28

[0162] The loss tangent of sample S6 was measured to be 4×10⁻⁵. L* was found to be 75.4 for S6 and 75.9 for S7. Adhesion strength for S6 was 24 MPa and 35 MPa for S7.

Example 4

[0163] Two yttria-alumina laminates were cold pressed as described for Sample S7 in Example 3. One laminate (S8) used AHPA alumina powder from Sasol with which about 0.5% AlF₃ had been dry mixed, and the other laminate (S9) used Baikowski SA-80 alumina powder from Baikowski-Malakoff (without AlF₃ additions). Each laminate was placed between sheets of molybdenum (Mo) foil.

[0164] Fluoride was added to S8 as a densification aid. The cold-pressed disks were hot pressed with the same stackup as in Example 2. The temperature cycle is shown in Table 9. The pressure cycle is same as for Table 6, previously shown.

TABLE 9

Temperature cycle for Example 4 Hot Pressing.				
Temperature, ° C.				
Time (min)	Ramp (/min)	Setpoint, ° C.	Soak (min)	Atmos.
0.0		20	1	Ar
1.0	5	1050		Ar
207.0		1050	10	Ar

TABLE 9-continued

Temperature cycle for Example 4 Hot Pressing.				
Temperature, ° C.				
Time (min)	Ramp (/min)	Setpoint, ° C.	Soak (min)	Atmos.
217.0	5	1200		Ar
247.0		1200	60	Ar
307.0	3	1400		Ar
373.7		1400	60	Ar
433.7	5	1050		Ar
503.7		1050	10	Ar
513.7	5	300		Ar
663.7	5	20		Ar
719.7		20	1	Ar

Ar = under argon atmosphere

[0165] The laminate made from the AHPA powder including AlF_3 additions was cracked in several places on removal and a porous interface between the yttria layer and the alumina layer was observed. The loss tangent of this sample (S8) was $2 \cdot 10^{-5}$. The loss tangent of S9 was 4.6×10^{-5} . L^* was found to be 48.6 for S8 and 76.0 for S9. Adhesion strength for S8 was less than 5 MPa and was 39 MPa for S9.

Example 5

[0166] Two yttria-alumina laminates were cold pressed as described for sample S9 in Example 4, except that a layer of ytterbium oxide (Yb_2O_3) powder about 0.04" was interposed between the yttria layer and the alumina layer. Both laminates used the CoorsTek 99512 powder described in Example 1. One laminate (S11) had one layer of 0.004" Mo foil placed on one side, while the other one (S10) did not.

[0167] The cold-pressed disks were hot pressed with the same stackup as in Example 2. The pressure and temperature cycles are the same as for example 4.

[0168] The loss tangent of S10 was found to be 15×10^{-5} , and its porosity was measured to be 1%. Substantially no microcracks or fissures were observed in the corrosion-resistant non-porous yttria layer. The as-hot-pressed layer thickness of Y_2O_3 was 920 μm and the thickness of the Yb_2O_3 layer was 530 μm after hot pressing. L^* was found to be 49.7 for S10. Adhesion strength for S10 was 28 MPa.

[0169] For S11, the as-hot-pressed layer thickness of Y_2O_3 was 700 μm and the thickness of the Yb_2O_3 layer was 450 μm after hot pressing.

Example 6

[0170] One yttria-alumina laminate (S43) was cold pressed as described in Example 5, except that the yttria and ytterbia powders were supplied by PIDC. The laminate used the APA powder from Sasol. Mo foil was placed on both sides of the laminate.

[0171] The cold-pressed disk was hot pressed with the same stackup as in Table 4 for Example 2. The temperature and pressure cycles are shown in Tables 10 and 11.

TABLE 10

Temperature Cycle for Example 6 Hot Pressing.				
Temperature, ° C.				
Time (min)	Ramp (/min)	Setpoint, ° C.	Soak (min)	Atmos.
0.0		20	1	Vac
1.0	5	1050		Vac
207.0		1050	10	Vac
217.0	3	1200		Vac
267.0		1200	1	Vac
268.0	3	1550		Vac
384.7		1550	60	Vac
444.7	5	1050		Vac
544.7		1050	10	Vac
554.7	5	300		Vac
704.7	5	20		Vac
760.7		20	1	Vac

TABLE 11

Pressure Cycle for Example 6 Hot Pressing.					
Pressure	Ramp	Soak	Time		
			total	segment	
Psi	(min)	(min)	min	h	m
0	0		0	0	0
0		217	217	3	37
2000	30		247	0	30
2000		198	445	3	18
0	110		555	1	50
0		151	706	2	

[0172] The as-hot-pressed layer thickness of Y_2O_3 for S43 was 2950 μm and the thickness of the Yb_2O_3 layer was 525 μm after hot pressing.

Example 7

[0173] One yttria-alumina laminate (S50) was cold pressed as described in Example 6. The laminate used the APA powder from Sasol. Mo foil was placed on both sides of the laminate. The yttria powder was mixed with 1 wt % ZrO_2 before use.

[0174] The cold-pressed disk was hot pressed with the same stackup as in Table 4 for Example 2. The pressure and temperature cycles are the same as for Example 6. The loss tangent of S50 was found to be $2.39 \cdot 10^{-5}$. The as-hot-pressed layer thickness of Y_2O_3 was 720 μm and the thickness of the Yb_2O_3 layer was 350 μm after hot pressing. The grain size of the yttrium oxide layer was estimated to be about 2 μm .

Example 8

[0175] Two yttria-alumina laminates were cold pressed as described in Example 7. One laminate (S54) used the APA powder by Sasol, along with PIDC yttria and a 40 μm thick ceramic tape of ytterbia, with the ytterbia powder also coming from PIDC. The second laminate (S55) used HPA alumina from Orbite Technologies, along with PIDC yttria and ytterbia. Both laminates had Mo foil on both faces.

[0176] The cold-pressed disks were hot pressed with the same stackup as in Table 4 for Example 2. The pressure and

temperature cycles are the same as for Example 6. The loss tangent of S54 was found to be 3.93×10^{-5} . The as-hot-pressed layer thickness of Y_2O_3 was 985 μm and the thickness of the Yb_2O_3 layer was 40 μm after hot pressing. For S55, the loss tangent was found to be 2.06×10^{-5} . The as-hot-pressed layer thickness of Y_2O_3 was 1000 μm and the thickness of the Yb_2O_3 layer was 315 μm after hot pressing. The grain size of the yttrium oxide layers for S54 and S55 were determined to be about 5 to 20 μm .

Example 9

[0177] Two yttria-alumina laminates were cold pressed as described in Example 8. One laminate (S57) used the APA powder by Sasol, along with PIDC yttria mixed with 3 vol % yttrium oxyfluoride (YOF) and PIDC ytterbia. The second laminate (S58) APA powder by Sasol, PIDC ytterbia, and PIDC yttria mixed with 3 vol % $Y_2Si_2O_7$. Both laminates had Mo foil on both faces.

[0178] The cold-pressed disks were hot pressed with the same stackup as in Table 4 for Example 2. The pressure and temperature cycles are the same as for Example 6. The loss tangent of S57 was found to be 4.50×10^{-5} . The as-hot-pressed layer thickness of Y_2O_3 was 1085 μm and the thickness of the Yb_2O_3 layer was 380 μm after hot pressing. The grain size of the yttrium oxide layer for S57 was determined to be about 50 μm . For S58, the loss tangent was found to be 7.73×10^{-5} . The as-hot-pressed layer thickness of Y_2O_3 was 980 μm and the thickness of the Yb_2O_3 layer was 425 μm after hot pressing. The grain size of the yttrium oxide layer for S58 was determined to be about 5 to 10 μm .

Example 10

[0179] One laminate (S49) was cold pressed as described in Example 6. The laminate used the APA powder from Sasol as the alumina base and a blend of 77 wt % yttria, 15 wt % zirconia, and 8 wt % alumina as the top layer. Mo foil was placed on both sides of the laminate.

[0180] The cold-pressed disk was hot pressed with the same stackup as in Table 4 for Example 2. The pressure and

temperature cycles are the same as for Example 6. The loss tangent of S49 was found to be 13.3×10^{-5} . The as-hot-pressed layer thickness of blended layer was 1215 μm . Adhesion of the laminate was found to be 32 MPa. The average grain size of the yttria-rich grains of the non-porous layer was estimated to be about 2 μm . At least one second phase, namely alumina-rich grains of the composition $Y_4Al_2O_9$, was observed in the microstructure and this second phase is believed to contribute to increased strength of the layer.

[0181] A summary of properties for Examples 1 through 10 is included in Table 12.

Listing of Elements

[0182]	100	corrosion-resistant component
[0183]	110	ceramic insulating substrate
[0184]	120	corrosion-resistant non-porous layer
[0185]	130	interposing layer
[0186]	150	corrosion-resistant non-porous layer
[0187]	t1	thickness of layer 120
[0188]	t2	thickness of layer 130
[0189]	200	plasma etch reactor assembly
[0190]	210	ceramic insulating substrate
[0191]	220	corrosion-resistant non-porous layer
[0192]	225	lid
[0193]	240	induction coil
[0194]	250	reactor
[0195]	300	heater apparatus
[0196]	320	corrosion-resistant non-porous layer
[0197]	330	interposing layer
[0198]	330	insulating ceramic
[0199]	340	heating element(s)
[0200]	360	radio-frequency (RF) shield
[0201]	380	supporting disk
[0202]	400	CVD reactor assembly
[0203]	410	showerhead
[0204]	420	corrosion-resistant non-porous layer
[0205]	440	heater
[0206]	450	wafer being processed

TABLE 12

Summary of Properties.									
Sample ID	Y_2O_3 Thickness (μm)	Yb_2O_3 Thickness (μm)	Porosity (%)	Loss Tangent ($\times 10^{-5}$)	L*	Adhesion (MPa)	Grain Size Alumina (μm)	Grain Size Yttria (μm)	Carbon (ppm)
1	908	—	0.24	9.1	53.9	30	1.7	—	640
4	799	—	0.5	11	49.7	20	0.76	0.4	—
5	626	—	0.69	15.7	66.1	26	0.92	—	—
6	—	—	—	4	75.4	24	—	—	—
7	—	—	—	53.2	75.9	35	—	—	—
8	—	—	—	2.3	76.0	<5	—	—	—
9	—	—	—	4.6	48.6	38	—	—	—
10	920	530	1	15	49.7	28	—	—	—
11	704	447	0.66	—	—	—	—	—	—
12	935	524	0.72	—	—	—	—	—	—
43	2950	525	—	—	—	—	—	—	—
49	1215	—	<1	13.3	—	32	—	2	—
	(top layer)								
50	720	350	—	2.4	—	—	—	2	—
54	985	40	—	3.9	—	—	—	5-20	—
55	1000	315	—	2.1	—	—	—	5-20	—
57	1085	380	—	4.5	—	—	—	50	—
58	980	425	—	7.7	—	—	—	5-10	—

Other Embodiments

[0207] A number of variations and modifications of the disclosure can be used. It would be possible to provide for some features of the disclosure without providing others.

[0208] The present disclosure, in various aspects, embodiments, and configurations, includes components, methods, processes, systems and/or apparatus substantially as depicted and described herein, including various aspects, embodiments, configurations, subcombinations, and subsets thereof. Those of skill in the art will understand how to make and use the various aspects, aspects, embodiments, and configurations, after understanding the present disclosure. The present disclosure, in various aspects, embodiments, and configurations, includes providing devices and processes in the absence of items not depicted and/or described herein or in various aspects, embodiments, and configurations hereof, including in the absence of such items as may have been used in previous devices or processes, for example, for improving performance, achieving ease and/or reducing cost of implementation.

[0209] The foregoing discussion of the disclosure has been presented for purposes of illustration and description. The foregoing is not intended to limit the disclosure to the form or forms disclosed herein. In the foregoing Detailed Description for example, various features of the disclosure are grouped together in one or more, aspects, embodiments, and configurations for the purpose of streamlining the disclosure. The features of the aspects, embodiments, and configurations of the disclosure may be combined in alternate aspects, embodiments, and configurations other than those discussed above. This method of disclosure is not to be interpreted as reflecting an intention that the claimed disclosure requires more features than are expressly recited in each claim. Rather, as the following claims reflect, inventive aspects lie in less than all features of a single foregoing disclosed aspects, embodiments, and configurations. Thus, the following claims are hereby incorporated into this Detailed Description, with each claim standing on its own as a separate preferred embodiment of the disclosure.

[0210] Moreover, though the description of the disclosure has included description of one or more aspects, embodiments, or configurations and certain variations and modifications, other variations, combinations, and modifications are within the scope of the disclosure, for example, as may be within the skill and knowledge of those in the art, after understanding the present disclosure. It is intended to obtain rights which include alternative aspects, embodiments, and configurations to the extent permitted, including alternate, interchangeable and/or equivalent structures, functions, ranges or steps to those claimed, whether or not such alternate, interchangeable and/or equivalent structures, functions, ranges or steps are disclosed herein, and without intending to publicly dedicate any patentable subject matter.

[0211] From the above description, one skilled in the art can easily ascertain the essential characteristics of the present invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions. Thus, other embodiments are also considered to be within the scope of the present claims.

What is claimed is:

1. A corrosion-resistant component configured for use with a semiconductor processing reactor, the corrosion-resistant component comprising:

- a) a ceramic insulating substrate; and,
 - b) a corrosion-resistant non-porous layer associated with the ceramic insulating substrate, the corrosion-resistant non-porous layer having a composition comprising at least 15% by weight of a rare earth compound based on total weight of the corrosion-resistant non-porous layer; and, the corrosion-resistant non-porous layer characterized by a microstructure substantially devoid of microcracks and fissures, and having an average grain size of at least about 100 nm and at most about 100 μm .
2. The corrosion-resistant component of claim 1, wherein the ceramic insulating substrate is selected from the group consisting of aluminum oxide, aluminum nitride, silicon nitride, silicate-based materials and mixtures of two or more thereof.
3. The corrosion-resistant component of claim 2, wherein the rare earth compound is selected from the group consisting of yttrium oxide (Y_2O_3), yttrium silicates, yttrium fluorides, yttrium oxyfluorides, yttrium aluminates, nitrides, complex nitride compounds, and combinations of two or more thereof.
4. The corrosion-resistant component of claim 3, wherein the corrosion-resistant non-porous layer is adhered to the ceramic insulating substrate, and the corrosion-resistant non-porous layer has:
- a. a porosity of at most 1%;
 - b. an adhesion strength of at least 20 MPa; and,
 - c. a thickness of at least 50 μm .
5. The corrosion-resistant component of claim 4, wherein the corrosion-resistant non-porous layer has:
- a. a porosity of at most 0.5%;
 - b. an adhesion strength of at least 30 MPa;
 - c. a thickness of at least 100 μm ; and,
 - d. an average grain size of at least about 300 nm and at most about 30 μm .
6. The corrosion-resistant component of claim 1, wherein the ceramic insulating substrate is aluminum oxide and the rare earth compound is a trivalent rare earth oxide.
7. The corrosion-resistant component of claim 1, wherein the ceramic insulating substrate is aluminum nitride and the corrosion-resistant non-porous layer is a rare earth silicate.
8. The corrosion-resistant component of claim 1, wherein the corrosion-resistant component is a lid configured for releasable engagement with a plasma etch reactor and has a loss tangent of less than 1×10^{-4} .
9. The corrosion-resistant component of claim 1, further comprising at least one interposing layer embedded in the ceramic insulating substrate, or layered between the ceramic insulating substrate and the corrosion-resistant non-porous layer.
10. The corrosion-resistant component of claim 9, wherein the at least one interposing layer is selected from the group consisting of rare earth oxides, rare earth silicates, rare earth aluminates, and mixtures of two or more thereof.
11. The corrosion-resistant component of claim 10, wherein the at least one interposing layer is ytterbium oxide (Yb_2O_3).
12. The corrosion-resistant component of claim 10, wherein the at least one interposing layer comprises conducting materials.
13. The corrosion-resistant component of claim 12, wherein the at least one interposing layer further comprises insulating materials.

14. The corrosion-resistant component of claim 11, wherein the at least one interposing layer is adhered to both the corrosion-resistant non-porous layer and to the ceramic insulating substrate, and the corrosion-resistant non-porous layer has:

- a. a porosity of at most 1%;
- b. an adhesion strength of at least 20 MPa; and,
- c. a thickness of at least 50 μm .

15. A green laminate configured for use with a semiconductor processing reactor, the green laminate comprising:

a first layer of green sinterable material selected from the group consisting of aluminum oxide, aluminum nitride, silicon nitride, silicate-based materials, and mixtures of two or more thereof;

a second layer of green sinterable material selected from the group consisting of yttrium oxide (Y_2O_3), yttrium silicates, yttrium fluorides, yttrium oxyfluorides, yttrium aluminates, nitrides, complex nitride compounds, and combinations of two or more thereof; and, wherein upon heat treatment of the green laminate, the second layer has a porosity of at most 1% and an average grain size of at least about 100 nm and at most about 100 μm .

16. The green laminate of claim 15, wherein upon heat treatment of the green laminate, the second layer has a porosity of at most 0.5% and an average grain size of at least about 300 nm and at most about 30 μm .

17. The green laminate of claim 16, further comprising at least one interposing layer between the first and second layers, wherein the at least one interposing layer comprises green sinterable material selected from the group consisting of rare earth oxides, rare earth silicates, rare earth aluminates, and mixtures of two or more thereof.

18. The green laminate of claim 16, wherein the heat treatment is selected from the group consisting of hot pressing and hot isostatic pressing.

19. An assembly configured for use in fabricating semiconductor chips, the assembly comprising:

- a. a reactor; and,
- b. a corrosion-resistant component including:
 - i. a ceramic insulating substrate; and,
 - ii. a corrosion-resistant non-porous layer associated with the ceramic insulating substrate, the corrosion-resistant non-porous layer of a composition comprising at least 15% by weight of a rare earth compound based on total weight of the corrosion-resistant non-porous layer and is characterized by a microstructure substantially devoid of microcracks and fissures, and having:
 - a thickness of at least 50 μm ;
 - a porosity of at most 1%; and,
 - an average grain size of at least 100 nm and at most 100 μm .

20. The assembly of claim 19, wherein the ceramic insulating substrate is selected from the group consisting of aluminum oxide, aluminum nitride, silicon nitride, silicate-based materials and mixtures of two or more thereof.

21. The assembly of claim 20, wherein the rare earth compound is selected from the group consisting of yttrium oxide (Y_2O_3), yttrium silicates, yttrium fluorides, yttrium oxyfluorides, yttrium aluminates, nitrides, complex nitride compounds, and combinations of two or more thereof.

22. The assembly of claim 21, wherein the corrosion-resistant non-porous layer is adhered to the ceramic insulating substrate and has an adhesion strength of at least 20 MPa.

23. The assembly of claim 22, wherein the corrosion-resistant non-porous layer has:

- a thickness of at least 100 μm ;
- a porosity of at most 0.5%;
- an adhesion strength of at least 30 MPa; and,
- an average grain size of at least about 300 nm and at most about 30 μm .

24. The assembly of claim 19, further comprising at least one interposing layer embedded in the ceramic insulating substrate, or layered between the ceramic insulating substrate and the corrosion-resistant non-porous layer.

25. The assembly of claim 24, wherein the at least one interposing layer is selected from the group consisting of rare earth oxides, rare earth silicates, rare earth aluminates, and mixtures of two or more thereof.

26. The assembly of claim 25, wherein the at least one interposing layer is ytterbium oxide (Yb_2O_3).

27. The assembly of claim 24, wherein the at least one interposing layer comprises conducting materials.

28. The assembly of claim 27, wherein the at least one interposing layer further comprises insulating materials.

29. The assembly of claim 24, wherein the at least one interposing layer is selected from the group consisting of ytterbium oxide (Yb_2O_3), molybdenum (Mo), tungsten (W), molybdenum disilicide (MoSi_2), tungsten carbide (WC), tungsten disilicide (WSi_2), and mixtures of two or more thereof.

30. The assembly of claim 19, wherein the reactor is a plasma etch reactor configured for plasma etching and the corrosion-resistant component is a lid configured for releasable engagement with the plasma etch reactor; and, wherein the lid has a loss tangent of less than 1×10^{-4} .

31. The assembly of claim 19, wherein the reactor is a deposition reactor configured for in-situ cleaning with halogen gases and the corrosion-resistant component is a heater.

32. The assembly of claim 19, wherein the reactor is a deposition reactor configured for in-situ cleaning with halogen gases and the corrosion-resistant component is a show-erhead.

33. The assembly of claim 31, wherein the substrate further includes at least one interposing conductive layer embedded therein, the conductive layer having a sheet resistivity of at most 10 Megaohm-cm and a coefficient thermal expansion difference of at most $4 \times 10^{-6}/\text{K}$ relative to the coefficients of thermal expansion for the ceramic insulating substrate and the corrosion-resistant non-porous layer.

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