

1 [0001] **APPARATUS AND METHOD WHICH REDUCE THE EROSION**
2 **RATE OF SURFACES EXPOSED TO HALOGEN-CONTAINING PLASMAS**

3 [0002] The present application is related to a series of applications filed by various
4 inventors of the present application, many of the applications relate to the use of a
5 yttrium-oxide comprising ceramic in the form of a coating, to provide a plasma-resistant
6 surface which is useful in semiconductor processing applications. The applications
7 include U.S. Application Serial No. 10/075,967 of Sun et al., filed February 14, 2002,
8 titled: "Yttrium Oxide Based Surface Coating For Semiconductor IC Processing Vacuum
9 Chambers", which issued as U.S. Patent No. 6,776,873 on August 17, 2004; U.S.
10 Application Serial No. 10/898,113 of Sun et al., filed July 22, 2004, titled: "Clean Dense
11 Yttrium Oxide Coating Protecting Semiconductor Apparatus", which is currently
12 pending; and U.S. Application Serial No. 10/918,232 of Sun et al., filed August 13,
13 2004, titled: "Gas Distribution Plate Fabricated From A Solid Yttrium Oxide-
14 Comprising Substrate", which is currently pending. Additional related applications
15 filed, which are a divisional and a continuation application of above-listed applications,
16 include: U.S. Application Serial No. 11/595,484 of Wang et al., filed November 10,
17 2006, titled: "Cleaning Method Used In Removing Contaminants From The Surface Of
18 An Oxide or Fluoride Comprising a Group III Metal", which is currently pending, and
19 which is a divisional application of U.S. Application Serial No. 10/898,113; and U.S.
20 Application No. 11/592,905 of Wang et al., filed November 3, 2006, titled: "Cleaning
21 Method Used In Removing Contaminants From A Solid Yttrium Oxide-Containing
22 Substrate", which is currently pending, and which is a continuation application of U.S.
23 Application Serial No. 10/918,232. The subject matter of all of these patents and
24 applications is hereby incorporated by reference.

1 [0003] **BACKGROUND**

2 [0004] 1. Field

3 [0005] The present invention relates to a specialized yttrium oxide comprising
4 solid solution ceramic which is highly resistant to plasmas in general, particularly
5 resistant to corrosive plasmas of the kind used in the etching of semiconductor
6 substrates.

7 [0006] 2. Description of the Background Art

8 [0007] This section describes background subject matter related to the disclosed
9 embodiments of the present invention. There is no intention, either express or implied,
10 that the background art discussed in this section legally constitutes prior art.

11 [0008] Corrosion (including erosion) resistance is a critical property for apparatus
12 components and liners used in semiconductor processing chambers, where corrosive
13 environments are present. Example of corrosive plasma environments include plasmas
14 used for cleaning of processing apparatus and plasmas used to etch semiconductor
15 substrates. Plasmas used for plasma-enhanced chemical vapor deposition processes
16 often tend to be corrosive as well. This is especially true where high-energy plasma is
17 present and combined with chemical reactivity to act upon the surface of components
18 present in the environment. The reduced chemical reactivity of an apparatus component
19 surface or of a liner surface is also an important property when corrosive gases alone are
20 in contact with processing apparatus surfaces.

21 [0009] Process chambers and component apparatus present within processing
22 chambers which are used in the fabrication of electronic devices and micro-electro-
23 mechanical structures (MEMS) are frequently constructed from aluminum and
24 aluminum alloys. Surfaces of a process chamber and component apparatus present
25 within the chamber are frequently anodized to provide a degree of protection from the
26 corrosive environment. However, the integrity of the anodization layer may be
27 deteriorated by impurities in the aluminum or aluminum alloy, so that corrosion begins

1 to occur early, shortening the life span of the protective coating. Ceramic coatings of
2 various compositions have been used in place of the aluminum oxide layer mentioned
3 above, and have been used over the surface of the anodized layer to improve the
4 protection of the underlying aluminum-based materials. However, current materials
5 used for protective layers deteriorate over time and eventually leave the aluminum alloy
6 subject to attack by the plasma, even though the life span of the protective layer is
7 extended over that of anodized aluminum.

8 [0010] Yttrium oxide is a ceramic material which has shown considerable promise
9 in the protection of aluminum and aluminum alloy surfaces which are exposed to
10 fluorine-containing plasmas of the kind used in the fabrication of semiconductor devices.
11 A yttrium oxide coating has been used and applied over an anodized surface of a high
12 purity aluminum alloy process chamber surface, or a process component surface, to
13 produce excellent corrosion protection (e.g. U.S. Patent Nol. 6,777,873 to Sun et al.,
14 mentioned above). In one application, the '873 Patent provides a processing chamber
15 component resistant to a plasma including fluorine and oxygen species. The processing
16 chamber component typically comprises: a high purity aluminum substrate, where
17 particulates formed from mobile impurities present in the aluminum are carefully
18 controlled to have a particular size distribution; an anodized coating on a surface of the
19 high purity aluminum substrate; and, a protective coating comprising yttrium oxide
20 overlying the anodized coating. The protective coating may include aluminum oxide up
21 to about 10 % by weight, and typically comprises 99.95 % by weight or greater yttrium
22 oxide. The protective coating is coating typically applied using a method such as spray
23 coating, chemical vapor deposition, or physical vapor deposition.

24 [0011] U.S. Patent No. 5,798,016, to Oehrlein et al., issued August 25, 1998,
25 describes the use of aluminum oxide as a coating layer for chamber walls or as a coating
26 layer for a chamber liner. The Oehrlein et al. reference further discloses that since
27 aluminum is reactive with a number of plasmas, it is recommended that "aluminum
28 oxide or a coating thereof be disposed on the liner or chamber walls", because aluminum

oxide tends to be chemically inert. In addition, a protective coating may be applied over the surfaces of the liner and/or chamber walls. Examples which are given include Al_2O_3 , Sc_2O_3 , or Y_2O_3 .

[0012] U.S. Patent Application Publication No. US 2001/0003271A1, of Otsuki, published June 14, 2001, and subsequently abandoned, discloses a film of Al_2O_3 , or Al_2O_3 and Y_2O_3 , formed on an inner wall surface of the chamber and on those exposed surfaces of the members within the chamber which require a high corrosion resistance and insulating property. An example is given of a processing chamber where a base material of the chamber may be a ceramic material (Al_2O_3 , SiO_2 , AlN , etc.), aluminum, or stainless steel, or other metal or metal alloy, which has a sprayed film over the base material. The film may be made of a compound of a III-B element of the periodic table, such as Y_2O_3 . The film may substantially comprise Al_2O_3 and Y_2O_3 . A sprayed film of yttrium-aluminum-garnet (YAG) is also mentioned. The sprayed film thickness is said to range from 50 μm to 300 μm .

[0013] In another application, a ceramic composition of matter comprising a ceramic compound (e.g. Al_2O_3) and an oxide of a Group IIIB metal (e.g. Y_2O_3) has been used for a dielectric window of a reactor chamber where substrates are processed in a plasma of a processing gas (e.g. U.S. Patent No. 6,352,611, to Han et al., issued March 5, 2002). The ceramic compound may be selected from silicon carbide, silicon nitride, boron carbide, boron nitride, aluminum nitride, aluminum oxide, and mixtures thereof; however, aluminum oxide is said to be available in a pure form which does not outgas. The Group IIIB metal may be selected from the group consisting of scandium, yttrium, the cerium subgroup, and the yttrium subgroup; however, yttrium is preferred, with the oxide being yttrium oxide. The preferred process for forming or producing the dielectric member is by thermal processing of a powdered raw mixture comprising the ceramic compound, the oxide of a Group IIIB metal, a suitable additive agent, and a suitable binder agent.

[0014] In another application, a protective coating for a semiconductor processing

1 apparatus component is described. The protective coating comprises aluminum or an
2 aluminum alloy, where the coating includes a material selected from, for example, but
3 not limited to: yttrium-aluminum-garnet (YAG); an oxide of an element selected from
4 the group consisting of Y, Sc, La, Ce, Eu, and Dy; a fluoride of an element selected from
5 the group consisting of Y, Sc, La, Ce, Eu, and Dy; and combinations thereof is used (e.g.
6 U.S. Patent Application Serial No.10/898,113 of Sun et al., filed July 22, 2004, and
7 entitled "Clean, Dense Yttrium Oxide Coating Protecting Semiconductor Apparatus",
8 mentioned above). The coating is applied to a substrate surface by thermal / flame
9 spraying, plasma spraying, sputtering, or chemical vapor deposition (CVD). The coating
10 is placed in compression by applying the coating at a substrate surface temperature of at
11 least about 150 - 200°C.

12 [0015] The kinds of protective coatings described above have been used to protect
13 exposed surfaces of a plasma source gas distribution plate of the kind used in
14 semiconductor and MEMS processing apparatus. However, due to the concentration of
15 reactive species which are present at the surface of the gas distribution plate, the lifetime
16 of the gas distribution plate has typically been limited, from about 8 processing days to
17 about 80 processing days, depending on the corrosivity of the plasma created in the
18 processing chamber. To increase the lifetime of a component such as a gas distribution
19 plate, a gas distribution plate was fabricated from a solid yttrium oxide-comprising
20 substrate, as described in U.S. Application No. 10/918,232 of Sun et al., mentioned
21 above. The solid yttrium oxide-comprising substrate contains up to about 10 %
22 aluminum oxide in some instances. The solid yttrium oxide-comprising substrate
23 typically comprises about 99.99 % yttrium oxide.

24 [0016] As device geometry continues to shrink, the on-wafer defect requirements
25 become more stringent, as particulate generation from apparatus within the processing
26 chamber increases in importance. For plasma dry etch chambers running various
27 halogen, oxygen, and nitrogen chemistries, such as F, Cl, Br, O, N, and various
28 combinations thereof, for example, the selection of the material used for apparatus

1 components and chamber liners becomes more critical. The materials with good plasma
2 resistance performance (which also have adequate mechanical, electrical and thermal
3 properties), can reduce particle generation, metal contamination, and provide prolonged
4 component life. This translates to low costs of manufacturing, reduced wafer defects,
5 increased lifetime, and increased mean time between cleaning. Ceramic materials which
6 have been used in such applications include Al_2O_3 , AlN , and SiC . However, the plasma
7 resistance properties of these ceramic materials is not adequate in many instances,
8 particularly when a fluorine plasma source gas is involved. The recent introduction of
9 Y_2O_3 ceramic shows improved plasma resistance properties, but this material generally
10 exhibits weak mechanical properties that limits its applications for general use in
11 semiconductor processing components, processing kits, and chamber liners.

12 [0017] SUMMARY

13 [0018] Semiconductor processing conditions expose semiconductor processing
14 apparatus, such as the interior of processing chambers and the surfaces of components
15 within the processing chambers, to a variety of chemical reagents and plasma ions which
16 attack processing apparatus surfaces. The effect of the attack on an apparatus surface is
17 frequently referred to as erosion of the apparatus surface. It is possible to reduce the
18 erosion rate by selecting a particular material composition for the apparatus surfaces. A
19 protective material may be applied as a coating over the apparatus surface; however, this
20 may not be the best solution to avoiding erosion. The coating is constantly getting
21 thinner (eroding) during a plasma etch, and there is an increased risk that the substrate
22 beneath the coating will be attacked by the plasma penetrating the coating layer. The
23 coating layer may flake off during plasma processing due to residual stress. While such
24 problems will be significantly reduced by using a coating of the erosion-resistant
25 materials described in embodiments herein, in many instances it may be advantageous to
26 form an entire apparatus component from the erosion-resistant materials. However,
27 frequently the materials which are more erosion-resistant are more crystalline, and an

1 improvement in erosion resistance comes at a cost, in the form of decreased mechanical
2 properties (such as ductility) of the apparatus. Ceramic materials which are formed from
3 an oxide of a Group IIIA, IIIB, IVB and VB element, or combinations thereof, have been
4 demonstrated to provide erosion resistance to halogen-comprising plasmas.

5 Embodiments of the present invention pertain to reducing the erosion rate of a ceramic
6 material, typically comprising a Group IIIA, IIIB, IVB, or a Group IVB element, or
7 combinations thereof, while maintaining acceptable mechanical properties or improving
8 mechanical properties of the component parts made of the ceramic material.

9 [0019] In one embodiment, sintered ceramics are formed which contain a single
10 solid solution phase or which are multi-phase, such as two phase and three phase. The
11 multi-phase ceramics typically contain a yttrium aluminate phase and one or two solid
12 solution phases formed from yttrium oxide, zirconium oxide and/or rare earth oxides.

13 The sintered ceramic has been evaluated under various plasma processing conditions to
14 determine erosion resistance. The materials which were erosion tested were also tested
15 for mechanical properties. For example, ceramic materials formed from starting

16 compositions in which the Y_2O_3 , yttrium oxide, molar concentration ranges from about
17 50 mole % to about 75 mole %; the ZrO_2 , zirconium oxide, molar concentration ranges
18 from about 10 mole % to about 30 mole %; and, the Al_2O_3 , aluminum oxide, molar
19 concentration ranges from about 10 mole % to about 30 mole % provide excellent

20 erosion resistance to halogen-containing plasmas while providing advanced mechanical
21 properties which enable handling of solid ceramic processing components with less

22 concern about damage to a component. In many embodiments, a starting composition
23 for the ceramic materials may be one that comprises Y_2O_3 molar concentration ranges

24 from about 55 mole % to about 65 mole %, ZrO_2 molar concentration ranges from about
25 15 mole % to about 25 mole %, and Al_2O_3 molar concentration ranges from about 10
26 mole % to about 25 mole %. When the erosion rate is of great concern, the starting

27 material concentration of the ceramic material may be one that comprises Y_2O_3 molar
28 concentration ranges from about 55 mole % to about 65 mole %, the ZrO_2 molar

1 concentration ranges from about 20 mole % to about 25 mole % and the Al_2O_3 molar
2 concentration 10 mole % to about 15 mole %. In one embodiment, to produce a solid
3 apparatus component, these starting material formulations are compacted into a
4 pelletized form and are sintered using a method selected from pressureless sintering, hot-
5 press sintering (HP), or hot isostatic press sintering (HIP). These sintering techniques are
6 well known in the art.

7 [0020] In other embodiments, the starting material compositions listed above may
8 be used to form a ceramic coating over the surface of a variety of metal and ceramic
9 substrates, including, but not limited to, aluminum, aluminum alloy, stainless steel,
10 alumina, aluminum nitride and quartz, using a technique well known in the art, such as
11 plasma spraying, for example and not by way of limitation. Typically the aluminum
12 alloy used is a high purity aluminum alloy of the kind described in U.S. Patent No.
13 6,766,873 to Sun et al., mentioned above. However, with the improved mechanical
14 properties which have been obtained, it is recommended that solid ceramic apparatus
15 components be used when possible, to avoid the eventual failure of the apparatus to
16 function properly due to interfacial problems between the coating and the underlying
17 substrate, or to prevent a sudden failure of plasma resistance due to the coating layer
18 flaking off, or to prevent plasma penetration of the coating layer through defects which
19 may be exposed from within the coating layer as the coating layer becomes thinner due
20 to erosion.

21 [0021] The addition of zirconium oxide powder to yttrium oxide powder at a
22 concentration of zirconium oxide, ranging from about 0.1 mole % to about 65 mole %,
23 after consolidation by conventional ceramic processing, provides a single solid solution
24 with a cubic yttria crystal structure phase or a cubic fluorite-type crystal structure phase,
25 or provides a mixed solid solution of cubic yttria crystal structure phase and cubic
26 fluorite-type crystal structure phase. For the cubic yttria crystal structure, the cell
27 parameter of the solid solution is smaller than that of the pure cubic yttrium oxide
28 crystalline structure, due to the formation of yttrium vacancy. For the cubic fluorite-type

1 crystal structure, the cell parameter of the solid solution is smaller than that of the pure
2 cubic fluorite-type structure, due to the formation of oxygen vacancy. The smaller cell
3 parameter improves the plasma resistance properties of the solid solution of zirconium
4 oxide in yttrium oxide. For example, the erosion rate of a pure solid yttrium oxide
5 ceramic in a CF_4/CHF_3 plasma is about $0.3 \mu\text{m/hr}$. The erosion rate (the rate at which a
6 surface is removed in μm (of thickness)/hr) of a solid ceramic of about 69 mole %
7 yttrium oxide and about 31 mole % zirconium oxide is about $0.1 \mu\text{m/hr}$, a 3 times slower
8 erosion rate than pure solid yttrium oxide. This unexpected decrease in erosion rate
9 extends the lifetime of a process chamber liner or an internal apparatus component within
10 the process chamber, so that the replacement frequency for such apparatus is reduced,
11 reducing apparatus down time; and, the particle and metal contamination level generated
12 during a plasma process is reduced, enabling a device fabrication with ever shrinking
13 geometry with reduced overall cost of the processing apparatus per wafer processed, on
14 the average.

15 [0022] While the $0.1 \mu\text{m/hr}$ erosion rate for the zirconium oxide-containing yttrium
16 oxide solid solution is surprisingly better than that of yttrium oxide at $0.3 \mu\text{m/hr}$, and
17 considerably better than of a solid aluminum oxide ceramic at $1.44 \mu\text{m/hr}$ in the
18 CF_4/CHF_3 plasma, the mechanical properties of the zirconium oxide-containing yttrium
19 oxide solid solution illustrate that an improvement in flexural strength and fracture
20 toughness would be helpful.

21 [0023] In one embodiment, the flexural strength and fracture toughness of the
22 zirconium oxide-containing yttrium oxide solid solution are achieved, by adding various
23 amounts of aluminum oxide to the formula for the solid solution ceramic to form an
24 additional yttrium aluminate phase. The mixture of oxides was pelletized by
25 unidirectional mechanical pressing or cold isostatic pressing of a granular powder formed
26 by spray drying, in combination with a typical content of binders. The green body was
27 then pressureless sintered using techniques generally known in the art. The addition of
28 10 mole % to 30 mole % of alumina significantly improved the mechanical properties of

1 the sintered ceramic composition in terms of flexural strength and fracture toughness, as
2 discussed subsequently herein. This surprising change in mechanical properties, which
3 indicates that fabricated parts could be handled with less risk of fracture, was achieved
4 with minimal effect on the plasma erosion rate of the ceramic material. For example, the
5 erosion rate of the ceramic containing 69 mole % yttrium oxide and 31 mole %
6 zirconium oxide, after exposure to a plasma containing CF_4 and CHF_3 , was about $0.1 \mu\text{m}$
7 / hr. For the ceramic containing about 14 mole % aluminum oxide, the erosion rate after
8 exposure to the same plasma was also about $0.1 \mu\text{m}$ / hr. For the ceramic containing
9 about 25 mole % aluminum oxide, the erosion rate after exposure to the same plasma was
10 about $0.2 \mu\text{m}$ / hr. The relationship between aluminum oxide content, increase in
11 flexural strength, and increase in erosion rate is not a linear relationship. However, one
12 of skill in the art can optimize the formula with minimal experimentation, in view of the
13 information provided herein.

14 [0024] As an alternative to adding aluminum oxide to a multi phase metal stable
15 composition containing yttrium oxide and zirconium oxide, it is possible to add HfO_2 ,
16 hafnium oxide; Sc_2O_3 , scandium oxide; Nd_2O_3 , neodymium oxide; Nb_2O_5 , niobium
17 oxide; Sm_2O_3 , samarium oxide; Yb_2O_3 , ytterbium oxide; Er_2O_3 , erbium oxide; Ce_2O_3 (or
18 CeO_2), cerium oxide, or combinations thereof. In the instance where one of these
19 alternative oxides is used, the concentration of the oxide in the starting material
20 formulation ranges from about 0.1 mole % to about 90 mole %, and typically ranges
21 from about 10 mole % to about 30 mole %.

22 [0025] After mixing of at least one of the alternative oxides listed above with the
23 Y_2O_3 and ZrO_2 powders used to form a solid solution, the combination of powders was
24 compacted by unidirectionally mechanical pressing or cold isostatic pressing of the
25 granular powder formed by spray drying with a typical content of binders. The green
26 body was then pressureless sintered using techniques known in the art. Upon cooling of
27 the sintered body, a single phase or two phase solid solution forms, where the solid
28 solution is a "multi-element-doped" solid solution. One solid solution exhibits a cubic

1 yttria crystal structure, and another solid solution exhibits the cubic fluorite-type crystal
2 structure. The solid solution has excellent plasma resistance, typically better erosion
3 resistance than that of the aluminum oxide-comprising solid solutions discussed herein.
4 However, the mechanical properties of the yttria-zirconia-alumina system are somewhat
5 better. All of these multi-doped solid solutions exhibit excellent plasma erosion
6 resistance and improved mechanical properties in comparison with previously known
7 yttrium oxide-zirconium oxide solid solutions.

8 [0026] **BRIEF DESCRIPTION OF THE DRAWINGS**

9 [0027] Figure 1 A shows a photomicrograph of the as-sintered surface of a solid
10 yttrium oxide ceramic at a magnification of 1,000 times.

11 [0028] Figure 1B shows a photomicrograph of the as-sintered surface of a solid
12 solution ceramic substrate formed from 63 mole % yttrium oxide, 23 mole % zirconium
13 oxide, and 14 mole % aluminum oxide, at a magnification of 1,000 times.

14 [0029] Figure 1C shows a photomicrograph of the as-sintered surface of a solid
15 solution ceramic substrate formed from 55 mole % yttrium oxide, 20 mole % zirconium
16 oxide, and 25 mole % aluminum oxide, at a magnification of 1,000 times.

17 [0030] Figure 2A shows a photomicrograph of the surface of a solid yttrium oxide
18 ceramic after a test etch using the processing plasmas and times typically used to etch the
19 various layers of a contact via feature in a semiconductor device. The magnification is
20 1,000 times.

21 [0031] Figure 2B shows a photomicrograph of the surface of a solid solution ceramic
22 formed from 63 mole % yttrium oxide, 23 mole % zirconium oxide, and 14 mole %
23 aluminum oxide after a test etch using the processing plasmas and times typically used to

1 etch the various layers of a contact via feature in a semiconductor device. The
2 magnification is 1,000 times.

3 [0032] Figure 2C shows a photomicrograph of the surface of a solid solution
4 ceramic formed from 55 mole % yttrium oxide, 20 mole % zirconium oxide, and 25 mole
5 % aluminum oxide after a test etch using the processing plasmas and times typically
6 used to etch the various layers of a contact via feature in a semiconductor device. The
7 magnification is 1,000 times.

8 [0033] Figure 3A shows a photomicrograph of the post-etch ceramic of Figure 2A,
9 but at a magnification of 5,000 times.

10 [0034] Figure 3B shows a photomicrograph of the post-etch ceramic of Figure 2B,
11 but at a magnification of 5,000 times.

12 [0035] Figure 3C shows a photomicrograph of the post-etch ceramic of Figure 2C,
13 but at a magnification of 5,000 times.

14 [0036] Figure 4A shows a photomicrograph of the as-sintered surface of a solid
15 solution ceramic formed from 63 mole % yttrium oxide, 23 mole % zirconium oxide, and
16 14 mole % aluminum oxide, at a magnification of 2,000 times.

17 [0037] Figure 4B shows a photomicrograph of the surface of the solid solution
18 ceramic shown in Figure 4A, after exposure of the test coupon to a trench etch process of
19 the kind described herein. The magnification is 2,000 times.

20 [0038] Figure 4C shows a photomicrograph of the as sintered surface of a solid
21 solution ceramic formed from 55 mole % yttrium oxide, 20 mole % zirconium oxide, and

1 25 mole % aluminum oxide, at a magnification of 2,000 times.

2 [0039] Figure 4D shows a photomicrograph of the surface of the solid solution
3 ceramic shown in Figure 4C, after exposure of the test coupon to a trench etch process of
4 the kind described herein. The magnification is 2,000 times.

5 [0040] Figure 5A shows a photomicrograph of a solid solution ceramic formed
6 from 63 mole % yttrium oxide, 23 mole % zirconium oxide, and 14 mole % aluminum
7 oxide after exposure of the test coupon to a metal etch process of the kind described
8 herein. The magnification is 5,000 times.

9 [0041] Figure 5B shows a photomicrograph of a solid solution ceramic formed
10 from 55 mole % yttrium oxide, 20 mole % zirconium oxide, and 25 mole % aluminum
11 oxide after exposure of the test coupon to an etch by a CF_4/CHF_3 plasma. The
12 magnification of 5,000 times.

13 [0042] **DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS**

14 [0043] As a preface to the detailed description, it should be noted that, as used in
15 this specification and the appended claims, the singular forms "a", "an", and "the"
16 include plural referents, unless the context clearly dictates otherwise.

17 [0044] When the word "about" is used herein, this is intended to mean that the
18 nominal value presented is precise within $\pm 10\%$.

19 [0045] Bulk yttrium oxide has been shown to have very good corrosion resistance
20 upon exposure to fluorine plasma and other corrosive plasmas which are typically used in
21 semiconductor manufacturing processes (such as etch processes and chemical vapor
22 deposition processes). However, pure crystalline yttrium oxide, while offering very good
23 corrosion resistance to various etchant plasmas, does not offer good mechanical

1 properties in terms of flexural strength and fracture toughness, for example. To improve
2 the overall performance and handling capabilities of semiconductor component parts and
3 liners, there is a need to improve the mechanical properties from those available in pure
4 crystalline yttrium oxide. To obtain the improvement in mechanical properties, it is
5 necessary to form an alloy of yttrium oxide with a compatible oxide. The improvement
6 in mechanical properties needed to be accomplished without harming the very good
7 plasma erosion properties of the pure yttrium oxide.

8 [0046] In consideration of the Gibbs Formation Free Energy of various ceramic
9 materials which might be compatible with yttrium oxide, we determined that it is more
10 difficult to form fluorides than oxides for yttrium and aluminum elements, so that yttrium
11 oxide and aluminum oxide are expected to provide good resistance to a fluorine-
12 containing plasma. The Gibbs Formation Free Energy of zirconium fluoride is similar to
13 that for yttrium fluoride. Further, in a homogeneous amorphous oxyfluoride, or a glass-
14 ceramic composite oxyfluoride, increasing the zirconium fluoride content can decrease
15 the free energy of the final oxyfluoride to make it more stable.

16 [0047] EXAMPLE EMBODIMENTS:

17 [0048] Example One: Etch Plasma Process Conditions For Erosion Rate Testing

18 [0049] Tables One - Three, below, provides the etch plasma compositions and etch
19 plasma processing conditions which were used for evaluation of a series of test coupon
20 materials. There were three basic different sets of etch plasma conditions which were
21 used for the erosion rate testing: 1) Trench etching, where the etch plasma source gas
22 and etch process conditions were representative of etching a trench feature size beyond
23 65 nm technology, i.e. smaller than 65 nm, into a multilayered semiconductor substrate.
24 Such a substrate typically includes an antireflective coating (ARC or BARC) layer, an
25 organic or inorganic dielectric layer, a metal layer, and an etch stop layer. Contact Via
26 etching, where the etch plasma source gas and etch process conditions were
27 representative of etching a contact via having an aspect ratio of about 30 in production

and 40 plus in the developed device substrate, and having a diameter of beyond 65 nm technology into a multilayered semiconductor substrate including a buried ARC (BARC) layer, a dielectric layer and a stop layer; and 3) Metal etching, here the etch plasma source gas and etch process conditions were representative of etching an overlying titanium nitride hard mask and an aluminum layer, where the etch plasma source gas and etch process conditions are beyond 65 nm technology.

[0050] The trench etching process and the contact via etching process were carried out in the ENABLER™ processing system, and the metal etching process was carried out in the DPS™ processing system, all available from Applied Materials, Inc. of Santa Clara, California.

[0051] Table One: Process Conditions for Trench Etch Erosion Rate Test

[0052]

Trench Etch Simulation	CF ₄ *	O ₂ *	CHF ₃ *	N ₂ *	Ar *	Plasma Source Power ¹	Pr ²	Subr Bias Power ³	Subr Temp ⁴	Time ⁵
Etch Step One	150		30				300	1,000	40	35
Etch Step Two				400		1200	220	400	40	40
Etch Step Three	175		15			1500	150	500	40	39
Etch Step Four		500				100	10	200	40	55

* All gas flow rates are in sccm.

1. Plasma Source Power in W.

2. Pressure in mTorr.

3. Substrate Bias Power in W.

4. Substrate Temperature in °C.

5. Time in seconds.

1 [0053] Table Two: Process Conditions for Via Etch Erosion Rate Test

2 [0054]

3 4	Via Etch Simulation	CF ₄ *	C ₄ F ₆ *	CHF ₃ *	CH ₂ F ₂ *	Ar *	O ₂ *	N ₂ *
5 6	Etch Step One	80						80
7 8	Etch Step Two		28	15	20	500	31	
9 10	Etch Step Three		40			650	30	
11 12	Etch Step Four					200		
13 14	Etch Step Five						500	
15 16	Via Etch Simulation	Plasma Source Power ¹	Pr ²	Substrate Bias Power ³	Substrate Temp ⁴	Time ⁵		
17	Etch Step One		80	400	40	50		
18	Etch Step Two	400	30	1700	40	60		
19	Etch Step Three		30	1700	40	60		
20	Etch Step Four	1000	50	100	40	45		

21 * All gas flow rates are in sccm.

22 1. Plasma Source Power in W.

23 2. Pressure in mTorr.

24 3. Substrate Bias Power in W.

25 4. Substrate Temperature in °C.

26 5. Time in seconds.

1 [0055] Table Three: Process Conditions for Metal Etch Erosion Rate Test

2 [0056]

3	4	5	6	7	8	9	10	11	12	13	14	15
Metal	Cl ₂	BCl ₃	C ₂ H ₄	Ar	CHF ₃	N ₂	Plasma	Subr	Pr	Subr	Time	
Etch	*	*	*	*	*	*	Source	Bias	3	Temp		
Simul.							Power	Power				
							1	2		4	5	
6	Etch	60		3		20		1000	100	8	40	30
7	Step											
8	One											
9	Etch	25	40	10		5		500	150	10	40	18
10	Step											
11	Two											
12	Etch	60	40	20				700	120	18	40	30
13	Step											
14	Three											
15	Etch	60	40	3				1000	200	8	40	23
16	Step											
17	Four											
18	Etch	30	60	5	50		5	800	170	6	40	15
19	Step											
20	Five											

21 * All gas flow rates are in sccm.

22 1. Plasma Source Power in W.

23 2. Substrate Bias Power in W.

24 3. Pressure in mTorr.

25 4. Substrate Temperature in °C.

26 5. Time in seconds.

27 [0057] Example Two: Comparative Relative Erosion Rates Of Various Ceramic
 28 Materials Compared With Aluminum Oxide

29 [0058] Aluminum oxide has frequently been used as a protective layer or liner when
 30 a semiconductor process makes use of an etchant plasma. Using aluminum oxide as the
 31 base comparative material, we determined the relative etch rates, in a Trench Etch
 32 (CF₄/CHF₃) environment. With aluminum oxide having a relative erosion rate of 1, we

1 found that the relative erosion rate of quartz was about 2.2 times that of aluminum oxide.
2 The relative erosion rate of silicon carbide was about 1.6 times that of aluminum oxide.
3 The relative erosion rate of zirconia was about 0.8 times that of aluminum oxide. The
4 relative erosion rate of pure yttrium oxide was about 0.19 times that of aluminum oxide.
5 The relative erosion rate of a yttrium oxide, zirconium oxide, aluminum oxide ceramic
6 composite, formed from 55 mole % yttrium oxide, 20 mole % zirconium oxide, and 25
7 mole % aluminum oxide was about 0.2 times that of aluminum oxide. The relative
8 erosion rate of a yttrium oxide, zirconium oxide, aluminum oxide ceramic composite,
9 formed from 63 mole % yttrium oxide, 23 mole % zirconium oxide, and 14 mole %
10 aluminum oxide was about 0.05 times that of aluminum oxide.

11 [0059] Example Three: Measured Erosion Rates for Trench Etching Process

12 [0060] With reference to the trench etching method described above, the sample
13 substrate test coupon erosion rates measured were as follows. The erosion rate of
14 aluminum oxide was 1.1 $\mu\text{m/hr}$. The erosion rate of bulk yttrium oxide was 0.3 $\mu\text{m/hr}$.
15 The erosion rate of a the a yttrium oxide, zirconium oxide, aluminum oxide ceramic
16 composite, formed from 55 mole % yttrium oxide, 20 mole % zirconium oxide, and 25
17 mole % aluminum oxide was 0.1 $\mu\text{m/hr}$. The erosion rate of a yttrium oxide, zirconium
18 oxide, aluminum oxide ceramic composite, formed from 63 mole % yttrium oxide, 23
19 mole % zirconium oxide, and 14 mole % aluminum oxide was 0.07 $\mu\text{m/hr}$.

20 [0061] Example Four: Measured Erosion Rates for Via Etching Process

21 [0062] With reference to the via etching method described above, the sample
22 substrate test coupon erosion rates measured were as follows. The erosion rate of
23 aluminum oxide was not measured. The erosion rate of bulk yttrium oxide was 0.16
24 $\mu\text{m/hr}$. The erosion rate of a the a yttrium oxide, zirconium oxide, aluminum oxide solid
25 solution, formed from 55 mole % yttrium oxide, 20 mole % zirconium oxide, and 25
26 mole % aluminum oxide was 0.21 $\mu\text{m/hr}$. The erosion rate of a yttrium oxide, zirconium

1 oxide, aluminum oxide solid solution, formed from 63 mole % yttrium oxide, 23 mole %
2 zirconium oxide, and 14 mole % aluminum oxide was 0.22 $\mu\text{m/hr}$.

3 [0063] Example Five: Measured Erosion Rates for Metal Etching Process

4 [0064] With reference to the metal etching method described above, the sample
5 substrate test coupon erosion rates measured were as follows. The erosion rate of
6 aluminum oxide was 4.10 $\mu\text{m/hr}$. The erosion rate for bulk yttrium oxide was 0.14
7 $\mu\text{m/hr}$. The erosion rate of a the a yttrium oxide, zirconium oxide, aluminum oxide
8 ceramic composite, formed from 55 mole % yttrium oxide, 20 mole % zirconium oxide,
9 and 25 mole % aluminum oxide was 0.10 $\mu\text{m/hr}$. The erosion rate of a yttrium oxide,
10 zirconium oxide, aluminum oxide ceramic composite, formed from 63 mole % yttrium
11 oxide, 23 mole % zirconium oxide, and 14 mole % aluminum oxide was 0.18 $\mu\text{m/hr}$.

12 [0065] Example Six: Photomicrographs Of Yttrium-Oxide-Based Ceramics After
13 Exposure to A Via Etch Process

14 [0066] Figures 1A through 1C show photomicrographs of the surface of a sintered
15 yttrium-oxide-containing ceramic composite prior to exposure to the via etch process
16 described herein. The yttrium-oxide-containing ceramic composites include: 1) yttrium
17 oxide-zirconium oxide solid solution; and 2) yttrium aluminate, when the composition
18 was yttrium oxide 100 parts by weight, zirconium oxide 20 parts by weight, and
19 aluminum oxide 10 parts by weight. (This composition is the same as 63 mole % yttrium
20 oxide, 23 mole % zirconium oxide, and 14 mole % aluminum oxide); and 3) yttrium
21 oxide - zirconium oxide - aluminum oxide solid solution, when the composition from
22 which the solid solution was formed was yttrium oxide 100 parts by weight, zirconium
23 oxide 20 parts by weight, and aluminum oxide 20 parts by weight. (This composition is
24 the same as 55 mole % yttrium oxide, 20 mole % zirconium oxide, and 25 mole %
25 aluminum oxide). All of the photomicrographs are at a magnification of 1,000 times.

26 [0067] Figures 2A through 2C show photomicrographs of the sintered yttrium-

1 oxide-containing ceramic composite subsequent to exposure to the via etch process
2 described herein. The yttrium-oxide-containing ceramic composites include: 1) yttrium
3 oxide-zirconium oxide solid solution; and 2) yttrium aluminate, when the composition
4 was yttrium oxide 100 parts by weight, zirconium oxide 20 parts by weight, and
5 aluminum oxide 10 parts by weight (This composition is the same as 63 mole % yttrium
6 oxide, 23 mole % zirconium oxide, and 14 mole % aluminum oxide); or when the
7 composition was yttrium oxide 100 parts by weight, zirconium oxide 20 parts by weight,
8 and aluminum oxide 20 parts by weight (This composition is the same as 55 mole %
9 yttrium oxide, 20 mole % zirconium oxide, and 25 mole % aluminum oxide). All of the
10 photomicrographs are at a magnification of 1,000 times.

11 [0068] The surface roughness of the bulk yttrium oxide shown in Figure 2A has
12 increased in roughness substantially. However, the overall surface roughness appears to
13 be less than that of the zirconium oxide and aluminum oxide containing sample coupons.
14 The surface roughness of the solid solution shown in Figure 2B, which contains 10 parts
15 by weight aluminum oxide appears to have hills and valleys which are flatter than the
16 hills and valleys of the solid solution shown in Figure 2C, which contains the 20 parts by
17 weight of aluminum oxide. However, the hills and valleys on the 10 parts by weight
18 aluminum oxide sample coupon shown in Figure 2B have more pitting on the surface
19 than in the 20 parts by weight sample coupon shown in Figure 2C.

20 [0069] Figures 3A through 3C show photomicrographs which correspond with
21 Figures 2A through 2C, respectively, but are at a magnification of 5,000 times. Looking
22 at the surface of the bulk yttrium oxide sample coupon shown in Figure 3A, the surface is
23 relatively smooth but does show some evidence of small pits. The Figure 3B solid
24 solution formed from yttrium oxide 100 parts by weight, zirconium oxide 20 parts by
25 weight, and aluminum oxide 10 parts by weight also shows some small scale pitting
26 present on the rougher surface shown in Figure 2B. The Figure 3C solid solution formed
27 from yttrium oxide 100 parts by weight, zirconium oxide 20 parts by weight, and
28 aluminum oxide 20 parts by weight shows negligible small scale pitting.

1 [0070] Looking at the erosion rates for the three test coupons, it appears that the
2 1,000 times magnification for the post-etch coupons shows better surface characteristics
3 related to the erosion rates of the coupons. The erosion rates were 0.16 $\mu\text{m/hr}$ for the
4 solid yttrium oxide shown in Figure 2A; 0.22 $\mu\text{m/hr}$ for the solid solution of yttrium
5 oxide - zirconium oxide - aluminum oxide which contained 10 parts by weight aluminum
6 oxide; and 0.21 $\mu\text{m/hr}$ for the solid solution of yttrium oxide - zirconium oxide -
7 aluminum oxide which contained 20 parts by weight aluminum oxide.

8 [0071] Example Seven: Photomicrographs Of Yttrium-Oxide-Containing Substrates
9 After Exposure to A Trench Etch Process

10 [0072] Figure 4A shows a photomicrograph of the as-sintered surface of a solid
11 solution ceramic composite containing 100 parts by weight yttrium oxide, 20 parts by
12 weight aluminum oxide, and 10 parts by weight aluminum oxide (63 mole % yttrium
13 oxide, 23 mole % zirconium oxide, and 14 mole % aluminum oxide), at a magnification
14 of 2,000 times. Figure 4B shows a photomicrograph of the surface of the solid ceramic
15 composite of Figure 4A after etching by a trench etch process of the kind shown herein.
16 Both photomicrographs are at a magnification of 2,000. The post-etched surface appears
17 to be flat and relatively homogeneous. This combination of photographs suggests that
18 after fabrication of an apparatus such as a chamber liner or a component part, it may be
19 advisable to “season” the part by exposing it to an exemplary plasma etch process prior to
20 introducing the apparatus into a semiconductor device production process. The erosion
21 rate for the solid solution ceramic composite containing the 10 parts by weight of
22 aluminum oxide, after exposure to the trench etch process, was about 0.08 $\mu\text{m/hr}$.

23 [0073] Figure 4C shows a photomicrograph of the as-sintered surface of a solid
24 solution ceramic composite containing 100 parts by weight yttrium oxide, 20 parts by
25 weight aluminum oxide, and 20 parts by weight aluminum oxide (55 mole % yttrium
26 oxide, 20 mole % zirconium oxide, and 25 mole % aluminum oxide). Figure 4D shows a

1 photomicrograph of the surface of the solid solution ceramic composite of Figure 4C after
2 etching by a trench etch process of the kind shown herein. Both photomicrographs are at
3 a magnification of 2,000. The post-etched surface appears to be flat and relatively
4 homogeneous. This combination of photographs suggests the same seasoning process
5 described above for newly fabricated apparatus. The erosion rate of the solid solution
6 ceramic composite containing the 20 parts by weight of aluminum oxide, after exposure
7 to the trench etch process, was about 0.07 $\mu\text{m/hr}$.

8 [0074] Example Eight: Photomicrographs Of Yttrium-Oxide-Containing Ceramic
9 Composites After Exposure To A Metal Etch Process

10 [0075] Figure 5A shows a photomicrograph of a two phase solid solution ceramic
11 composite formed from 100 parts by weight of yttrium oxide, 20 parts by weight of
12 zirconium oxide and 10 parts by weight of aluminum oxide (63 mole % yttrium oxide, 23
13 mole % zirconium oxide, and 14 mole % aluminum oxide) after exposure of the test
14 coupon to a metal etch process of the kind described herein. The magnification is 5,000
15 times. Figure 5B shows a photomicrograph of a two phase solid solution ceramic
16 composite formed from 100 parts by weight of yttrium oxide, 20 parts by weight of
17 zirconium oxide, and 10 parts by weight of aluminum oxide (55 mole % yttrium oxide,
18 20 mole % zirconium oxide, and 25 mole % aluminum oxide) after exposure of the test
19 coupon to a metal etch process of the kind described herein. The magnification is 5,000
20 times. A comparison of these two photomicrographs shows that the two phase solid
21 solution containing the higher content of aluminum oxide has an increased amount of the
22 darker phase, which is yttrium aluminate. The erosion rate of the two phase solid
23 solution ceramic composites containing the 10 parts by weight of aluminum oxide, after
24 exposure to the trench etch process, was about 0.18 $\mu\text{m/hr}$, while the erosion rate of the
25 two phase solid solution ceramic composite containing the 20 parts by weight of
26 aluminum oxide, after exposure to the trench process was about 0.10 $\mu\text{m/hr}$.

1 [0076] Example Nine: Relative Physical and Mechanical Properties Of Yttrium-Oxide-
2 Containing Substrates

3 [0077] Table Four below shows comparative physical and mechanical properties for
4 the bulk, pure yttrium oxide ceramic and for various yttrium-oxide containing solid
5 solution ceramics.

6 [0078] Table Four

7 [0079]

8	Material	Y ₂ O ₃	Al ₂ O ₃	100 ZrO ₂	100 Y ₂ O ₃	100 Y ₂ O ₃	100 Y ₂ O ₃
9	Starting			3 Y ₂ O ₃	20 ZrO ₂	20 ZrO ₂	20 ZrO ₂
10	Composition			parts by	parts by	10 Al ₂ O ₃	20 Al ₂ O ₃
				weight	weight.	parts by	parts by
						weight	weight
11	Flexural	100 - 150	400	1200±100	137	215	172
12	Strength						
13	(MPa)						
14	Vickers						
15	Hardness	5.7	17.2	11.9	9.3	9.4	9.6
16	(5Kgf)(GPa)						
17	Young's						
18	Modulus	140 - 170	380	373	190	190	202
19	(GPa)						
20	Fracture						
21	Toughness	1.0 - 1.3	3.5	10.9	1.3	1.6	1.7
22	(Mpa · m ^{1/2})						
23	Thermal						
24	Conductivity	13.7	33	2.9	4.7	3.5	
25	(W/m/°K)						
26	Thermal						
27	Shock	130-200	200		130-200	150-	
28	Resistance					200	
29	(ΔT) °C						

1	Material	Y_2O_3	Al_2O_3	100 ZrO ₂	100 Y ₂ O ₃	100 Y ₂ O ₃	100 Y ₂ O ₃
2	Starting			3 Y ₂ O ₃	20 ZrO ₂	20 ZrO ₂	20 ZrO ₂
3	Composition			parts by weight	parts by weight.	10 Al ₂ O ₃	20 Al ₂ O ₃
4	Thermal					parts by weight	parts by weight
5	Expansion	7.2	7.7	9.4	9.0	8.5	
6	$\times 10^{-6}/K$						
7	(20 - 900 °C)						
8	Dielectric						
9	Constant	12.3 - 13	9.9	—	15.0	15.5	
10	(20 °C 13.56 MHZ)						
11	Dielectric Loss						
12	Tangent $\times 10^{-4}$	< 20	0.5	—	< 20	< 20	—
13	(20 °C 13.56 MHZ)						
14	Volume						
15	Resistivity	$10^{12} - 10^{13}$	10^{15}	—	10^{11}	$10^{16} - 10^{22}$	—
16	at RT ($\Omega \cdot cm$)						
17	Density	4.92	3.95	5.89	5.19	4.90	4.86
18	(g/cm ³)						
19	Mean Grain						
20	Size	10 - 25	—	0.5 - 1.0	5 - 10	3 - 6	3 - 6
21	(μm)						
22	Phase	Y_2O_3	Al_2O_3	$Zr_{1-x}Y_xO_2$	F/C-Y ₂ O ₃	F/C-Y ₂ O ₃	F/C-Y ₂ O ₃
23	Composition				ss	ss and Y ₄ Al ₂ O ₉	ss Y ₄ Al ₂ O ₉ and YAlO ₃
24	Plasma Erosion						
25	Rate ($\mu m/hr$)	0.3	1.44	0.3	0.1	0.1	0.2
26	(CF ₄ /CHF ₃)						

* All of the solid solution ceramic substrates were sintered using a pressureless sintering technique under a hydrogen protected atmosphere.

[0080] A review of the plasma erosion rate clearly shows the advantages of the solid solution yttrium oxide, zirconium oxide, aluminum oxide ceramics which have been described herein. We have demonstrated that it is possible to reduce the erosion rate of a

1 ceramic material of this kind, while maintaining acceptable mechanical properties, which
2 enable easier handling of the apparatus without risk of damage to the apparatus.

3 [0081] Combinations of yttrium oxide, zirconium oxide and aluminum oxide have
4 been evaluated, and we have discovered that ceramic materials formed from starting
5 compositions in which the Y_2O_3 , yttrium oxide, molar concentration ranges from about 50
6 mole % to about 75 mole %; the ZrO_2 , zirconium oxide, molar concentration ranges from
7 about 10 mole % to about 30 mole %; and, the Al_2O_3 , aluminum oxide, molar
8 concentration ranges from about 10 mole % to about 30 mole %, provide excellent
9 erosion resistance to halogen containing plasmas while providing advanced mechanical
10 properties which enable handling of solid ceramic processing components with less
11 concern about damage to a component. In many applications, a starting composition for
12 the ceramic materials may be one in which Y_2O_3 molar concentration ranges from about
13 55 mole % to about 65 mole %, the ZrO_2 molar concentration ranges from about 10 mole
14 % to about 25 mole % and the Al_2O_3 molar concentration ranges from about 10 mole %
15 to about 20 mole %. When the erosion rate is of great concern, starting material
16 concentration of the ceramic material may be one in which Y_2O_3 molar concentration
17 ranges from about 55 mole % to about 65 mole %, the ZrO_2 molar concentration ranges
18 from about 20 mole % to about 25 mole % and the Al_2O_3 molar concentration 5 mole %
19 to about 10 mole %.

20 [0082] Starting material compositions of the kind described above may be used to
21 form a ceramic coating over the surface of a variety of metal or ceramic substrates,
22 including but not limited to aluminum, aluminum alloy, stainless steel, alumina,
23 aluminum nitride, and quartz, using a technique well known in the art, such as plasma
24 spray, for example and not by way of limitation. However, with the improved
25 mechanical properties which have been obtained, it is recommended that solid ceramic
26 apparatus components be used when possible, to prevent sudden failure of plasma
27 resistance due to coating layer flaking off, or defects in the coating which appear as the
28 coating thins, or the formation of metal contamination by mobile impurities from the
29 underlying substrate which migrate into the coating.

1 [0083] The addition of a concentration of zirconium oxide, ranging from about 0.1
2 mole % to about 65 mole % to what was a pure yttrium oxide, provides a solid solution of
3 yttrium oxide and zirconium oxide with the cubic yttria crystal structure or cubic fluorite-
4 type crystal structure, where the cell parameter is smaller than that of the pure structure,
5 due to the formation of yttrium vacancy/oxygen vacancy, respectively. The smaller cell
6 parameter of the solid solution crystal structure improves the plasma resistance properties
7 of the solid solution of zirconium oxide in yttrium oxide. For example, the erosion rate
8 of a solid yttrium oxide ceramic in a CF_4/CHF_3 plasma of the kind used to etch a trench in
9 a multilayered semiconductor substrate is about $0.3 \mu\text{m/hr}$. The erosion rate of a solid
10 solution ceramic of about 69 mole % yttrium oxide and about 31 mole % zirconium oxide
11 is about $0.1 \mu\text{m/hr}$, a 3 times slower etch rate than solid yttrium oxide. This unexpected
12 decrease in etch rate extends the lifetime of a process chamber liner or an internal
13 apparatus component within the process chamber, so that: the replacement frequency for
14 such apparatus is reduced, reducing apparatus down time; the particle amount generated
15 during a process is reduced, improving the product properties; the metal contamination
16 generated during a process is reduced, advancing the product properties; and the overall
17 will reduce the overall cost of the processing apparatus per wafer processed will be
18 reduced, on the average.

19 [0084] While the $0.1 \mu\text{m/hr}$ erosion rate for the zirconium oxide-containing yttrium
20 oxide solid solution is surprisingly better than that of yttrium oxide at $0.3 \mu\text{m/hr}$, and
21 considerably better than of a solid aluminum oxide ceramic at $1.44 \mu\text{m/hr}$ in the
22 CF_4/CHF_3 plasma, the mechanical properties of the zirconium oxide-containing yttrium
23 oxide solid solution illustrate that an improvement in flexural strength and fracture
24 toughness would be helpful.

25 [0085] In one embodiment, the flexural strength and fracture toughness of the
26 zirconium oxide-containing yttrium oxide solid solution are achieved, by adding various
27 amounts of aluminum oxide to the formula for the solid solution ceramic to form an
28 additional yttrium aluminate phase. The mixture of oxides was compacted by
29 unidirectional mechanical pressing or cold isostatic pressing of a granular powder formed

1 by spray drying, in combination with a typical content of binders. The green body was
2 then pressureless sintered using techniques generally known in the art. The addition of
3 10 mole % to 30 mole % of alumina significantly improved the mechanical properties of
4 the sintered ceramic composition in terms of flexural strength and fracture toughness.
5 For example, the erosion rate of the ceramic containing 69 mole % yttrium oxide and 31
6 mole % zirconium oxide, after exposure to a plasma containing CF_4 and CHF_3 , was about
7 $0.1 \mu\text{m} / \text{hr}$. For the ceramic containing about 14 mole % aluminum oxide, the erosion
8 rate after exposure to the same plasma was also about $0.1 \mu\text{m} / \text{hr}$. For the ceramic
9 containing about 25 mole % aluminum oxide, the erosion rate after exposure to the same
10 plasma was about $0.2 \mu\text{m} / \text{hr}$. With respect to the mechanical properties, for example,
11 an overall starting composition which is about 69 mole % yttrium oxide and about 31
12 mole % zirconium oxide, after sintering exhibits a flexural strength of about 137 Mpa,
13 and a fracture toughness of $1.3 \text{ Mpa} \cdot \text{m}^{1/2}$, as discussed above. When the overall ceramic
14 composition is about 63 mole % yttrium oxide, about 23 mole % zirconium oxide, and
15 about 14 mole % aluminum oxide, after sintering the flexural strength is about 215 Mpa
16 and the fracture toughness is about $1.6 \text{ Mpa} \cdot \text{m}^{1/2}$. When the overall ceramic
17 composition is about 55 mole % yttrium oxide, about 20 mole % zirconium oxide, and
18 about 25 mole % aluminum oxide, after sintering the flexural strength is about 172 Mpa
19 and the fracture toughness is about $1.7 \text{ Mpa} \cdot \text{m}^{1/2}$. The relationship between aluminum
20 oxide content, increase in flexural strength, and increase in erosion rate is not a linear
21 relationship. However, one of skill in the art can optimize the formula with minimal
22 experimentation, in view of the information provided herein.

23 [0086] As an alternative to adding aluminum oxide to a multi phase metal stable
24 composition containing yttrium oxide and zirconium oxide is to add HfO_2 , hafnium
25 oxide; Sc_2O_3 , scandium oxide; Nd_2O_3 , neodymium oxide; Nb_2O_5 , niobium oxide; Sm_2O_3 ,
26 samarium oxide; Yb_2O_3 , ytterbium oxide; Er_2O_3 , erbium oxide; Ce_2O_3 (or CeO_2), cerium
27 oxide, or combinations thereof. In the instance where these alternative compounds are
28 used, the concentration of the alternative compound in the starting material formulation
29 ranges from about 0.1 mole % to about 90 mole %. Typically the concentration used

1 will range from about 10 mole % to about 30 mole %.

2 [0087] After mixing of at least one of the alternative oxides listed above with the
3 Y_2O_3 and ZrO_2 powders used to form a solid solution, the combination of powders was
4 compacted by unidirectionally mechanical pressing or cold isostatic pressing of the
5 granular powder formed by spray drying with a typical content of binders. The green
6 body was then pressureless sintered using techniques known in the art. Upon cooling of
7 the sintered body, a single phase or two phase solid solution forms, where the solid
8 solution is a "multi-element-doped" solid solution. One solid solution exhibits a cubic
9 yttria crystal structure, and another solid solution exhibits the cubic fluorite-type crystal
10 structure. The solid solution has excellent plasma resistance, typically better erosion
11 resistance than that of the aluminum oxide-comprising solid solutions discussed herein.
12 However, the mechanical properties of the yttria-zirconia-alumina system are somewhat
13 better. All of these multi-doped solid solutions exhibit excellent plasma erosion resistance
14 and improved mechanical properties in comparison with previously known yttrium oxide-
15 zirconium oxide solid solutions.

16 [0088] Typical applications for a yttrium oxide-comprising substrate of the kind
17 described herein include, but are not limited to components used internal to a plasma
18 processing chamber, such as a lid, lid-liner, nozzle, gas distribution plate or shower head,
19 electrostatic chuck components, shadow frame, substrate holding frame, processing kit,
20 and chamber liner. All of these components are well known in the art to those who do
21 plasma processing.

22 [0089] The above described exemplary embodiments are not intended to limit the
23 scope of the present invention, as one skilled in the art can, in view of the present
24 disclosure, expand such embodiments to correspond with the subject matter of the
25 invention claimed below.

[0090]

CLAIMS

[0091] We claim:

- 1 1. A ceramic article which is resistant to erosion by halogen-containing
2 plasmas used in semiconductor processing, said ceramic article including ceramic having
3 at least two phases, said ceramic formed from yttrium oxide at a molar concentration
4 ranging from about 50 mole % to about 75 mole %; zirconium oxide at a molar
5 concentration ranging from about 10 mole % to about 30 mole %; and at least one other
6 component selected from the group consisting of aluminum oxide, hafnium oxide,
7 scandium oxide, neodymium oxide, niobium oxide, samarium oxide, ytterbium oxide,
8 erbium oxide, cerium oxide, and combinations thereof, said at least one other component
9 concentration ranging from about 10 mole % to about 30 mole %.
- 1 2. A ceramic article in accordance with Claim 1, wherein said ceramic is formed
2 from yttrium oxide at a concentration ranging from about 55 mole % to about 65 mole %,
3 zirconium oxide at a concentration ranging from about 15 mole % to about 25 mole %
4 and said at least one other component at a concentration ranging from about 10 mole % to
5 about 25 mole %.
- 1 3. A ceramic article in accordance with Claim 2, wherein said ceramic is formed
2 from yttrium oxide at a concentration ranging from about 55 mole % to about 65 mole %,
3 zirconium oxide at concentration ranging from about 20 mole % to about 25 mole %, and
4 said at least one other component at a concentration ranging from about 10 mole % to
5 about 20 mole %.
- 1 4. A ceramic article in accordance with Claim 1, or Claim 2, or Claim 3, wherein
2 said at least one other component is aluminum oxide.

- 1 5. A ceramic article in accordance with Claim 4, wherein a mean grain size of said
2 ceramic ranges from about 0.5 μ m to about 10 μ m.
- 1 6. A ceramic article in accordance with Claim 1, wherein a flexural strength of said
2 ceramic ranges from about 150 MPa to about 250 MPa.
- 1 7. A ceramic article in accordance with Claim 1, wherein a fracture toughness of said
2 ceramic ranges from about 1.5 MPa $\cdot$ m^{1/2} to about 2.0 MPa $\cdot$ m^{1/2}.
- 1 8. A ceramic article in accordance with Claim 1, wherein said article is selected
2 from the group consisting of a lid, a lid liner, a nozzle, a gas distribution plate, a shower
3 head, an electrostatic chuck component, a shadow frame; a substrate holding frame, a
4 processing kit, and a chamber liner.
- 1 9. A ceramic article in accordance with Claim 4, wherein said article is selected
2 from the group consisting of a lid, a lid liner, a nozzle, a gas distribution plate, a shower
3 head, an electrostatic chuck component, a shadow frame, a substrate holding frame, a
4 processing kit, and a chamber liner.
- 1 10. A method of reducing the plasma erosion of a semiconductor processing
2 apparatus contacted by a halogen-containing plasma, comprising: employing a ceramic-
3 comprising article, said ceramic formed from yttrium oxide at a molar concentration
4 ranging from about 50 mole % to about 75 mole %; zirconium oxide at a molar
5 concentration ranging from about 10 mole % to about 30 mole %; and at least one other
6 component selected from the group consisting of aluminum oxide, hafnium oxide,
7 scandium oxide, neodymium oxide, niobium oxide, samarium oxide, ytterbium oxide,
8 erbium oxide, cerium oxide, and combinations thereof, said at least one other component
9 concentration ranging from about 10 mole % to about 30 mole %.

1 11. A method in accordance with Claim 10, wherein said ceramic-comprising
2 article is formed from yttrium oxide at a molar concentration ranging from about 55 mole
3 % to about 65 mole %, zirconium oxide at a concentration ranging from about 15 mole %
4 to about 25 mole % and said at least one other component at a concentration ranging from
5 about 10 mole % to about 25 mole %.

1 12. A method in accordance with Claim 11, wherein said ceramic-comprising
2 article is formed from yttrium oxide at a concentration ranging from about 55 mole % to
3 about 65 mole %, zirconium oxide at concentration ranging from about 20 mole % to
4 about 25 mole %, and said at least one other component at a concentration ranging from
5 about 10 mole % to about 20 mole %.

1 13. A method in accordance with Claim 10, or Claim 11, or Claim 12, wherein said
2 at least one other component is selected to be aluminum oxide.

1 14. A method in accordance with Claim 10, wherein said plasma erosion rate for a
2 surface of said semiconductor processing apparatus upon exposure to a halogen-
3 comprising plasma is less than about 0.3 $\mu\text{m/hr}$.

1 15. A method in accordance with Claim 14, wherein said plasma erosion rate for a
2 surface of said semiconductor processing apparatus upon exposure to a halogen-
3 comprising plasma ranges from about 0.1 $\mu\text{m/hr}$ to about 0.3 $\mu\text{m/hr}$.

1 16. A method in accordance with Claim 13, wherein said plasma erosion rate for a
2 surface of said semiconductor processing apparatus upon exposure to a halogen-
3 comprising plasma is less than about 0.3 $\mu\text{m/hr}$.

1 17. A method in accordance with Claim 16, wherein said plasma erosion rate for a

2 surface of said semiconductor processing apparatus upon exposure to a halogen-
3 comprising plasma ranges from about 0.1 $\mu\text{m/hr}$ to about 0.3 $\mu\text{m/hr}$.

1 18. A semiconductor processing apparatus which has at least one surface exposed to
2 a halogen-comprising plasma during said semiconductor processing, wherein said
3 semiconductor processing apparatus surface is a ceramic, said ceramic being resistant to
4 erosion by halogen-containing plasmas, wherein said ceramic includes at least two phases
5 and is formed from yttrium oxide at a molar concentration ranging from about 50 mole %
6 to about 75 mole %; zirconium oxide at a molar concentration ranging from about 10
7 mole % to about 30 mole %; and at least one other component selected from the group
8 consisting of aluminum oxide, hafnium oxide, scandium oxide, neodymium oxide,
9 niobium oxide, samarium oxide, ytterbium oxide, erbium oxide, cerium oxide, and
10 combinations thereof, said at least one other component concentration ranging from about
11 10 mole % to about 30 mole %.

1 19. A semiconductor processing apparatus in accordance with Claim 18, wherein
2 underlying said ceramic is a high purity aluminum alloy.

1 20. A semiconductor processing apparatus in accordance with Claim 19, wherein
2 said apparatus is selected from the group consisting of a lid, a lid liner, a nozzle, a gas
3 distribution plate, a shower head, an electrostatic chuck component, a shadow frame, a
4 substrate holding frame, a processing kit, and a chamber liner.

1 21. A semiconductor processing apparatus in accordance with Claim 18, wherein
2 said apparatus is a solid ceramic semiconductor processing apparatus.

1 22. A semiconductor processing apparatus in accordance with Claim 21, wherein
2 said apparatus is selected from the group consisting of a lid, a lid liner, a nozzle, a gas
3 distribution plate, a shower head, an electrostatic chuck component, a shadow frame, a

4 substrate holding frame, a processing kit, and a chamber liner.

1 23. A ceramic article which is resistant to erosion by halogen-containing
2 plasmas used in semiconductor processing, said article comprising: a ceramic formed
3 from a combination of yttrium oxide and zirconium oxide, with yttrium oxide at a molar
4 concentration ranging from about 90 mole % to about 70 mole %, and zirconium oxide at
5 a molar concentration ranging from about 10 mole % to about 30 mole %, wherein a
6 mean grain size of said ceramic ranges from about 2 μm to about 8 μm .

1 24. A ceramic article in accordance with Claim 23, wherein said ceramic is formed
2 from yttrium oxide at a concentration ranging from about 90 mole % to about 80 mole %,
3 and zirconium oxide at a concentration ranging from about 10 mole % to about 20 mole
4 %.

1 25. A ceramic article in accordance with Claim 23 or Claim 24, wherein a mean
2 grain size of said ceramic ranges from about 2 μm to about 8 μm .

1 26. A ceramic article in accordance with Claim 23, wherein a flexural strength of
2 said ceramic ranges from about 120 MPa to about 140 MPa.

1 27. A ceramic article in accordance with Claim 23, wherein a fracture toughness of
2 said ceramic ranges from about 1.1 MPa $\cdot$ m^{1/2} to about 1.3 MPa $\cdot$ m^{1/2}.

1 28. A ceramic article in accordance with Claim 23 or Claim 24, wherein said article
2 is selected from the group consisting of a lid, a lid liner, a nozzle, a gas distribution plate,
3 a shower head, an electrostatic chuck component, a shadow frame, a substrate holding
4 frame, a processing kit, and a chamber liner.

1 29. A method of reducing the plasma erosion of a semiconductor processing

2 apparatus contacted by a halogen-containing plasma, comprising: selecting said
3 semiconductor processing apparatus to comprise ceramic, said ceramic formed from
4 yttrium oxide at a molar concentration ranging from about 90 mole % to about 70 mole
5 %, and zirconium oxide at a molar concentration ranging from about 10 mole % to about
6 30 mole %.

1 30. A method in accordance with Claim 29, further comprising selecting said
2 ceramic for said semiconductor processing apparatus to be formed from yttrium oxide at
3 a molar concentration ranging from about 90 mole % to about 80 mole %, and zirconium
4 oxide at a concentration ranging from about 10 mole % to about 20 mole %.

1 31. A method in accordance with Claim 29 or 30, wherein said plasma erosion rate
2 for a surface of said semiconductor processing apparatus upon exposure to a halogen-
3 comprising plasma is less than about 0.2 $\mu\text{m/hr}$.

1 32. A method in accordance with Claim 31, wherein said plasma erosion rate for a
2 surface of said semiconductor processing apparatus upon exposure to a halogen-
3 comprising plasma ranges from about 0.1 $\mu\text{m/hr}$ to about 0.2 $\mu\text{m/hr}$.

1 33. A semiconductor processing apparatus having at least one surface exposed to a
2 halogen-comprising plasma during a process, wherein said semiconductor processing
3 apparatus surface is a ceramic which is resistant to erosion by halogen-containing
4 plasmas, wherein said ceramic is formed from yttrium oxide at a molar concentration
5 ranging from about 90 mole % to about 70 mole %, and zirconium oxide at a molar
6 concentration ranging from about 10 mole % to about 30 mole %.

1 34. A semiconductor processing apparatus in accordance with Claim 33, wherein
2 underlying said ceramic is a high purity aluminum alloy.

1 35. A method in accordance with Claim 33, wherein said semiconductor processing
2 apparatus is a solid ceramic semiconductor processing apparatus.

1 36. A semiconductor processing apparatus, said apparatus having at least one
2 surface exposed to a halogen-comprising plasma during a process, wherein said surface is
3 a ceramic which is resistant to erosion by halogen-containing plasmas, wherein said
4 ceramic is formed from zirconium oxide at a molar concentration ranging from about 96
5 mole % to about 94 mole %, and yttrium oxide at a molar concentration ranging from
6 about 4 mole % to about 6 mole %.

1 37. A semiconductor processing apparatus in accordance with Claim 36, wherein
2 underlying said ceramic is a high purity aluminum alloy.

1 38. A semiconductor processing apparatus in accordance with Claim 36, wherein
2 said apparatus is a solid ceramic apparatus.

1 39. A semiconductor processing apparatus in accordance with Claim 36, wherein
2 said apparatus is selected from the group consisting of a lid, a lid liner, a nozzle, a gas
3 distribution plate, a shower head, an electrostatic chuck component, a shadow frame, a
4 substrate holding frame, a processing kit, and a chamber liner.

1 40. A semiconductor processing apparatus in accordance with Claim 36,
2 wherein a mean grain size of said ceramic ranges from about 0.5 μm to about 8.0 μm .

1 41. A semiconductor processing apparatus in accordance with Claim 36, wherein a
2 flexural strength of said ceramic ranges from about 1100 MPa to about 1300 MPa.

1 42. A semiconductor processing apparatus in accordance with Claim 36, wherein a
2 fracture toughness of said ceramic ranges from about 10 MPa $\cdot$ m^{1/2} to about 12 MPa $\cdot$

3 $m^{1/2}$.

1 43. A method of reducing the plasma erosion of a semiconductor processing
2 apparatus contacted by a halogen-containing plasma, comprising: selecting said
3 semiconductor processing apparatus to be a ceramic-comprising article, said ceramic
4 formed from zirconium oxide at a molar concentration ranging from about 96 mole % to
5 about 94 mole %, and yttrium oxide at a molar concentration ranging from about 4 mole
6 % to about 6 mole %.

7
8 44. A method in accordance with Claim 43, wherein said plasma erosion rate for a
9 surface of said semiconductor processing apparatus, upon exposure to a halogen-
10 comprising plasma, is less than about 0.4 $\mu\text{m/hr}$.

1 45. A method in accordance with Claim 44 wherein said plasma erosion rate for a
2 surface of said semiconductor processing apparatus, upon exposure to a halogen-
3 comprising plasma, ranges from about 0.1 $\mu\text{m/hr}$ to about 0.4 $\mu\text{m/hr}$.

1 46. A method in accordance with Claim 43, wherein at least one surface of said
2 semiconductor processing apparatus, which surface is said ceramic, is exposed to said
3 halogen-comprising plasma during said semiconductor processing.

1 47. A method in accordance with Claim 46, wherein underlying said ceramic is a
2 high purity aluminum alloy.

1 48. A method in accordance with Claim 46, wherein said semiconductor processing
2 apparatus is a solid ceramic semiconductor processing apparatus.