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(54) **Title:**
CERAMIC COATING COMPRISING YTTRIUM WHICH IS RESISTANT TO A REDUCING PLASMA

(57) **Abstract:**
 ABSTRACT CERAMIC COATING COMPRISING YTTRIUM WHICH IS RESISTANT TO A REDUCING PLASMA Particulate generation has been a problem in semiconductor device processing in highly corrosive plasma environments. The problem is exacerbated when the plasma is a reducing plasma. Empirically produced data has shown that the formation of a plasma spray coated yttrium-comprising ceramic such as yttrium oxide, Y2O3 - 7rO2 solid solution, YAG, and YF3 provides a low porosity coating with smooth and compacted surfaces when such ceramics are spray coated from a powder feed having an average effective diameter ranging from about 22pm to about 0.1 pm. These spray- coated materials reduce the generation of particulates in corrosive reducing plasma environments. Figure 6

ABSTRACT

CERAMIC COATING COMPRISING YTTRIUM WHICH IS RESISTANT TO A REDUCING PLASMA

Particulate generation has been a problem in semiconductor device processing in highly corrosive plasma environments. The problem is exacerbated when the plasma is a reducing plasma. Empirically produced data has shown that the formation of a plasma spray coated yttrium-comprising ceramic such as yttrium oxide, Y_2O_3 - ZrO_2 solid solution, YAG, and YF_3 provides a low porosity coating with smooth and compacted surfaces when such ceramics are spray coated from a powder feed having an average effective diameter ranging from about $22\mu m$ to about $0.1\ \mu m$. These spray-coated materials reduce the generation of particulates in corrosive reducing plasma environments.

Figure 6

1 [0001] **CERAMIC COATING COMPRISING YTTRIUM WHICH**
2 **IS RESISTANT TO A REDUCING PLASMA**

3 [0002] The present application is related to two other applications pertaining to
4 semiconductor processing components which make use of a spray-coated, yttrium-
5 comprising ceramic material. The spray-coated, yttrium-comprising ceramic material is
6 frequently applied over an aluminum or aluminum alloy substrate. The related
7 applications are U.S. Application 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; and,
10 Application No. 10/898,113 of Sun et al., filed July 22, 2004, titled: "Clean Dense
11 Yttrium Oxide Coating Protecting Semiconductor Apparatus", which was published as
12 US 2005/0037193 A1 on February 17, 2005, and which is currently pending. The
13 subject matter of the referenced patent and application is hereby incorporated by
14 reference into the present description.

15 [0003] **BACKGROUND**

16 [0004] 1. Field

17 [0005] Embodiments of the present invention relate to a plasma or flame sprayed
18 yttrium-comprising coating useful as a protective coating over processing surfaces in a
19 semiconductor processing environment. The plasma or flame sprayed yttrium-
20 comprising coating is particularly useful in a reducing plasma to prevent particulate
21 contamination of a substrate which is being processed.

22 [0006] 2. Background

23 [0007] This section describes background subject matter related to the disclosed
24 embodiments of the present invention. There is no intention, either express or implied,
25 that the background art discussed in this section legally constitutes prior art.

26 [0008] Corrosion (including erosion) resistance is a critical property for apparatus

1 components and liners used in semiconductor processing chambers, where corrosive
2 environments are present. Although corrosive plasmas are present in the majority of
3 semiconductor processing environments, including plasma enhanced chemical vapor
4 deposition (PECVD) and physical vapor deposition (PVD), the most corrosive plasma
5 environments are those used for cleaning of processing apparatus and those used to etch
6 semiconductor substrates. This is especially true where high-energy plasma is present
7 and combined with chemical reactivity to act upon the surface of components present in
8 the environment. When the high-energy plasma is a reducing plasma, such as a hydrogen
9 species-containing plasma, the formation of particulates in the processing chamber has
10 been observed to be a problem. The particulates often contaminate the surfaces of
11 devices contained in a substrate which is processed in the semiconductor processing
12 chamber.

13 **[0009]** Process chamber liners and component apparatus present within the processing
14 chambers used to fabricate electronic devices and micro-electro-mechanical systems
15 (MEMS) are frequently constructed from aluminum and aluminum alloys. Surfaces of
16 the process chamber and component apparatus (present within the chamber) are
17 frequently anodized to provide a degree of protection from the corrosive environment.
18 However, the integrity of the anodization layer may be deteriorated by impurities in the
19 aluminum or aluminum alloy, so that corrosion begins to occur early, shortening the life
20 span of the protective coating. The plasma resistance properties of aluminum oxide are
21 not positive in comparison with some other ceramic materials. As a result, ceramic
22 coatings of various compositions have been used in place of the aluminum oxide layer
23 mentioned above; and, in some instances, have been used over the surface of an anodized
24 layer present on an aluminum alloy substrate, to improve the protection of the underlying
25 aluminum-based materials.

26 **[0010]** Yttrium oxide is a ceramic material which has shown considerable promise in
27 the protection of aluminum and aluminum alloy surfaces which are exposed to halogen-

1 containing plasmas of the kind used in the fabrication of semiconductor devices. A
2 spray-coated yttrium oxide coating has been applied over an anodized surface of a high
3 purity aluminum alloy process chamber surface, or a process component surface, to
4 produce excellent corrosion protection (e.g. U.S. Patent No. 6,777,873 to Sun et al.,
5 mentioned above).

6 [0011] The substrate base material of the chamber wall or liner, of an apparatus
7 component may be a ceramic material (Al_2O_3 , SiO_2 , AlN , etc.), may be aluminum, or
8 stainless steel, or may be another metal or metal alloy. Any of these may have a sprayed
9 film over the base material. The film may be made of a compound of a III-B element of
10 the periodic table, such as Y_2O_3 . The film may substantially comprise Al_2O_3 and Y_2O_3 .
11 A sprayed film of yttrium-aluminum-garnet (YAG) has also been mentioned. Examples
12 of a sprayed film thickness range from 50 μm to 300 μm , for example.

13 [0012] There have been problems with aluminum and aluminum alloys which have
14 been spray coated with a yttrium oxide-comprising film to provide corrosion and erosion
15 resistance. In particular, as part of the rigorous challenges in integrated circuit (IC) etch
16 for the 45 nm and 32 nm technology nodes (as well as future technology nodes),
17 particulates and contaminants produced during the IC fabrication operations have
18 reduced the yield of acceptable devices.

19 [0013] There is a need in the semiconductor industry to reduce the amount of
20 particulates and contamination generated during plasma processing as part of the
21 manufacture of IC components, particularly when the plasma is a reducing plasma.

22 [0014] **DESCRIPTION**

23 [0015] It had been observed that particulates were becoming a problem during
24 semiconductor device processing in highly corrosive plasma environments. The
25 particulates affected semiconductor device yields. Empirically generated data has shown
26 that the ceramic protective coatings used to protect semiconductor processing chamber

1 surfaces and apparatus components present within the chamber were the source of a large
2 amount of the particulates. Empirically generated data has shown that by polishing the
3 surface of a ceramic-coated process chamber liner or an apparatus component, prior to
4 use of the ceramic-coated apparatus; the amount of particulate generation could be
5 reduced. Still, the amount of particulates generated affected semiconductor yields
6 significantly.

7 [0016] The problem of particulate generation was particularly bad when the
8 environment in a plasma processing chamber was a reducing atmosphere. A number of
9 plasma processes make use of hydrogen among other reactive species, and this reducing
10 environment produces increased particulates over those observed when hydrogen is not
11 present. An extensive development project was carried out which resulted in
12 embodiments of the present invention which pertain to forming an improved protective
13 ceramic coating which produces fewer particulates in a reducing environment. The
14 development program was based on yttrium-comprising ceramics. These yttrium-
15 comprising ceramics included yttrium oxide (Y_2O_3), $Y_2O_3-ZrO_2$ solid solution, YAG, and
16 YF_3 in addition to more exotic ceramic coating compositions designed to provide
17 particular mechanical, physical or electrical properties.

18 [0017] Photomicrographs of specimens cut from aluminum substrates coated with a
19 yttrium oxide coating, which was applied using known in the art plasma spray coating
20 techniques, showed a substantial increase in porosity and surface roughness after
21 exposure to a plasma containing reducing species. It was empirically determined that a
22 substantial reduction in porosity and surface roughness of the spray-coated yttrium oxide
23 surface could be obtained by using a smaller average particle size yttrium oxide powder
24 feed to the plasma spray coating apparatus used to apply the coating. Embodiments of
25 the present invention employ smaller (than conventionally used) average particle size
26 Y_2O_3 , $Y_2O_3-ZrO_2$ solid solution, YAG, and YF_3 powder to spray coat a substrate. For
27 example, the conventional effective particle diameter of yttrium oxide powder fed to the

1 plasma spray-coating apparatus prior to the present invention was about 25 μm or larger.
2 An unexpected improvement in corrosion/erosion resistance to reducing plasmas was
3 obtained when the effective particle diameter fed to a plasma spray-coating apparatus
4 was reduced to less than about 22 μm , and typically less than about 15 μm , with the
5 effective particle diameter frequently ranging between about 15 μm and about 5 μm .
6 Smaller effective particle diameter powders, down to 0.1 μm , may be used in instances
7 when the spray-coating system can be adapted to handle such particles. Substrates spray-
8 coated using the reduced particle size powders show a corresponding substantial and
9 unexpected reduction in the average porosity of the yttrium-comprising spray coating.
10 This reduction in average porosity has been observed in coating embodiments for Y_2O_3 ,
11 $\text{Y}_2\text{O}_3\text{-ZrO}_2$ solid solution, YAG, and YF_3 deposited over an aluminum alloy substrate
12 surface. For example, for a 200 μm thick coating, the average porosity of the yttrium
13 oxide coating produced using the previous spray coating technique, which employed an
14 effective powder diameter for the yttrium oxide of 25 μm or larger, ranges from above
15 1.5 % to about 4 %, measured using Image-Pro PlusTM Version 6.0 software in
16 combination with an SEM microstructure image. This compares with an average
17 porosity ranging from less than 1.5 % down to about 0.15 % for a yttrium oxide coating
18 produced using a plasma spray coating embodiment of the present invention in which the
19 average effective powder diameter fed to the plasma spray apparatus ranged from about
20 22 μm down to about 5 μm . By way of example, a yttrium oxide coating having an
21 average porosity of about 0.47 % was achieved using a 15 μm effective powder diameter.
22 In addition, the average surface roughness of the yttrium oxide coating produced using
23 the 25 μm effective diameter powder was about 200 $\mu\text{-inch Ra}$ (5.0 $\mu\text{m Ra}$) compared
24 with an average surface roughness of only 51.2 $\mu\text{-inch Ra}$ (1.28 $\mu\text{m Ra}$) for the yttrium
25 oxide coating produced using the 15 μm diameter powder yttrium oxide feed to the laser
26 spray coating apparatus. In embodiments of the invention in general, the average
27 surface roughness may range from about 3 $\mu\text{m Ra}$ to about 0.6 $\mu\text{m Ra}$.

1 [0018] With respect to the 200 μm thick yttrium oxide coating described above, using
2 a standard HCl bubble test which is described subsequently herein, the yttrium oxide
3 coating produced using the 25 μm effective diameter yttrium oxide powder performed
4 well for about 7.5 - 8 hours, while the yttrium oxide coating produced using the 15 μm
5 (or smaller) diameter powder performed well for a time period in excess of 10 hours.
6 Further, the break down voltage (V_{BD}) for the yttrium oxide coating produced using the
7 25 μm diameter powder was 750 V/mil, while the break down voltage for the yttrium
8 oxide coating produced using the 15 μm diameter powder was at least 875 V/mil.

9 [0019] One of skill in the art can select any of the plasma spray-coating apparatus
10 commonly used in the industry for spray coating of yttrium-comprising coatings and
11 obtain similar relative results, with minimal experimentation.

12 [0020] The use of a smaller effective diameter yttrium-comprising powder provides a
13 less efficient coating of the substrate, with more powder consumed per thickness of
14 coating deposited. Since the yttrium-containing powders are expensive, no effort was
15 made to develop the use of smaller diameter yttrium-comprising powders for spray
16 coating. The unexpected relative advantages in performance properties of the coatings
17 produced when effective powder diameters ranging from about 22 μm down to about 0.1
18 μm , according to embodiments of the present invention, are used more than justifies the
19 use of the smaller effective powder diameters. For example, the sprayed coatings having
20 a thickness of 300 μm or less exhibit porosities ranging from about 0.15 % to less than
21 about 1.5 %, measured using the Image-Pro PlusTM software in the manner previously
22 described. Empirically generated data showed that a spray-coated yttrium oxide
23 processing component produced using the improved spray coating technique employing
24 the smaller effective diameter powders, according to embodiments of the present
25 invention, was even more resistant to erosion in a reducing plasma and produced fewer
26 particulates than a solid yttrium oxide component. This was presumed to be due to the
27 fact that the solid yttrium oxide component required the use of a sintering additive, which

1 produced an intergranular glassy phase, where the intergranular glassy phase is a source
2 of particulate formation.

3 [0021] While working to improve the performance of the yttrium oxide coating in a
4 reduced plasma, we discovered that the mechanism of attack of the yttrium oxide surface
5 is through the formation of yttrium hydroxide, $Y(OH)_3$. When reactive plasma species of
6 hydrogen or hydrogen and oxygen are present, the $Y(OH)_3$ compound is formed. When
7 reactive plasma species of hydrogen, fluorine, and oxygen are present, the $Y(OH)_3$
8 compound is formed, and YF_3 compound is formed as well, with the YF_3 formation being
9 preferentially formed based on thermodynamic considerations.

10 [0022] The $Y(OH)_3$ formed in a reducing atmosphere on a yttrium oxide surface is the
11 main reason particulates are generated. Once this discovery was made, further
12 experimentation showed that there are several exemplary methods, in accordance with
13 embodiments of the invention, which can be used to reduce the quantity of particulates
14 formed: 1) Continue to use a yttrium oxide coating, but produce a denser, smoother Y_2O_3
15 plasma sprayed coating which is attacked at a slower rate by the reducing species. This
16 is achieved by reducing the effective particle size diameter powder for the spray-coating
17 formation to range from about 22 μm to about 0.1 μm . 2) Substitute a YAG (Yttrium
18 Aluminum Garnet, which is commonly used in a $Y_3Al_5O_{12}$ form), or a Y_2O_3 - ZrO_2 solid
19 solution, or a YF_3 composition (or a combination thereof) to the plasma spray-coating
20 apparatus to form a YAG, or Y_2O_3 - ZrO_2 solid solution, or YF_3 (or a combination thereof)
21 coating. These materials reduce or avoid, respectively the formation of $Y(OH)_3$. And, 3)
22 Substitute a YAG, or a Y_2O_3 - ZrO_2 solid solution, or a YF_3 (or a combination thereof)
23 material for the Y_2O_3 and reduce the size of the YAG, or Y_2O_3 - ZrO_2 solid solution, or
24 YF_3 (or combinations thereof) effective diameter powder to the plasma spray-coating
25 apparatus to range between about 22 μm to 0.1 μm . More practically, a powder diameter
26 ranging from about 15 μm to about 5 μm is used. Coating thicknesses ranging from 5
27 μm to 400 μm have been produced. More commonly, a coating thickness ranging from

1 about 25 μm to about 300 μm is used.

2 [0023] **BRIEF DESCRIPTION OF THE DRAWINGS**

3 [0024] So that the manner in which the exemplary embodiments of the present
4 invention are attained is clear and can be understood in detail, with reference to the
5 particular description provided above, and with reference to the detailed description of
6 exemplary embodiments, applicants have provided illustrating drawings. It is to be
7 appreciated that drawings are provided only when necessary to understand the invention
8 and that certain well known processes and apparatus are not illustrated herein in order not
9 to obscure the inventive nature of the subject matter of the disclosure.

10 [0025] Figure 1 is a cross-sectional schematic 100 of one type of plasma spraying
11 system of the kind known in the art which may be used to apply coatings of the present
12 invention.

13 [0026] Figures 2A, 2B, and 2C show comparative photomicrographs 200, 210, and
14 220 of the surface of a previously known as-coated plasma sprayed yttrium oxide coating
15 at magnifications of 300X, 1000X, and 5000X, respectively.

16 [0027] Figures 2D, 2E, and 2F show photomicrographs 230, 240, and 250 of the
17 surface of the as-coated plasma sprayed yttrium oxide coating illustrated in Figures 2A
18 through 2C after exposure to a reducing chemistry plasma. Figure 2D is at a
19 magnification of 300X, Figure 2E is at a magnification of 1000X, and Figure 2F is at a
20 magnification of 5000X.

21 [0028] Figures 3A, 3B, and 3C show photomicrographs 300, 310, and 320 of the
22 surface of a lapped (polished) as-coated plasma sprayed yttrium oxide coating at

1 magnifications of 300X, 1000X, and 5000X respectively.

2 [0029] Figures 3D, 3E, and 3F show photomicrographs 330, 340, and 350 of the
3 surface of the lapped (polished) sprayed yttrium oxide coating illustrated in Figures 3A
4 through 3C after exposure to a reducing chemistry plasma. Figure 3D is at a
5 magnification of 300X, Figure 3E is at a magnification of 1000X, and Figure 3F is at a
6 magnification of 5000X.

7 [0030] Figure 4A is a comparative example which shows a graph 400 of the range of
8 the surface roughness in microns from a centerline 410 along the surface of an as-coated
9 plasma sprayed yttrium oxide coating produced using the technology available prior to
10 the present invention.

11 [0031] Figure 4B shows a graph 420 of the range of the surface roughness in microns
12 from a centerline 430 along the surface of an as-coated plasma sprayed yttrium oxide
13 coating produced using the technology of embodiments of the present invention.

14 [0032] Figures 5A and 5B are comparative photomicrographs 510 and 520, which
15 show a top view of the morphology of a plasma sprayed yttrium oxide coating prepared
16 using plasma spray technology prior to the present invention, at magnifications of 200X
17 and 1000X, respectively.

18 [0033] Figures 5C and 5D are photomicrographs 530 and 540, which show a top view
19 of the morphology of plasma sprayed yttrium oxide coating prepared using the plasma
20 spray technology of an embodiment of the present invention, at magnifications of 200X
21 and 1000X, respectively.

1 [0034] Figure 6A is a photomicrograph 600 showing a cross-sectional side view of an
2 aluminum alloy substrate 602 having a yttrium oxide coating 606 deposited over the
3 surface 604 of the aluminum alloy substrate 602. This is a comparative photomicrograph
4 which shows the characteristics of this structure which was prepared using plasma spray
5 technology prior to the present invention, at a magnification of 200X.

6 [0035] Figure 6B is a photomicrograph 610 showing a cross-sectional side view of an
7 aluminum alloy substrate 612 having a yttrium oxide coating 616 deposited over the
8 surface 614 of the aluminum alloy substrate 612. This photomicrograph shows the
9 characteristics of this structure which was prepared using plasma spray technology which
10 is an embodiment of the present invention, at a magnification of 200X.

11 [0036] Figure 7A shows a block diagram 700 which compares an erosion rate for a
12 plasma sprayed yttrium oxide coating (over an aluminum alloy substrate) applied using
13 the prior art spray coating technology 704, with the erosion rate for a bulk substrate of
14 yttrium oxide 706, with the erosion rate for a plasma sprayed yttrium oxide coating (over
15 an aluminum substrate) applied using an embodiment of the present invention 708, where
16 each of these test specimen substrates was exposed to the same plasma containing
17 reducing species.

18 [0037] Figure 7B shows a block diagram 720 which compares an erosion rate for a
19 series bulk, sintered materials. Each of these test specimen substrates was exposed to the
20 same plasma containing reducing species.

21 [0038] Figure 8 shows a Table 800, listing the compositions of the various bulk
22 materials for which the erosion rates are presented in Figure 7B.

1 [0039] Figure 9 shows a phase diagram 900 showing the majority of the materials
2 which are listed in Table 800.

3 [0040] **DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS**

4 [0041] As a preface to the detailed description, it should be noted that, as used in this
5 specification and the appended claims, the singular forms "a", "an", and "the" include
6 plural referents, unless the context clearly dictates otherwise.

7 [0042] When the word "about" is used herein, this is intended to mean that the
8 nominal value presented is precise within $\pm 10\%$.

9 [0043] To facilitate understanding, identical reference numerals have been used,
10 where possible, to designate identical elements that are common to the figures. It is
11 contemplated that elements and features of one embodiment may be beneficially
12 incorporated in other embodiments without further recitation. It is to be noted that the
13 appended drawings illustrate only exemplary embodiments of the invention where a
14 drawing would be particularly helpful in understanding the embodiment. Not all
15 embodiments require a drawing for understanding, and therefore the drawings are not to
16 be considered as limiting of the scope of the invention, for the invention may admit to
17 other equally effective embodiments.

18 [0044] As discussed above, it had been observed that particulates were becoming a
19 problem during semiconductor device processing in highly corrosive plasma
20 environments. Empirically generated data showed that the ceramic protective coatings
21 used to protect various semiconductor apparatus processing surfaces within the chamber
22 were the source of a large amount of the particulates. In addition, when erosion rates
23 were compared for various semiconductor processing plasmas, it became apparent that
24 when the plasma was a reducing plasma, one which contained reducing species,
25 particularly hydrogen, the production of particulates was increased.

26 [0045] The yield of devices per fabrication processes was decreasing as the device

1 sizes became smaller and the presence of particulates on the semiconductor substrate
2 surface became more significant with respect to device function. A program was
3 initiated to reduce the production of particulates by the coatings used to protect the
4 semiconductor processing apparatus surfaces.

5 [0046] The development program was based on yttrium-comprising ceramics. These
6 yttrium-comprising ceramics included yttrium oxide, Y_2O_3 - ZrO_2 solid solution, YAG,
7 and YF_3 in addition to other more exotic yttrium-comprising ceramic materials which
8 were designed to provide particular mechanical or electrical properties.

9 [0047] Figure 1 shows a cross-sectional schematic 100 of a type of plasma spraying
10 system which is useful in applying the coatings of the present invention. The particular
11 apparatus illustrated in Figure 1 is an APS 7000 Series Aeroplasma Spraying System
12 available from Aeroplasma K.K. (Tokyo, Japan). The apparatus 100 includes the
13 following components: first DC main electrode 102; first auxiliary electrode 104; first
14 argon source 106; first air source 108; spray material powder source 110; cathode torch
15 112; accelerator nozzle 114; plasma arc 116; second DC main electrode 118; second
16 auxiliary electrode 120; anode torch 122; spray base material source 124; second argon
17 source 126; second air source (plasma trimming) 128 (128A and 128B); spray film 130;
18 plasma jet 132; molten powder source 134; third argon source 136; and twin anode α
19 torch 138.

20 [0048] Twin anode α torch 138 consists of two anode torches, so that each of the
21 anode torches bears half of the thermal load. Using twin anode torch α 138, a high
22 voltage can be obtained with relatively low current, so that the thermal load on each of
23 the torches will be low. Each nozzle and electrode rod of the torches is water-cooled
24 separately, and the arc starting point and ending point are protected by inert gas, so that
25 stable operation at 200 hours or more is ensured, the service life of consumed parts is
26 extended, and maintenance costs are reduced.

27 [0049] A stable high temperature arc is formed between the cathode torch 112 and the

1 anode torch 122, and spray material can be fed directly into the arc. The spray material
2 is completely melted by the high temperature arc column. The arc starting and ending
3 points are protected by inert gas, so that air or oxygen can be used for the plasma gas
4 introduced through the accelerator nozzle 114.

5 [0050] A plasma trimming function 128 is used for twin anode α . Plasma trimming
6 trims the heat of the plasma jet that does not contribute to melting of the spray material,
7 and reduces the thermal load on the substrate material and film to make spraying at short
8 distances possible.

9 [0051] While one kind of plasma spray coating apparatus is shown in Figure 1, one
10 skilled in the art will recognize that other kinds of coating apparatus can be used to carry
11 out the present invention as well. With the understanding of the information presented
12 subsequently herein, one of skill in the art of plasma spray coating and flame spray
13 coating can, with minimal experimentation, carry out the invention using varying coating
14 deposition equipment.

15 [0052] Figures 2A, 2B, and 2C show comparative photomicrographs 200, 210, and
16 220 of the upper surface of an as-coated plasma sprayed yttrium oxide coating having a
17 thickness of about 200 μm , which was deposited using the technology prior to the present
18 invention. The photomicrographs are at magnifications of 300X, 1000X, and 5000X,
19 respectively. The flaky surface texture, which would enable direct particulate formation
20 is readily apparent at all of the magnifications, but particularly at the 5000X
21 magnification.

22 [0053] Figures 2D, 2E, and 2F show photomicrographs 230, 240, and 250 of the
23 surface of the as-coated plasma sprayed yttrium oxide coating illustrated in Figures 2A
24 through 2C after exposure to a reducing chemistry plasma. Figure 2D is at a
25 magnification of 300X, Figure 2E is at a magnification of 1000X, and Figure 2F is at a
26 magnification of 5000X. The reducing plasma recipe was and is as shown in Table One,
27 for the data in Figures 2, 3, and Figure 7B, in a 300 mm eMaxTM CT+ chamber of the

1 kind available from Applied Materials, Inc., Santa Clara, California. The test specimen
 2 substrate evaluated was located on the wafer and then put at the ESC location within the
 3 processing chamber. It is clear that a large amount of the flaky topography which was
 4 illustrated in Figures 2A, 2B, and 2C has been removed during exposure to the reducing
 5 plasma. It is likely that the material which was removed is accountable for particulates
 6 which appear on the surface of a device-containing semiconductor structure processed
 7 using the reducing chemistry plasma.

8 [0054] TABLE ONE

Step	Ar	H ₂	CH ₃ F ₃	O ₂	CF ₄	CHF ₃	CO	N ₂	Press	RF H	RF L	RF S	B fld
	SCCM	SCCM	SCCM	SCCM	SCCM	SCCM	SCCM	SCCM	mTorr	W	W	W	G
STAB 1				14	150	50			200				
B/S				14	150	50			200	300	300		
Pump	800								FO*				
CHMO		250						200	30	750		500	
STAB 2				26	100	100			50				
ME				26	100	100			50	700	300		
STAB 3			40	28		50	200		250				
OE			40	28		50	200		250	1000			
STAB 4				2020					250				50
ICC HP				2020					250			2500	50
ICC LP				2020					50			2500	50
Pump Purge	1500								FO*				

* Fully Open

The substrate temperature during exposure to the processing recipe shown above was about 25 °C.

1 [0055] It is readily apparent that the flaky topography has been removed from the
2 yttrium oxide coating surface during exposure to the plasma, as illustrated by comparing
3 Figure 2C with Figure 2F. This, in combination with a chemical composition of the
4 particulates found on processed semiconductor device surfaces confirmed that the bulk
5 of particulates were generated from the yttrium oxide coating.

6 [0056] A study in which the spray-coated yttrium oxide layer was examined as the
7 depth into the coating thickness was increased, showed that the overall crystalline
8 structure of the yttrium oxide and the porosity of the yttrium oxide coating was relatively
9 constant throughout the thickness of the coating. However, as is illustrated by a
10 comparison of the Figures 2A - 2C with 2D - 2F, it would be possible to avoid an initial
11 heavy particle generation period when a newly-coated apparatus is introduced into a
12 process chamber by removing the flaky upper surface of the as coated apparatus prior to
13 using the apparatus to produce semiconductor devices.

14 [0057] The flaky upper surface could be removed by exposure to the very reducing
15 plasma which was described with respect to Figures 2D through 2F. However, this would
16 require approximately 50 hours of exposure to the plasma, so this was not practical.
17 Instead, the surface of the yttrium oxide plasma spray coated apparatus was polished
18 using a lapping technique commonly known in the art for polishing ceramic materials.
19 Figures 3A, 3B, and 3C show photomicrographs 300, 310, and 320 of the surface of a
20 lapped (polished) as-coated plasma sprayed yttrium oxide coating at magnifications of
21 300X, 1000X, and 5000X respectively. It is readily apparent that the flaky material has
22 been removed from the upper surface of the coating.

23 [0058] Figures 3D, 3E, and 3F show photomicrographs 330, 340, and 350 of the
24 surface of the lapped (polished) plasma sprayed yttrium oxide coating illustrated in
25 Figures 3A through 3C after exposure to a reducing chemistry plasma. Figure 3D is at a
26 magnification of 300X, Figure 3E is at a magnification of 1000X, and Figure 3F is at a
27 magnification of 5000X. The reducing plasma was produced in the manner described in

1 Table One. The exposure time was 50 hours. It is readily apparent that the flaky
2 topography has been removed from the yttrium oxide coating surface during exposure to
3 the plasma, as illustrated by comparing Figure 3C with Figure 3F. However, as can be
4 seen from Figure 3F, the exposed coating surface (as the gradual erosion of the protective
5 layer of yttrium oxide occurs) over processing time in a corrosive environment is still
6 relatively susceptible to particulate formation, due to the cracks in the surface and the
7 grain structure in general of the spray coated ceramic material. A further improvement in
8 the spray coated yttrium oxide, to provide a dense and porosity-reduced body structure
9 and a smooth and compact coating surface would be helpful in reducing particulate
10 generation.

11 **[0059]** Another embodiment of the present invention pertains to improvement of the
12 spray coating technique, to obtain a more dense spray coating which would be less
13 susceptible to attack by reducing plasmas. After considerable experimentation, where
14 numerous variables of the plasma spray coating process were examined, it was
15 discovered that a substantial, unexpected reduction in porosity and surface roughness of
16 the spray-coated yttrium oxide surface could be obtained by using a smaller particle size
17 yttrium oxide powder feed to the plasma spray coating apparatus which was used to apply
18 the coating to the aluminum alloy substrate.

19 **[0060]** For example, the average, conventional effective particle diameter of yttrium
20 oxide powder fed to the plasma spray-coating apparatus prior to the present invention was
21 larger than 25 μm in diameter. Empirical data was developed which showed that a
22 reduction in this average powder diameter to about 22 μm or smaller, typically ranging
23 between about 15 μm and about 0.1 μm , significantly reduced the porosity of the yttrium
24 oxide coating produced on the aluminum alloy substrate surface.

25 **[0061]** Table Two, below shows the improvement in the physical properties of a
26 plasma sprayed yttrium oxide coating, which properties were achieved using an
27 embodiment of the present invention in which the size of the yttrium oxide powder feed

1 to the plasma spray coating apparatus was changed in the manner described above.

2 [0062] TABLE TWO

Coating Deposition Technique	Coating Thickness		Coating Surface Roughness Ra		Break Down Voltage	HCl Bubble Test*	Porosity **	Hardness ***
	(mil)	(μm)	$\mu\text{-inch}$	μm				
Prior Technique	8	200	200	5.0	750	7.5 - 8	1.5 to 4	≤ 4
Present Invention Embodiment	8	200	51.2	1.28	875	> 10	<1.5 to 0.15	4.1

*The bubble test was performed to an Applied Materials Technical Specification, Part No. 0250-39691, which is generally known in the semiconductor industry. Currently, the failure standard for this test is the appearance of 4 hydrogen bubbles per second on a continuous basis.

** The volume porosity of the yttrium oxide coating was measured using an Image-Pro PLUS, version 6.0 (available from Media Cybernetics, Bethesda, MD) applied to a photomicrograph of the surface of the coating.

*** The hardness was measured using the Vickers Hardness (Hv) test, and the HV value was calculated based on ASTM E92-82.

3 [0063] As illustrated in Table Two, for a 200 μm thick coating, the average porosity of
 4 the yttrium oxide coating produced using the conventional 25 μm diameter yttrium oxide
 5 powder ranged from about 1.5 % to about 4%, while the average porosity of the yttrium
 6 oxide coating produced using a size-reduced equivalent diameter yttrium oxide powder
 7 size ranged from less than 1.5 % down to about 0.15 %. By way of example, a 15 μm
 8 equivalent diameter powder produced a coating having a porosity of about 0.47 %. This
 9 decrease in porosity is particularly significant as an indicator of the ease of
 10 attack of the plasma containing reducing species. In addition, the average surface
 11 roughness Ra of the yttrium oxide coating produced using the conventional 25 μm
 12 diameter powder was about 200 $\mu\text{-inch}$ Ra (5.0 μm Ra) compared with an average

1 surface roughness of only 51.2 μ -inch Ra (1.28 μ m Ra) for the yttrium oxide coating
2 produced using the size-reduced 15 μ m diameter yttrium oxide powder feed to the
3 plasma spray coating apparatus. Using the standard HCl bubble test, a 200 μ m thick
4 yttrium oxide coating produced using the conventional 25 μ m equivalent diameter
5 powder performed well for about 7.5 - 8 hours, while a 200 μ m thick yttrium oxide
6 coating produced using the size-reduced 15 μ m diameter powder performed well for a
7 time period in excess of 10 hours. Further, the break down voltage (V_{BD}) for the yttrium
8 oxide coating produced using the conventional 25 μ m equivalent diameter powder was
9 only 750 V/mil, while the break down voltage for the yttrium oxide coating produced
10 using the size-reduced 15 μ m equivalent diameter powder was higher than 875 V/mil.
11 One of skill in the art can select any of the apparatus commonly used in the industry for
12 spray coating of yttrium-comprising coatings and obtain similar relative results with
13 minimal experimentation.

14 [0064] Figure 4A is a comparative example which shows a graph 400 of the range of
15 the surface roughness in microns from a centerline 410 along the surface of an as-coated
16 plasma sprayed yttrium oxide coating produced using the technology available prior to
17 the present invention. The distance of travel along the surface is shown in millimeters on
18 axis 402, while the height above or depth beneath the centerline of the range in microns is
19 shown on axis 404. The range in surface distance from the centerline of the range was
20 from about + 23 microns to about - 17 microns.

21 [0065] Figure 4B shows a graph 420 of the range of the surface roughness in microns
22 from a centerline 430 along the surface of an as-coated plasma sprayed yttrium oxide
23 coating. The plasma-sprayed coating was produced using the embodiment of the
24 invention in which a reduced effective diameter powder is fed to the plasma spraying
25 apparatus. The distance of travel along the surface is shown in millimeters on axis 422,
26 while the height above or depth beneath the centerline of the range in microns is shown

1 on axis 424. The range in surface distance from the centerline of the range was from
2 about + 6 microns to about - 4.5 microns. This significant change in the range of the
3 height and depth of the surface variation substantially reduces the surface area of the
4 protective coating which is exposed to the corrosive reducing plasma.

5 [0066] Figures 5A and 5B are comparative photomicrographs 510 and 520, which
6 show a top view of the morphology of a plasma sprayed yttrium oxide coating prepared
7 using plasma spray technology prior to the present invention, at magnifications of 200X
8 and 1000X, respectively. Figures 5C and 5D are photomicrographs 530 and 540, which
9 show a top view of the morphology of plasma sprayed yttrium oxide coating prepared
10 using the embodiment of the present invention in which a reduced effective diameter
11 powder is fed to the plasma spraying apparatus. Figures 5C and 5D are at magnifications
12 of 200X and 1000X, respectively. A comparison of Figures 5A and 5B with Figures 5C
13 and 5D illustrates the reduction in surface area which is subject to attack by the plasma.
14 The surface morphology in Figures 5A and 5B shows increased vulnerability to attack
15 (compared with the surface morphology in Figures 5C and 5D) by a reducing plasma, due
16 to the increased exposure in a two dimensional direction by the vertical variation in the
17 height and depth of the surface, as well as the increased surface area due to the spherical
18 structures extending above the coating surface.

19 [0067] Figure 6A is a comparative photomicrograph 600 showing a cross-sectional
20 side view of an aluminum alloy substrate 602 having a yttrium oxide coating 606
21 deposited over the surface 604 of the aluminum alloy substrate 602. This comparative
22 photomicrograph shows the characteristics of the structure which was prepared using
23 plasma spray technology prior to the present invention, to produce a yttrium oxide
24 coating having a thickness of about 200 μm . The magnification in the photomicrograph
25 is 200X. The aluminum alloy substrate 602 of the test specimen is shown at the base of
26 the photomicrograph 600. The roughness of the surface 604 of the aluminum alloy is
27 clearly defined. The general porosity of the spray coated yttrium oxide 606 is also

1 apparent, as is the surface roughness of the coating which was prepared using the
2 prior art plasma spray technology, where the conventional 25 μm average effective
3 diameter yttrium oxide powder was fed to the plasma spray coater.

4 [0068] Figure 6B is a photomicrograph 610 which shows the improvement in the
5 plasma spray-coated yttrium oxide coating achieved when the reduced effective diameter
6 powder size yttrium oxide is fed to the plasma sprayer. Figure 6B shows a cross-
7 sectional side view of an aluminum alloy substrate 612 having a yttrium oxide coating
8 616 deposited over the surface 614 of the aluminum alloy substrate. Again, the
9 magnification is 200X. The aluminum alloy substrate 612 of the test specimen is shown
10 at the base of the photomicrograph 610. The roughness of the surface 614 of the
11 aluminum alloy is clearly defined, and is similar to that shown in Figure 6A. The general
12 porosity of the spray coated yttrium oxide 616 is considerable less than that for the
13 coating produced using the prior art process, which is shown in Figure 6A. The surface
14 roughness of the coating which was prepared using the embodiment of the present
15 invention is far smoother than that produced using the prior art plasma spray technology.
16 Photomicrographs 600 and 610 further support the data contained in the above Table
17 Two.

18 [0069] Figure 7A shows a block diagram 700 which compares an erosion rate for a for
19 various yttrium oxide-comprising substrates. The erosion rate for each of the yttrium
20 oxide-comprising substrates is shown in $\mu\text{m/hr}$ on axis 702 of the block diagram 700.
21 Block 704 shows the erosion rate for a plasma sprayed yttrium oxide coating (over an
22 aluminum alloy substrate) applied using the previous spray coating method, which
23 employed yttrium oxide particle feed to the plasma sprayer which had an average
24 effective particle diameter of 25 μm or larger. Block 706 shows the erosion rate for a
25 bulk specimen substrate (of the kind previously known in the art) of yttrium oxide 706.
26 Block 708 shows the erosion rate for a plasma sprayed yttrium oxide coating (over an
27 aluminum substrate, where the yttrium oxide coating was applied using an embodiment

1 of the present invention employing the reduced size powder yttrium oxide feed to the
 2 plasma spraying apparatus. Each of these test substrates was exposed to the same plasma
 3 containing reducing species. The plasma processing recipe used to produce the data
 4 shown in Figure 7A is shown below in Table Three. The average temperature during the
 5 processing ranged between about 20 °C and 90 °C, depending on the process step. The
 6 time period of exposure to the plasma was 87 hours. We determined, unexpectedly, that
 7 a spray-coated yttrium oxide processing component of the kind produced using the
 8 reduced powder yttrium oxide feed to the plasma spraying apparatus generated fewer
 9 particulates than a solid yttrium oxide component. This is thought to be due to the fact
 10 that the solid yttrium oxide component required the use of a sintering additive. Use of a
 11 sintering additive, which produces an intergranular glassy phase is a source of particulate
 12 formation.

13 [0070]

TABLE THREE

Step	Ar	N ₂	CH ₂ F ₂	O ₂	CF ₄	CHF ₃	Bias Power	Source Power	Press	NSTU *	CSTU in/out **	He in/out ***
	SCCM	SCCM	SCCM	SCCM	SCCM	SCCM	W	W	mTorr	ratio	A _{app}	SCCM
BARC					150	30	1000		300	1.3	2/0	10-10
TRANS		400					100	100	220	1.35	14/0	10-10
ORG		400					400	1200	220	1.35	14/0	10-10
TRANS					175	15	100	100	150	3	10/-2	10-10
ME					175	15	500	1500	150	3	10/-2	10-10
TRANS	500			250			100	100	10	1.35	10/0	20-20
PET				500			200	1000	10	1.35	10/0	20-20

* NSTU: Neutral Species Tuning Unit (ratio).

**CSTU: Changed Species Tuning Unit (Ampere).

*** Helium coolant feed to the substrate support platform, to the inside fluid circulation ring and to the outside fluid circulation ring at the support platform surface.

1 [0071] Figure 7B shows a block diagram 720 which compares an erosion rate for a
2 series of bulk materials, each having a different chemical composition. Each of these test
3 specimens was exposed to the same plasma containing reducing species per the recipe
4 provided in Table One, in the 300 mm eMax CT+ processing chamber. The performance
5 of YAG bulk material confirmed the theories about the avoidance of the formation of
6 $Y(OH)_3$ in a reducing plasma as a method of improving erosion resistance. Block 724
7 represents an HF01 substrate; Block 726 represents an NB04 substrate; Block 728
8 represents a Y-ZrO₂ substrate; Block 730 represents an NB01 substrate; Block 732
9 represents an HPM substrate; Block 734 represents a YA3070 substrate; Block 736
10 represents a Y₂O₃ substrate; Block 738 represents a YZ20 substrate; and Block 740
11 represents a YAG substrate. Blocks 736, 738, and 740 are of the highest interest, because
12 they represent bulk substrates for Y₂O₃, a Y₂O₃-ZrO₂ solid solution containing 20 atomic
13 % ZrO₂, and YAG, respectively. These three materials have been shown to be
14 particularly resistant to a reducing plasma when applied by plasma spray coating in
15 accordance with one of the embodiments of the present invention.

16 [0072] Figure 8 shows a Table 800, which lists the chemical compositions of various
17 starting powders of various bulk materials, the erosion rates of which are illustrated in
18 Figure 7B.

19 [0073] Figure 9 shows a phase diagram 900 which illustrates the chemical
20 compositions of starting powders and phases in the final materials formed, where the
21 materials are listed in Table 800.

22 [0074] While working to improve the performance of the yttrium oxide coating, the
23 discovery was made that the mechanism of attack of the yttrium oxide surface is through
24 the formation of yttrium hydroxide, $Y(OH)_3$. When reactive plasma species of hydrogen
25 and oxygen are present, the $Y(OH)_3$ compound is formed. When reactive plasma species
26 of hydrogen, fluorine, and oxygen are present, the $Y(OH)_3$ compound is formed. In
27 theory, by looking at the thermodynamics data (Gibbs formation free energy) for various

1 compounds, it is possible to determine the probability that the $Y(OH)_3$ compound will be
2 formed. In experimentation, high resolution XPS has been used to detect the formation
3 of $Y(OH)_3$. Experimentation has shown that the use of (Yttrium Aluminum Garnet),
4 which is commonly in a $Y_3Al_5O_{12}$ form, and also the use of Y_2O_3 - ZrO_2 solid solution
5 avoids the formation of $Y(OH)_3$. In addition, further study has indicated that YF_3 is
6 thermodynamically stable and resistant to the formation of $Y(OH)_3$, making this material
7 desirable for use as a protective coating in an plasma environment which contains
8 reducing active species. Thus YAG, Y_2O_3 - ZrO_2 solid solution, or YF_3 , or combinations
9 thereof, are excellent materials for use as a protective coating in a plasma environment
10 which contains reducing active species. To provide an advantageous porosity in the
11 range of about 0.5 % or less, and a break down voltage (V_{BD}) of 875 or greater, the
12 average (equivalent diameter) particle size of the powder used to deposit a plasma
13 sprayed YAG, Y_2O_3 - ZrO_2 solid solution, or YF_3 coating ranges from about 22 μm to
14 about 5 μm . Again, equivalent diameter particle sizes down to about 0.1 μm may be used
15 if the spray-coating apparatus can be adapted to handle particles of this size. Use of this
16 size-reduced powder should reduce porosity of a plasma-sprayed coating and provide a
17 more dense structure in the same manner as observed with the use of the size-reduced
18 powder in plasma-sprayed Y_2O_3 -comprising coatings.

19 [0075] While the foregoing is directed to embodiments of the present invention,
20 other and further embodiments of the invention may be devised in view of the present
21 disclosure, without departing from the basic scope of the invention, and the scope thereof
22 is determined by the claims which follow.

[0076]

CLAIMS

[0077] We claim:

- 1 1. An article which is resistant to corrosion or erosion by chemically active
2 reducing plasmas, said article comprising a metal or metal alloy substrate having on its
3 surface a spray coated yttrium-comprising ceramic material, wherein a porosity of said
4 ceramic coating is less than 1.5 %.
- 1 2. An article in accordance with Claim 1, wherein said porosity ranges from less
2 than 1.5 % to about 0.1 %.
- 1 3. An article in accordance with Claim 2, wherein said porosity ranges from about
2 1% to about 0.1 %.
- 1 4. An article in accordance with Claim 1, wherein an exposed surface of said spray
2 coated yttrium-comprising ceramic material has a surface roughness of less than about
3 3 $\mu\text{m Ra}$.
- 1 5. An article in accordance with Claim 3, wherein said surface roughness ranges
2 from less than about 1.5 $\mu\text{m Ra}$ to about 0.6 $\mu\text{m Ra}$.
- 1 6. An article in accordance with Claim 1, wherein the break down voltage of said
2 spray-coated yttrium-comprising ceramic material is at least above 650 V/mil.
- 1 7. An article in accordance with Claim 6, wherein said break down voltage ranges
2 from about 650 V/mil to greater than 900 V/mil.

- 1 8. An article in accordance with Claim 1 or Claim 4, or Claim 6, wherein said
2 spray coated yttrium-comprising ceramic material has a thickness ranging from about 5
3 μm to about 400 μm .
- 1 9. An article in accordance with Claim 8, wherein said material thickness ranges
2 from about 25 μm to about 300 μm .
- 1 10. An article in accordance with Claim 8, wherein said yttrium-comprising
2 ceramic material is selected from the group consisting of Y_2O_3 , Y_2O_3 - ZrO_2 solid
3 solution, YAG, YF_3 and combinations thereof.
- 1 11. A method of fabricating an article which is resistant to corrosion or erosion by
2 chemically active reducing plasmas, comprising: fabricating said article by plasma
3 spray-coating a metal or metal alloy substrate with a yttrium-comprising ceramic
4 material, wherein said yttrium-comprising ceramic material is in the form of a powder
5 having an average equivalent diameter ranging from about 22 μm to about 0.1 μm .
- 1 12. A method of fabricating an article in accordance with Claim 11, wherein said
2 powder has an average equivalent diameter ranging from about 15 μm to about 5 μm .
- 1 13. A method of fabricating an article in accordance with Claim 11 or Claim 12,
2 wherein said yttrium comprising material is selected from the group consisting of Y_2O_3 ,
3 Y_2O_3 - ZrO_2 solid solution, YAG, YF_3 and combinations thereof.
- 1 14. A method in accordance with Claim 11, wherein said yttrium comprising
2 material is selected from the group consisting of Y_2O_3 - ZrO_2 solid solution, YAG, YF_3
3 and combinations thereof.

1 15. A method of fabricating an article which is resistant to corrosion or erosion by
2 chemically active reducing plasmas, comprising: fabricating said article by plasma spray-
3 coating a metal or metal alloy substrate with a yttrium-comprising ceramic material,
4 wherein said yttrium-comprising ceramic material is selected from the group consisting of
5 Y_2O_3 - ZrO_2 solid solution, YF_3 and combinations thereof.

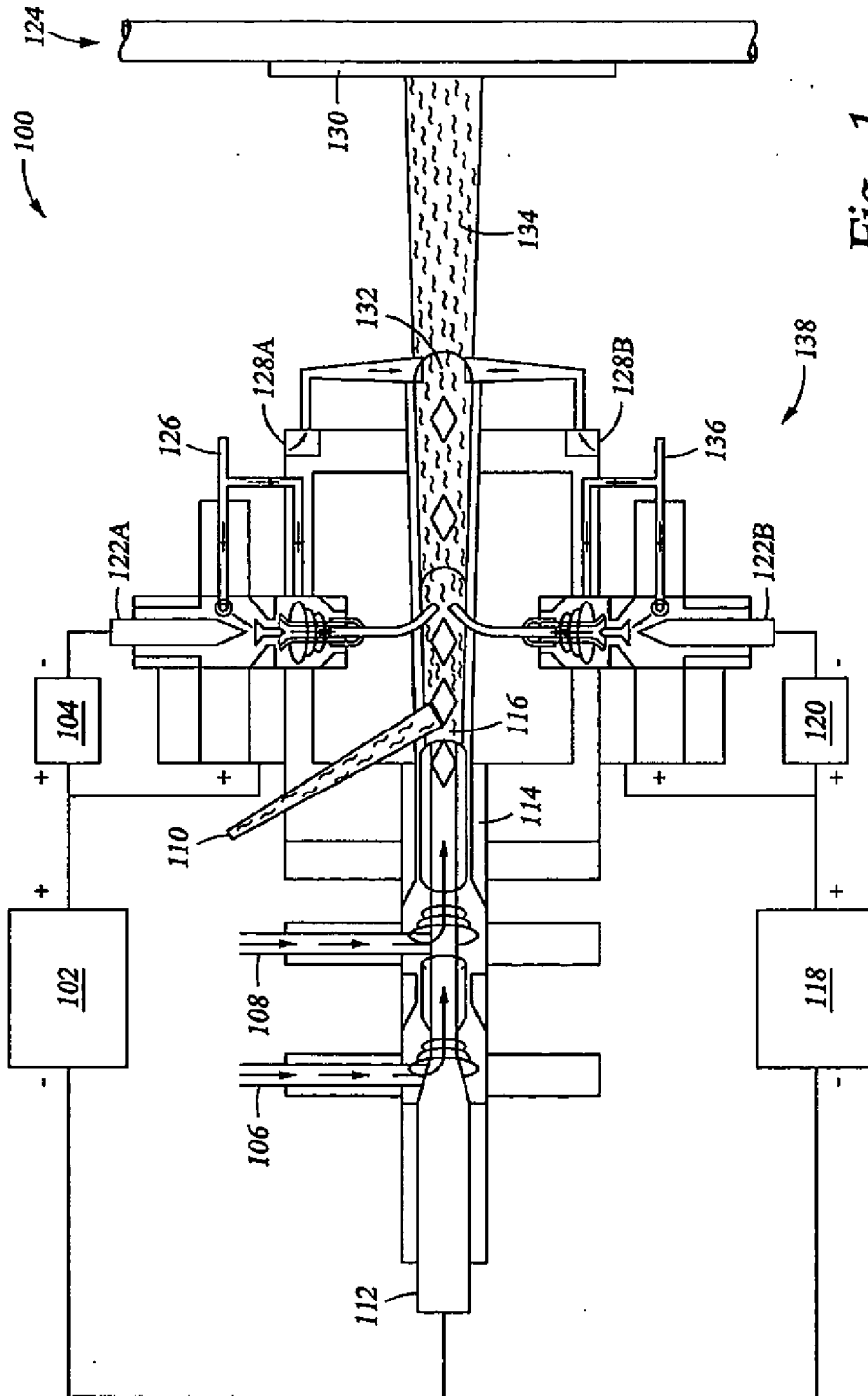


Fig. 1
(PRIOR ART)

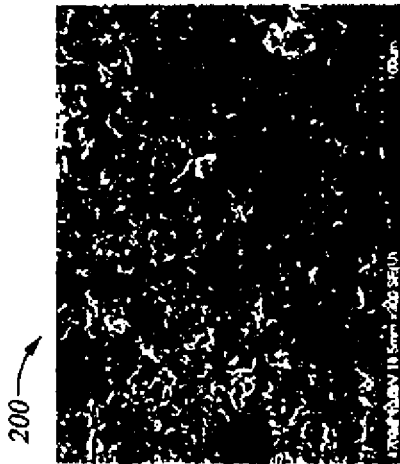
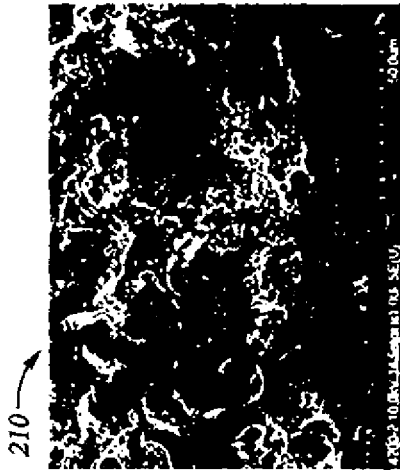


Fig. 2C
(PRIOR ART)

Fig. 2B
(PRIOR ART)

Fig. 2A
(PRIOR ART)

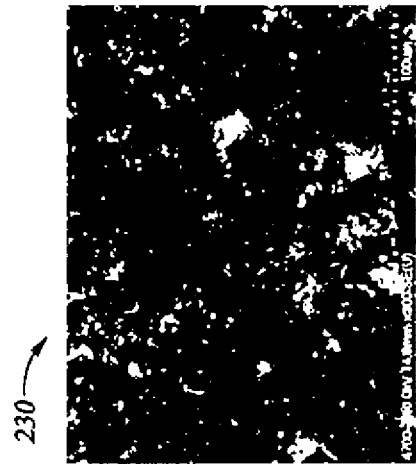
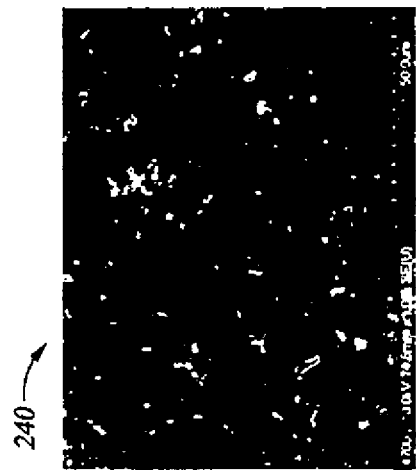


Fig. 2F

Fig. 2E

Fig. 2D

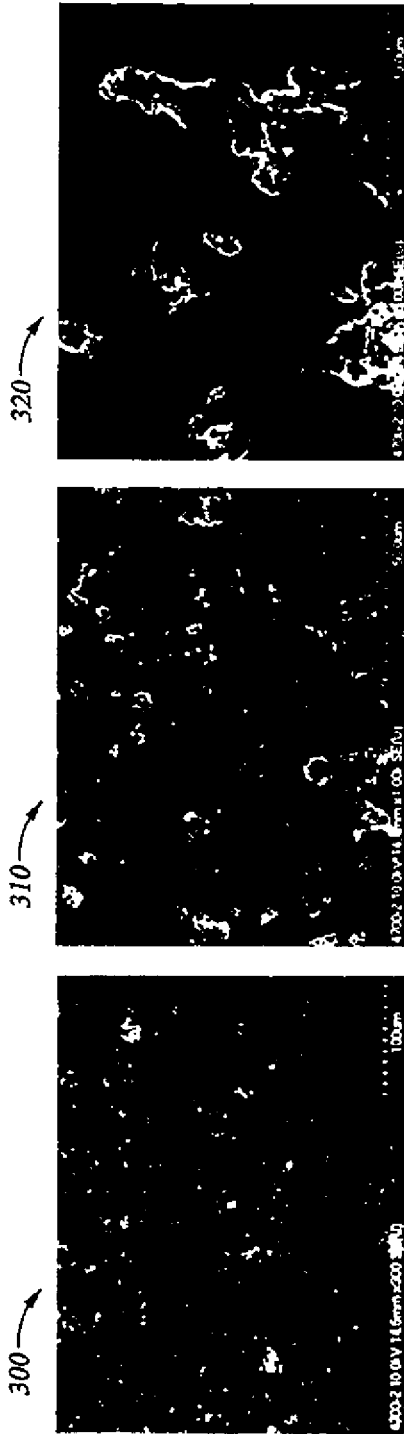


Fig. 3A

Fig. 3B

Fig. 3C

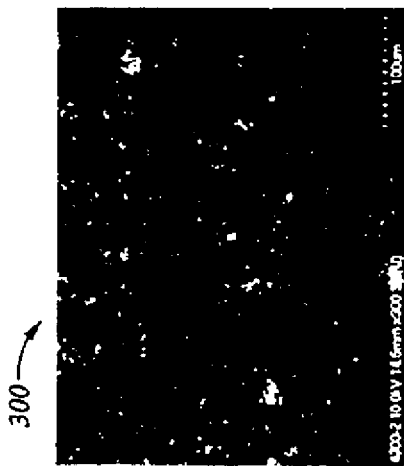


Fig. 3D

Fig. 3E

Fig. 3F

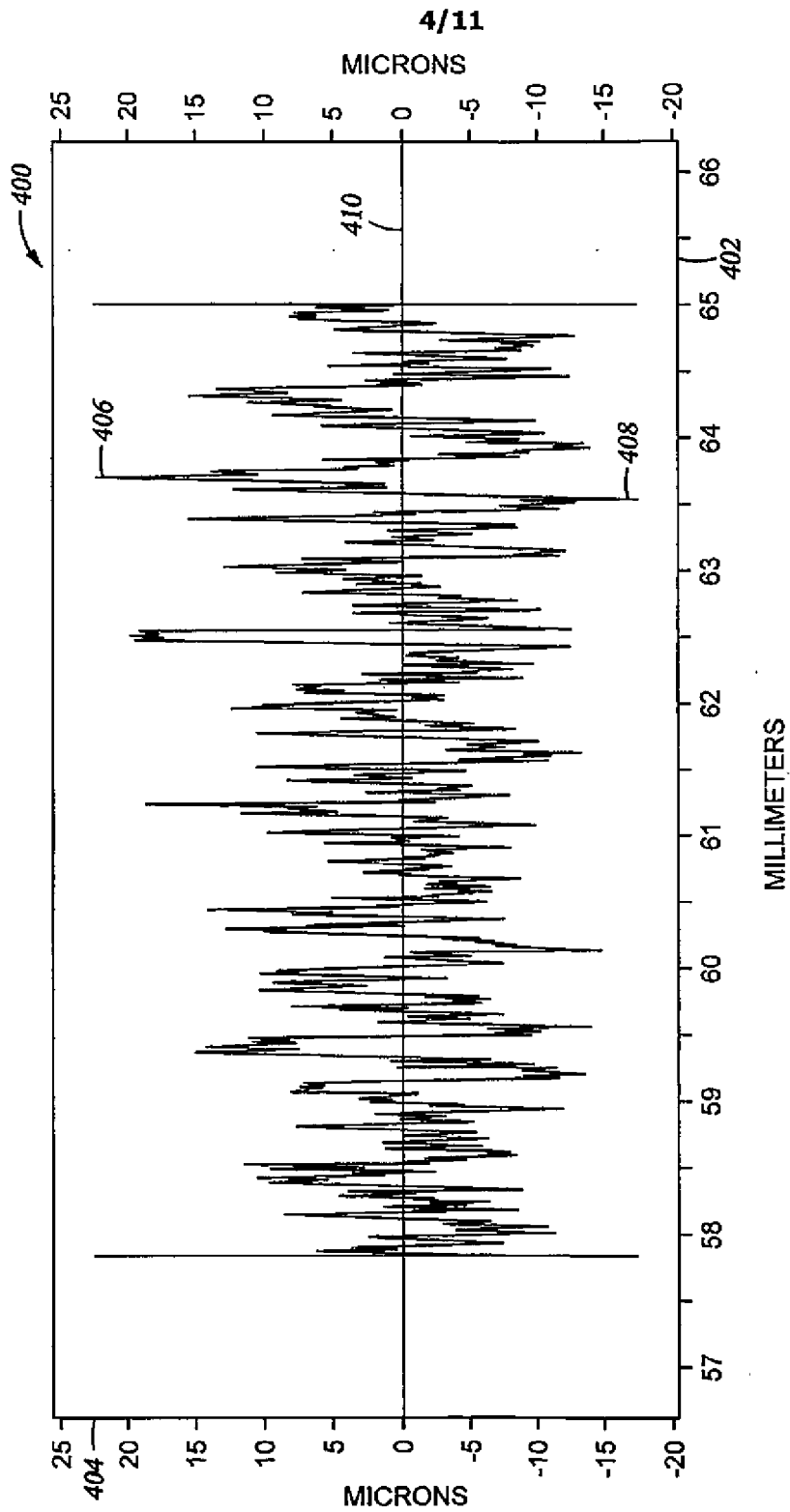


Fig. 4A
(PRIOR ART)

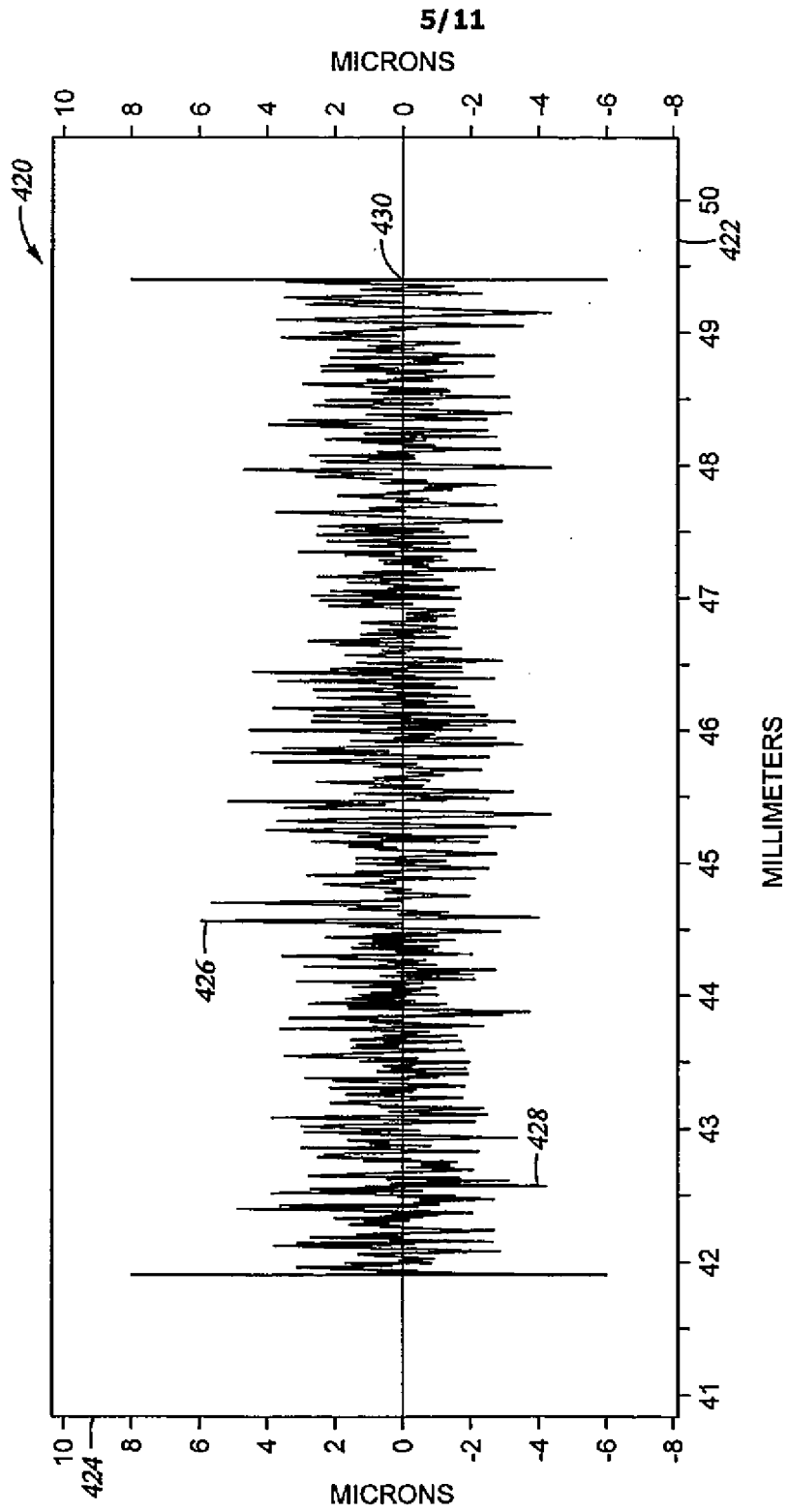


Fig. 4B

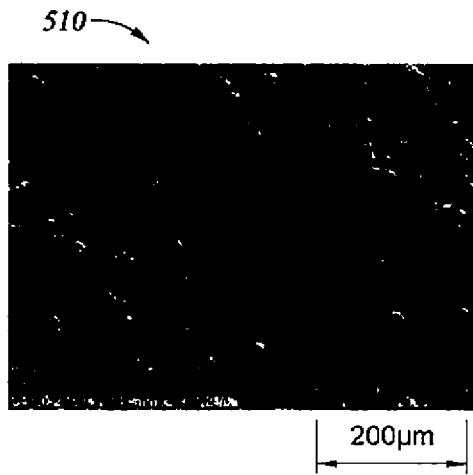


Fig. 5A

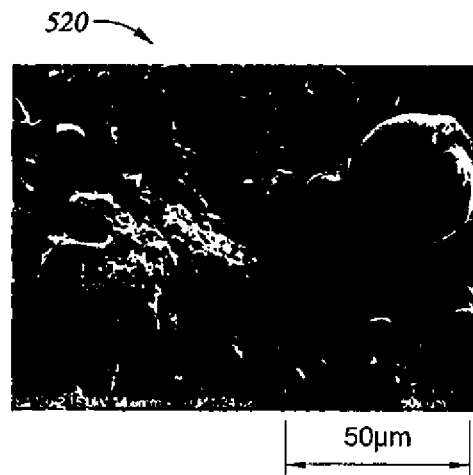


Fig. 5B

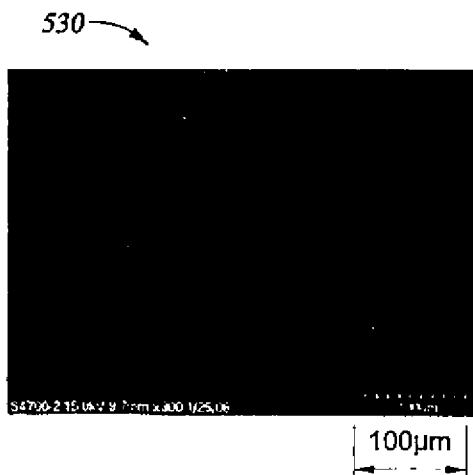


Fig. 5C

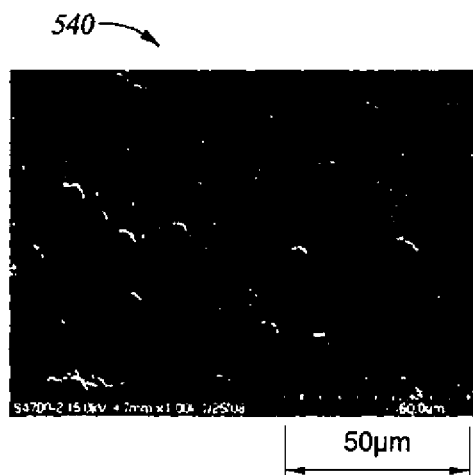


Fig. 5D

7/11

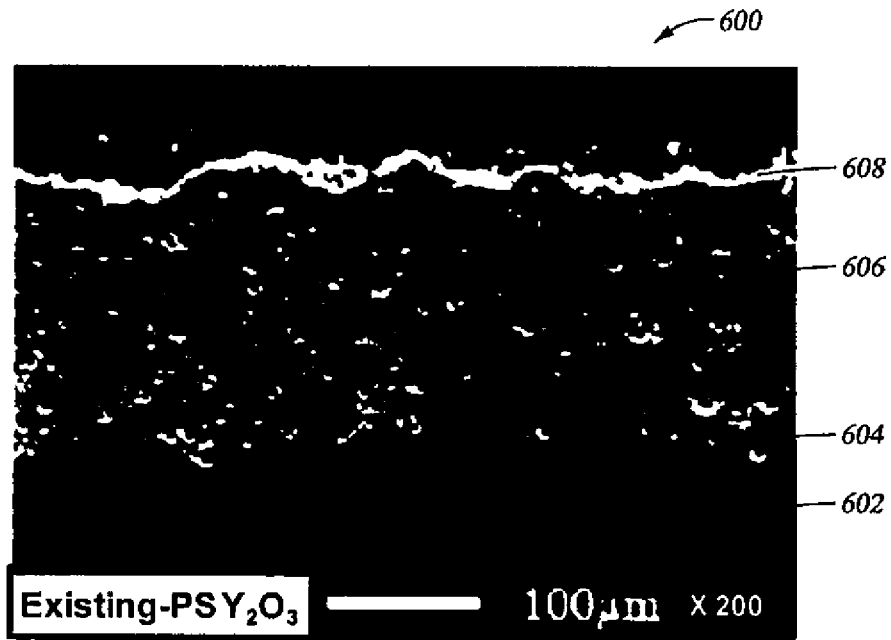


Fig. 6A

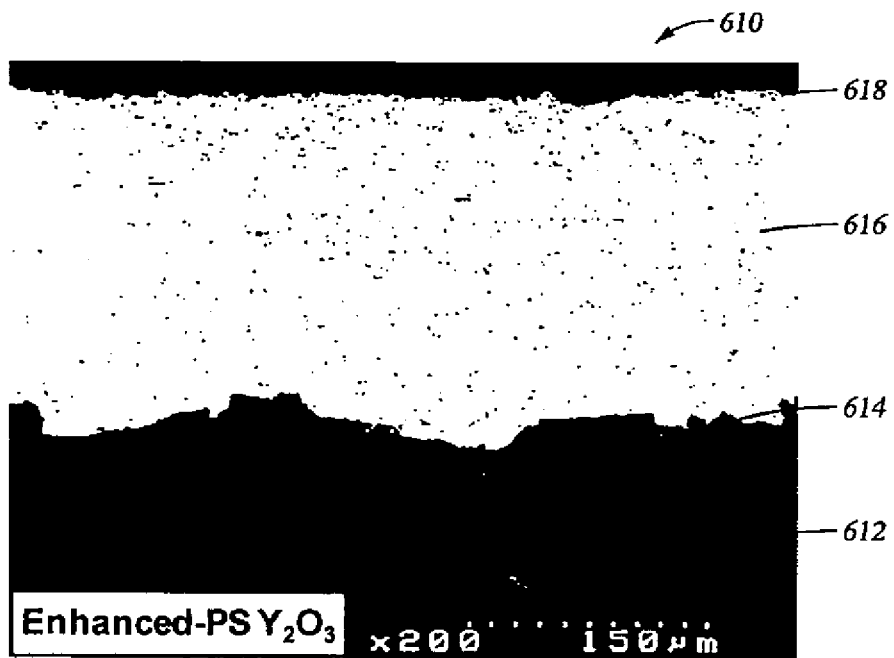


Fig. 6B

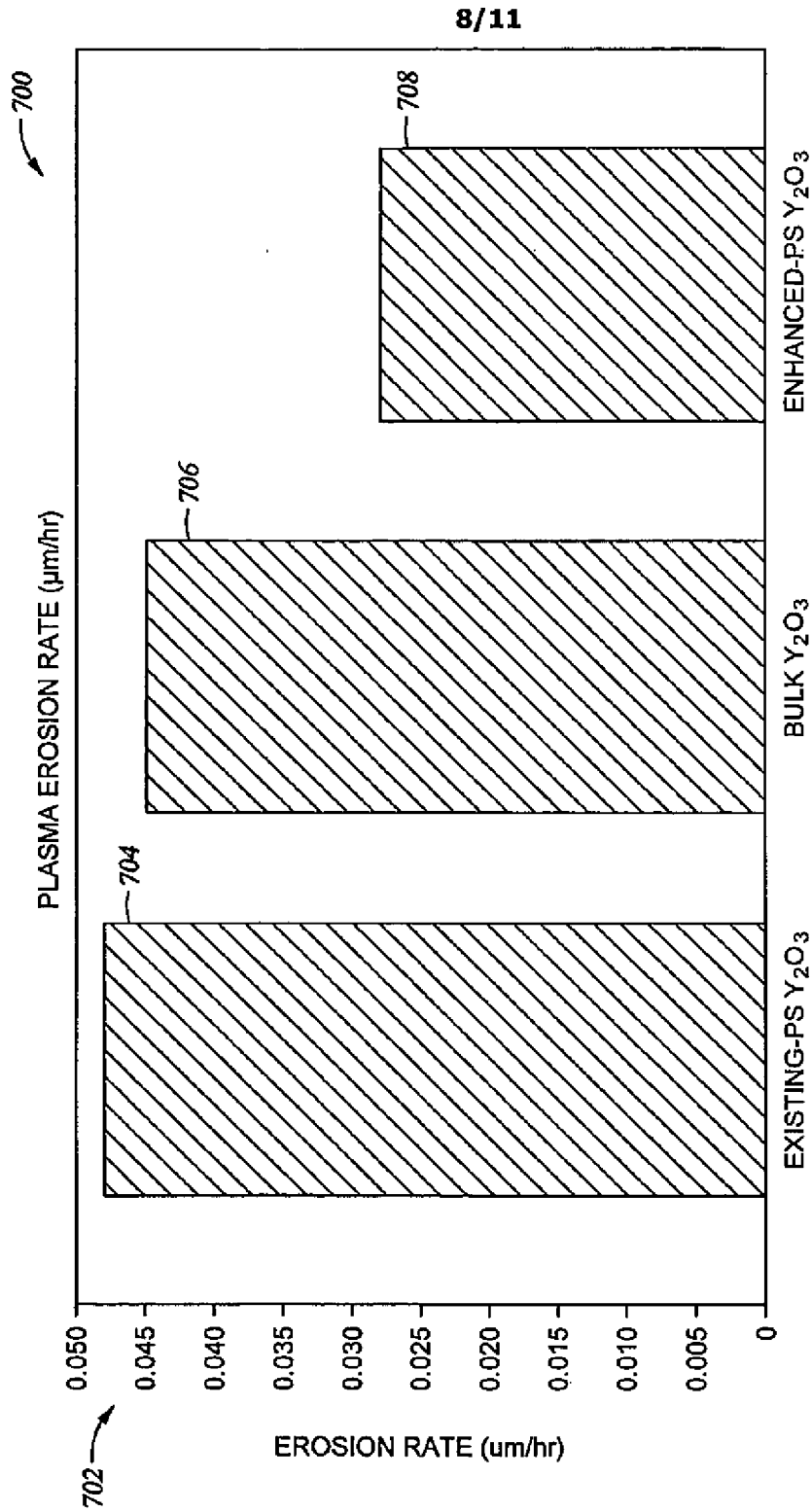


Fig. 7A

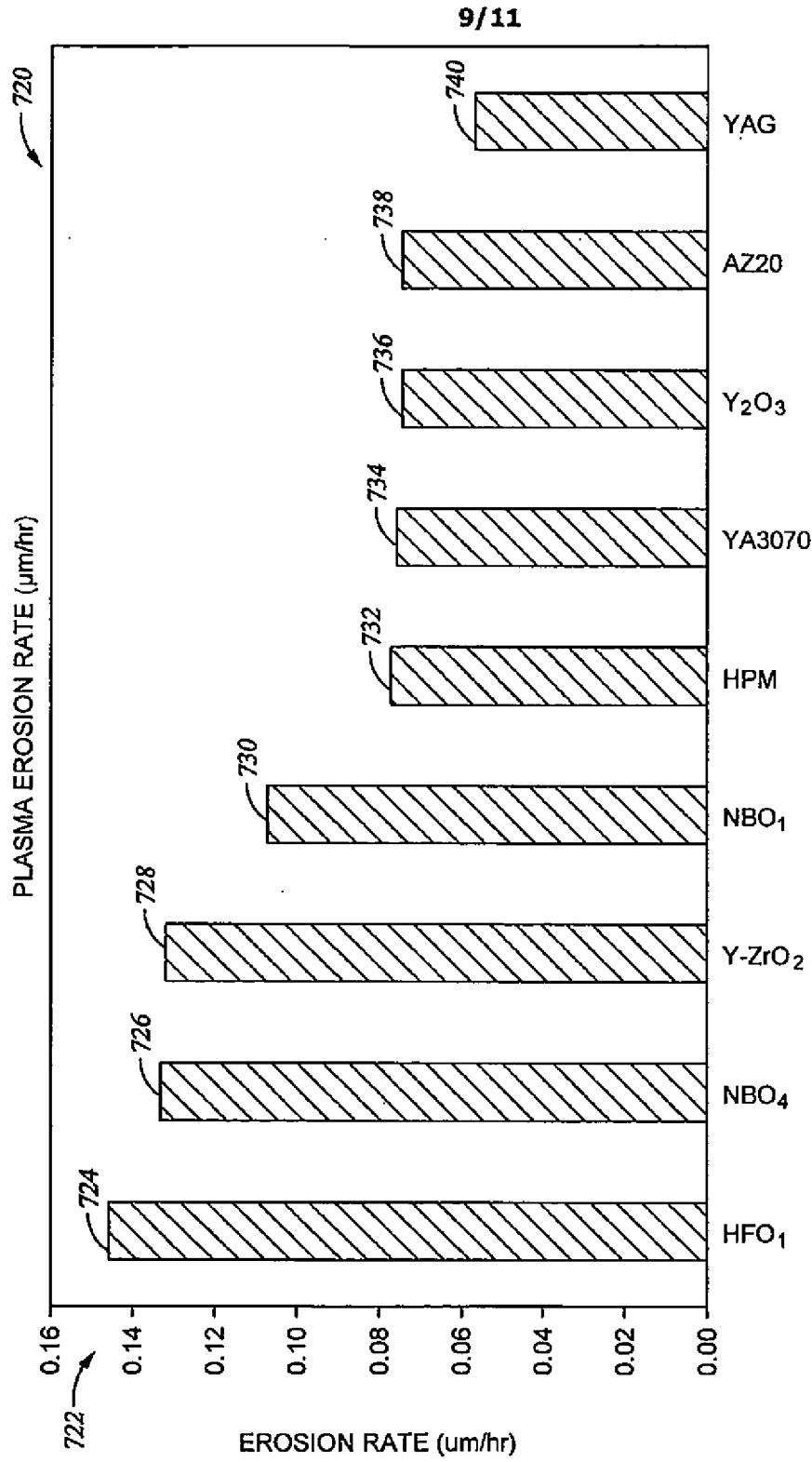


Fig. 7B

10/11

800

EROSION RATE AND CHEMICAL COMPOSITION OF DIFFERENT MATERIALS

NEW NAME	EROSION RATE ($\mu\text{m/hr}$)	COMPOSITION
YAG	0.057	37.5mol% Y_2O_3 62.5mol% Al_2O_3
YZ20	0.074	73.2mol% Y_2O_3 26.8mol% ZrO_2
Y2O3	0.074	100mol% Y_2O_3
YA3070	0.076	8.5mol% Y_2O_3 91.5mol% Al_2O_3
HPM	0.077	63mol% Y_2O_3 , 14mol% Al_2O_3 , 23mol% ZrO_2
NBO1	0.107	70mol% Y_2O_3 , 10mol% Nb_2O_5 , 20mol% ZrO_2
Y-ZrO2	0.132	3mol% Y_2O_3 , 97mol% ZrO_2
NBO4	0.133	60mol% Y_2O_3 , 20mol% Nb_2O_5 , 20mol% ZrO_2
HFO1	0.146	75mol% Y_2O_3 , 20mol% HfO_2 , and 5mol% ZrO_2

Fig. 8

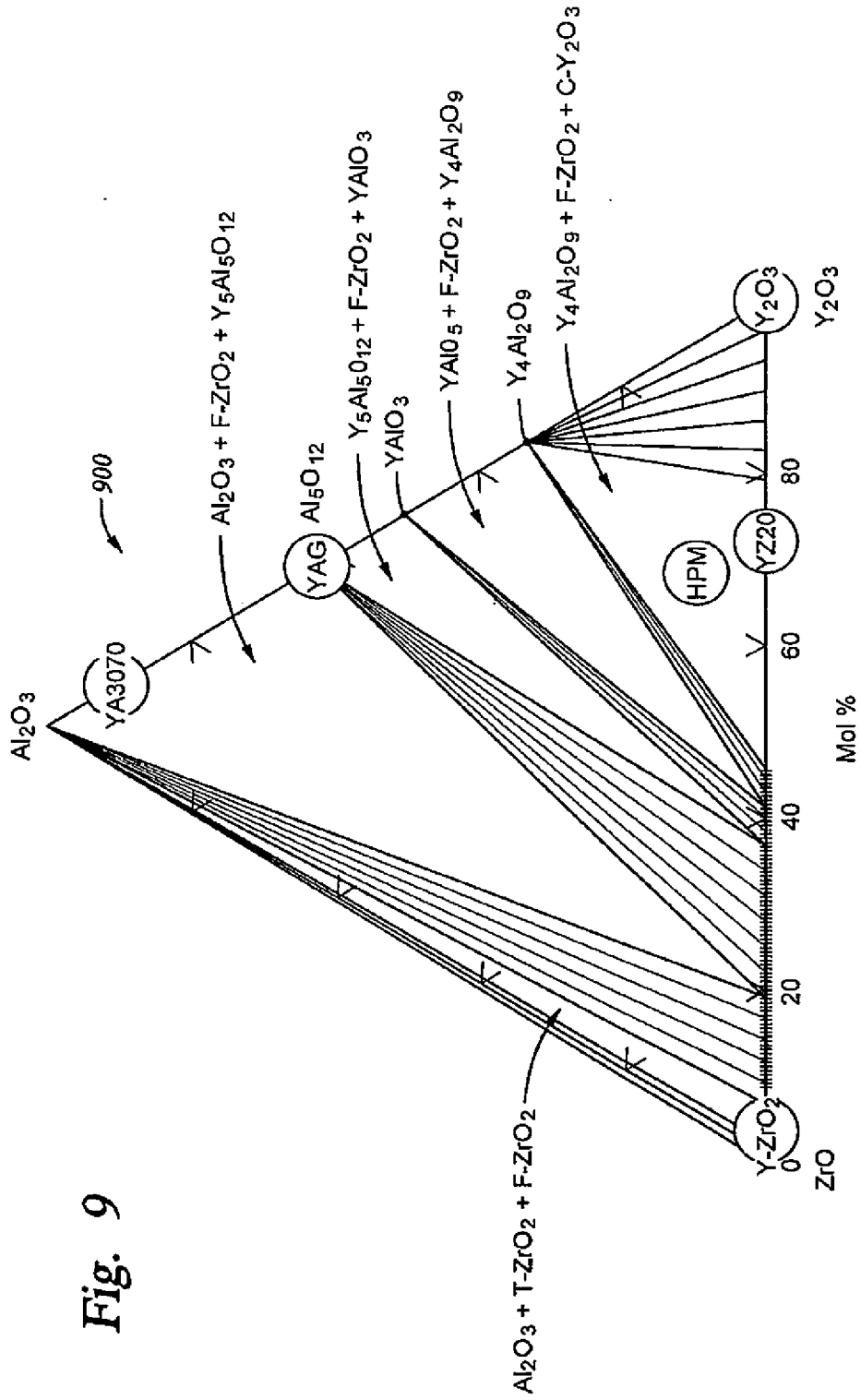


Fig. 9