Embellishments of the invention relate to compositions including a yttrium-based fluoride crystal phase, or a yttrium-based oxyfluoride crystal phase, or an oxyfluoride amorphous phase, or a combination of these materials. The compositions may be used to form a solid substrate for use as a semiconductor processing apparatus, or the compositions may be used to form a coating which is present upon a surface of substrates having a melting point which is higher than about 1600°, substrates such as aluminum oxide, aluminum nitride, quartz, silicon carbide and silicon nitride, by way of example.
**Fig. 1**
Fig. 3A

Al2O3 SUBSTRATE

Fig. 3B

YF3 GLASS-CERAMICS
Plasma chemistry CF$_4$/CHF$_3$

Normalized erosion rate (Al$_2$O$_3$=1)

Fig. 4
Fig. 5

Fig. 6
Fig. 7
SEMICONDUCTOR PROCESSING APPARATUS WITH PROTECTIVE COATING INCLUDING AMORPHOUS PHASE

[0001] This application is a divisional application of U.S. application Ser. No. 12/590,200, entitled “Protective Coatings Resistant To Reactive Plasma Processing”, which was filed on Nov. 3, 2009; which claims priority under U.S. Provisional Application Ser. No. 61/199,127, entitled: “Protective Coatings Resistant To Reactive Plasma Processing”, which was filed on Nov. 12, 2008.

FIELD

[0002] Embodiments of the invention relate to compositions of metal oxyfluoride comprising glazes, glass ceramics, and combinations thereof which are useful as plasma-resistant protective solid substrates or plasma resistant coatings over other substrates. In addition, embodiments of the invention relate to methods of applying bulk materials or coatings of the compositions over a substrate to provide various processing components which are useful as part of reactive plasma processing apparatus.

BACKGROUND

[0003] This section describes background subject matter related to the disclosed embodiments of the present invention. There is no intention, either express or implied, that the background art discussed in this section legally constitutes prior art.

[0004] A glaze is a specialized form of glass and therefore can be described as an amorphous solid. Glazing is the process of coating the part with a layer of glaze. A glass ceramic is a specialized form of ceramics, which is formed first as a glass and then made to crystallize partly through a designed heat treatment which involves controlled cooling.

[0005] Unlike traditional sintered ceramics, glass ceramics do not have pores between crystal grains. The spacing between grains is filled with the glass. Glass ceramics share many properties with both glass and traditional crystalline ceramics. After adjusting the composition of glass ceramics by processing technique, the final material may exhibit a number of advanced properties that the traditional ceramics do not have.

[0006] Glazes and glass ceramics have long been used to provide protective coatings. To form the protective coatings, typically a powder of an oxide, which may be in combination with a non-oxide, is placed into a suspending medium, to which a binder composition may be added, this combination of ingredients produces a slurry which is applied over a substrate which is to be coated, and then the slurry is sintered under controlled temperature and environmental conditions. During sintering, when the fluid coating material is cooled rapidly, typically a glaze is produced; when the coating material is cooled slowly, a glass-ceramic is obtained.

[0007] The physical properties of the coating obtained, such as thermal conductivity, thermal expansion coefficient, hardness, and toughness, for example, can be adjusted by changing the composition of the ceramic powder, and/or the processing technique. The thickness of the coating, for a given application process, may be “fine tuned” by adjusting the slurry viscosity, pH, and binder, for example. Depending on the composition of the coating and the substrate, and the application process, a transition layer may be formed between the substrate and portion of the coating which is in contact with the substrate. A transition layer formed in-situ during application of the coating to the substrate surface may provide better chemical bonding between the substrate and the coating and may also dissipate the stress due to thermal expansion difference between the substrate and the coating.

[0008] To apply a coating, a slurry containing the ceramic powder, suspension medium, binder and possibly dopants of various kinds is typically applied over the surface of a substrate using a technique known in the art, such as painting, dipping, spraying, screen printing, or spin-on, by way of example. The substrate must be able to withstand the sintering temperature required to form the coating. The coating is then sintered at a sufficient temperature and for a period of time to permit the coating to form. The coating performance in a given application is limited by the composition of the coating and the processing conditions used to apply the coating.

[0009] Processing chamber liners and component apparatus present within processing chambers which are used in the fabrication of electronic devices and micro-electromechanical structures (MEMS), for example and not by way of limitation, are frequently constructed from ceramics such as aluminum oxide and aluminum nitride. While the plasma erosion resistance for these materials in a fluorine containing plasma of the kind typically used for etching silicon-containing electronic device structures is better than a number of materials which were used in the processing art even 5 years ago, there is constantly an effort to try to improve the erosion resistance of etch processing components, as a means of extending the lifetime of the processing apparatus and of reducing metal contamination and particle formation during device processing. Not only is the processing apparatus very expensive, the production down time caused by the need to replace apparatus which is not functioning well due to erosion is also very expensive.

[0010] Solid yttrium oxide component structures have demonstrated considerable advantages when used as semiconductor apparatus components in reactive plasma processing. A yttrium oxide solid component substrate typically comprises at least 99.0% by volume yttrium oxide, has a density of at least 4.92 g/cm³, and a water absorbency of about 0.02% or less. The average crystalline grain size of the yttrium oxide is within a range of about 10 μm to about 25 μm. The co-inventors of the present invention developed a yttrium oxide-containing substrate which includes impurities which are equal to or less than the following maximum concentrations: 90 ppm Al; 10 ppm Ca; 5 ppm Cr; 5 ppm Cu; 10 ppm Fe; 5 ppm K; 5 ppm Mg; 5 ppm Na; 5 ppm Ni; 120 ppm Si; and 5 ppm Ti. This yttrium oxide-containing substrate provided improvements over substrates previously known in the art. A yttrium oxide-comprising substrate of this general composition which included up to about 10% by volume of aluminum oxide was also developed.

[0011] In a reactive plasma etch rate test, where the reactive etchant plasma contains plasma species generated from a plasma source gas of CF₃ and CH₃, a solid Yttrium oxide substrate component resists etch by the plasma better than solid aluminum oxide substrate or solid aluminum nitride substrate, but not as well as the components of the present invention either in solid form or as coatings over underlying substrates.
BRIEF DESCRIPTION OF THE DRAWINGS

[0012] So that the manner in which the exemplary embodiments of the present invention are attained is clear and can be understood in detail, with reference to the particular description provided above, and with reference to the detailed description of exemplary embodiments, applicants have provided illustrating drawings. It is to be appreciated that drawings are provided only when necessary to understand exemplary embodiments of the invention and that certain well known processes and apparatus are not illustrated herein in order not to obscure the inventive nature of the subject matter of the disclosure.

[0013] FIG. 1 is a schematic 100 representative of the use of a glaze/glass ceramic as a coating layer over a ceramic substrate such as aluminum oxide or aluminum nitride.

[0014] FIG. 2A shows a photomicrograph 200 illustrating the crystal structure of an aluminum substrate 202 directly adjacent a transition area 204, which is directly adjacent a yttrium fluoride glass ceramic 206.

[0015] FIG. 2B shows a photomicrograph 220 illustrating the crystal structure of the yttrium fluoride glass ceramic 206 at a magnification which is two times that shown in FIG. 2A.

[0016] FIG. 3A shows a photomicrograph 300 of the crystaline structure of an aluminum oxide substrate 302 directly adjacent a transition area 304, which is directly adjacent a yttrium fluoride glass ceramic doped with neodymium fluoride 306.

[0017] FIG. 3B shows a photomicrograph 320 of the crystaline structure of the neodymium-doped yttrium fluoride glass ceramic 306 at a magnification which is five times that shown in FIG. 3A.

[0018] FIG. 4 shows a bar graph 400 which illustrates the relative normalized erosion rates of various solid substrates including aluminum nitride 402, aluminum oxide 404, a series of three yttrium oxides (406, 408, 410) and 412 available from different vendors, and a yttrium oxyfluoride glass ceramic 414.

[0019] FIG. 5 shows a photomicrograph 500 which illustrates a transition layer 502 directly adjacent an aluminum oxide substrate (not shown on the left), which is directly adjacent a yttrium oxyfluoride glass ceramic 504. A crack 506 passing through transition area 502 stops at the yttrium oxyfluoride glass ceramic coating.

[0020] FIG. 6 shows a sintering profile 600 for a coating of yttrium oxyfluoride glass ceramic applied over an aluminum oxide substrate. The sintering time is shown in minutes on axis 602 and the temperature is shown on axis 604.

[0021] FIG. 7 shows a sintering profile 700 for a coating of neodymium fluoride doped yttrium oxyfluoride glass ceramic applied over an aluminum oxide substrate. The sintering time is shown in minutes on axis 702 and the temperature is shown on axis 704.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0022] As a preface to the detailed description, it should be noted that, as used in this specification and the appended claims, the singular forms "a", "an", and "the" include plural references, unless the context clearly dictates otherwise.

[0023] When the word "about" is used herein, this is intended to mean that the nominal value presented is precise within ±10%.

[0024] The materials and methods described herein are useful in designing and in fabrication of component apparatus for semiconductor and MEMS processing equipment. In particular, the materials and methods of fabricating components produce component apparatus which is resistant to halogen plasmas in general and to the fluoride-containing plasmas which are so problematic in terms of reaction with and erosion of surfaces of the components. Example component parts of the kind which particularly benefit from the materials and methods described herein include plasma processing chamber apparatus such as shower heads for gas distribution, process chamber lid interiors, process chamber liners, and electrostatic chuck surfaces, by way of example and not by way of limitation. Use of the materials described herein and the method of fabricating parts from these materials will decrease the amount of particles formed and metal contamination which occurs during the performance lifetime of the component part, and extend the lifetime of the component part as well.

[0025] A protective coating composition of the kind described herein is useful over a surface of an aluminum oxide, aluminum nitride, quartz, silicon carbide, silicon nitride, and other ceramic or glass substrates with a melting point higher than about 1600° C. The protective coating is a sintered composition including a yttrium-based fluoride crystal, or a yttrium-based oxyfluoride crystal, or an oxyfluoride amorphous phase, or a combination thereof. The materials which are selected for formation of the coating depend on the plasma resistance and mechanical, thermal, and electrical properties required for a given component. The starting materials typically comprise compound powders, a suspension medium, and a binder. A majority % of the compound powders (typically about 30% by weight or greater) is a yttrium compound, which may be an oxyfluoride, a fluoride, or combinations of these. This majority compound may be doped with a minority component powder, for example, an oxide, fluoride, or oxyfluoride of: neodymium, cerium, samarium, erbium, aluminum, scandium, lanthanum, hafnium, niobium, zirconium, ytterbium, hafnium, and combinations thereof. Properties such as thermal conductivity, thermal expansion coefficient, hardness, toughness, dielectric strength, dielectric constant, loss tangent, electrical resistivity, and erosion resistance will be determined in large part by the compounds selected for combination in forming a sintered coating.

[0026] The suspension medium may be selected from water or organic chemicals, including but not limited to methanol and ethanol, and combinations thereof, by way of example. Typically, when the suspension medium is methanol or ethanol, the concentration of this suspension medium in the suspension ranges from about 30 weight % to about 90 weight %. The binder may be selected from polyvinyl alcohol (PVA) and polymeric cellulose ether, or combinations thereof, by way of example and not by way of limitation.

[0027] Once the materials have been selected, there are a number of other variables which must be determined. These include the relative weight or volume percentages (or ratios) of the powdered materials, and the size of the starting powdered materials; the relative weight percentage of suspension medium; and the relative weight % of binder. Determination of these variables will affect the properties of the suspension such as the viscosity and the manner in which the suspension may be applied over a substrate surface.
of these variables affect the properties including thickness of the coating on the substrate prior to sintering, and ultimately affect the properties including thickness of the sintered coating. The sintering time and temperature profile determines the composition which is formed and the final crystalline structure of the sintered coating. As was discussed initially, when the cooling rate is fast, a glaze is formed, and when the cooling rate is slow, a glass-ceramic is formed. In addition, the ambient environment (atmosphere) in which the sintering takes place may introduce additional elements into the coating surface. For example, when oxygen is present in the sintering atmosphere, oxygen will be introduced into the sintered body. The time and temperature profile of the sintering will affect the depth to which the oxygen penetrates into the coating and the compounds which are formed. Initially, a large amount of empirical work was required to establish the guidelines from which satisfactory products of the present invention were produced.

Example One

[0032] FIG. 1 is a schematic representative of the use of a glaze/glass ceramic as a coating layer over a ceramic substrate such as aluminum oxide or aluminum nitride. FIG. 1 shows the coating 106 overlying a transition layer (transition area) 104, which overlies the substrate 102. In Example One, the substrate was aluminum oxide, Al₂O₃, but one of skill in the art will recognize that the substrate could be AlN. The powder used to form the glaze/glass-ceramic coating layer 106 was pure YF₃. We discovered that a different sintering time and temperature profile led to different phase compositions for the sintered coating. The sintering was carried out in flowing argon protective gas at atmospheric pressure. The glass ceramic coating described in this example was sintered from pure YF₃ powder having an average powder size of about 100 nm. Powder having an average particle size within the range of about 30 nm up to about 1 µm may be used. The YF₃ powder was suspended in an ethanol suspension media, where the weight % YF₃ powder was about 30%, and the weight % ethanol in the suspension was about 70%. As previously mentioned, as an alternative, the suspension media may be water where a binder is used. A binder such as PVA works well. The coating was applied over an aluminum oxide substrate using a dipping technique of the kind known in the art. The substrate can be dipped in the suspension a number of times to achieve a desired coating thickness. In the present instance, the coating thickness prior to sintering was about 100 µm.

[0033] The sintering process was carried out in flowing argon protective gas at atmospheric pressure. The sintering time/temperature profile for the coating present over an aluminum oxide substrate having a thickness of about 25 µm is shown in FIG. 6. The graph 600 shows the time period in minutes on axis 602 and the temperature in °C on axis 604. As indicated, the substrate with coating applied was rapidly increased in temperature at a linear rate from room temperature to 1000 °C over a time period of about 60 minutes as illustrated in area 606. The heating rate was then slowed, as indicated by region 608 of the curve, during which the temperature was increased from 1000 °C to 1410 °C over a time period of about 140 minutes. The sintering was then held at a constant temperature of 1410 °C as illustrated in area 610 of the curve for a time period of about 180 minutes. Finally, the coated substrate was cooled at a linear rate from 1410 °C to room temperature over a time period of about 275 minutes, as indicated by region 612 of the curve. The thickness of the sintered coating produced was about 25 µm.

[0034] Four crystal phases were found in the x-ray diffraction of the glass-ceramic coating structure which was sintered at 1410 °C. The coating layer composition near and at the coating surface included YOF and Y₂O₃. There was a transition area between the coating and the aluminum oxide substrate which was AlF₃, followed by Al₂O₃ adjacent to and in contact with the substrate. There is about 22 molar % of Y-Al-O-F amorphous phase distributed between crystal grains in the surface layer and the transition layer. The Composition of Phases, Phase Composition %, and Grain Size for the coating structure are shown below in Table One.

### TABLE ONE

<table>
<thead>
<tr>
<th>Composition</th>
<th>Phase Composition molar %</th>
<th>Grain Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous</td>
<td>22.04</td>
<td>—</td>
</tr>
<tr>
<td>Y-Al-O-F</td>
<td>18.6</td>
<td>46</td>
</tr>
<tr>
<td>YOF</td>
<td>41.58</td>
<td>2.9</td>
</tr>
<tr>
<td>AlF₃</td>
<td>3.89</td>
<td>28.7</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>28.7</td>
<td>&gt;1100</td>
</tr>
</tbody>
</table>

Example Two

[0035] The composition of the starting suspension was the same for Example Two as described for Example One. The thickness of the unsintered coating on the substrate was about 100 µm. The sintering was carried out in flowing argon
The sintering profile, including heat up rate and cool down rate were the same as for Example One. However, the sintering temperature increase to 1430°C, and the reduction in dwell time to 2 hours had a very significant and surprising effect on the overall structure of the coating. FIG. 7 shows the sintering conditions, which produced a coating where there is no amorphous material present, and the grain sizes of the various compounds is significantly altered. For example, the grain size of the YOF phase increased from about 46 nm to greater than 100 nm. The YF₃ crystalline phase did not form in the previous sintering profile where the maximum temperature was 1410°C, but did form when the sintering profile where the maximum temperature was 1430°C. The grain size for YF₃ crystalline phase was greater than 100 nm. The AlF₃ grain size has increased from 2.9 nm to 58.6 nm. While the grain sizes of all of these crystalline components increased, the grain size of the Al₂O₃ crystalline component decreased from greater than 100 nm to about 59.4 nm. The difference in composition in the resulting glass-ceramic coating produced was surprising, in terms of the amount of shifting in phase composition and grain size for the various phases. In addition, the transition area from the substrate to the coating has significantly changed, where the composition of the transition area has become mainly AlF₃ (23.88% AlF₃ and 9.13% Al₂O₃) compared with the transition area of the coating discussed in Example One, where the transition area was mainly Al₂O₃ (28.7% Al₂O₃ and 3.89% AlF₃). This difference in composition led to the different thermal and mechanical properties of the transition layer.

This change in the transition area determines both the ability of the coating to withstand temperature fluctuations which cause stress due to differences in coefficient of expansion between the substrate. The stresses created can cause cracking of the coating, as will be discussed subsequently.

Example Three

FIGS. 2A and 2B show photomicrographs which illustrate the fracture surface observation for a coated aluminum oxide substrate which was produced in the manner described in Example One. In FIG. 2A, the structure 200 includes the aluminum oxide substrate 202 which is comprised of crystals which demonstrate obvious porosity potential. The average crystal size of the aluminum oxide is greater than 100 nm. In direct contact with these crystals is the transition area 204. Transition area 204 comprises some aluminum oxide adjacent the aluminum oxide substrate 202, but extending away from the substrate is an AlF₃ composition which has a much smaller crystal size, on the average of about 2.9 nm. This smaller crystal is able to provide a more densely packed structure, as shown in the photomicrograph. Moving away from the transition area 204 is the coating layer 206 which includes a combination of Y₂O₃ and YOF. The average crystal size of the Y₂O₃ is about 18.6 nm and the average crystal size of the YOF is about 46 nm. The presence of the amorphous Y—Al—O—F phase, which acts as a matrix to surround the Y₂O₃ and YOF crystals provides an impervious coating. FIG. 2B shows a photomicrograph of structure 220, where the coating 202 is the Y₂O₃ and YOF crystal grains interspersed with amorphous Y—Al—O—F phase, shown at a magnification of 2x the magnification shown for area 206 in FIG. 2A. The finished coating surface (not shown) is dense and free from loose particulates, as would be expected looking at the non-fractured area 206 towards the right of structure 220.

The oxygen present in the Y₂O₃ and YOF crystaline portion of the coating matrix was generally supplied from the oxide substrate. During the sintering process, flowing argon was circulated through the sintering furnace. The AlF₃ transition layer was formed according to the following mechanism: The 1410°C to 1430°C sintering temperature is higher than the melting temperature of YF₃, a Y—Al—O—F melt is formed. However, the melt composition is not homogeneous and, in the area close to the Al₂O₃ substrate, there is a higher Al content. During cooling of the melt, the nucleation of AlF₃ (heterogeneous) starts in the location of the boundary between the Al₂O₃ substrate and the melt, and the growth continues during cooling, to produce the AlF₃ crystal grains.

Example Four

In Example Four, the substrate was also Al₂O₃, but one of skill in the art will recognize that the substrate could be aluminum oxide or aluminum nitride. The ceramic powder used to produce the coating was a mixture of 80% by weight YF₃ and 20% by weight NdF₃. Again, we determined that a different sintering time/temperature profile led to

<table>
<thead>
<tr>
<th>Composition</th>
<th>Phase Composition</th>
<th>Grain Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anomalous</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y—Al—O—F</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>11.46</td>
<td>17.5</td>
</tr>
<tr>
<td>YOF</td>
<td>37.43</td>
<td>&gt;1100</td>
</tr>
<tr>
<td>YF₃</td>
<td>18.1</td>
<td>&gt;1100</td>
</tr>
<tr>
<td>AlF₃</td>
<td>23.88</td>
<td>58.6</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>9.13</td>
<td>59.4</td>
</tr>
</tbody>
</table>
different phase compositions for the sintered ceramic coating. The sintering was carried out in flowing argon protective gas at atmospheric pressure. The glass-ceramic coatings sintered from the 80% by weight YF₃ and 20% by weight NdF₃ mixture were first sintered using the sintering profile described with respect to Example One and illustrated in FIG. 6. The YF₃ powder had an average powder size of about 100 nm. The NdF₃ powder had an average powder size of about 100 nm. The powders were suspended in an ethanol suspension media, where the weight % of the powder mixture was about 30%, and the ethanol in the suspension was about 70 weight %. The coating was applied over an aluminum oxide substrate using a dipping technique, to produce a resulting unsintered coating thickness over the substrate of about 100 μm.

[0042] As previously mentioned, the sintering time/temperature profile for the coating present over an aluminum oxide substrate having a thickness of about 25 μm is shown in FIG. 6.

[0043] Five crystal phases were found in the x-ray diffraction of the glass-ceramic coating structure. The coating layer included YOF, Nd₂O₃, Nd₃Al₂O₉, NdAlO₃, and Al₂O₃. There is about 20 molar % of amorphous Y—Nd—Al—O—F phase distributed between the crystalline grains. The YOF and Nd₂O₃ were from the upper portion of the coating, nearer the surface of the coating. The NdAlO₃ and Nd₃Al₂O₉ were from the transition layer, and the Al₂O₃ was adjacent the Al₂O₃ substrate surface. Amorphous Y—Nd—Al—O—F phase was present throughout the upper portion and the transition area of the coating. The Phase Composition and Grain Size analyzed by XRD for the coating structure are shown below in Table three.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Phase Composition</th>
<th>Grain Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous Y—Nd—Al—O—F</td>
<td>20.26</td>
<td></td>
</tr>
<tr>
<td>YOF</td>
<td>23.92</td>
<td>5.9</td>
</tr>
<tr>
<td>Nd₂O₃</td>
<td>36.27</td>
<td>22.2</td>
</tr>
<tr>
<td>NdAlO₃</td>
<td>1.48</td>
<td>16.5</td>
</tr>
<tr>
<td>Nd₃Al₂O₉</td>
<td>16.72</td>
<td>&gt;1100</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.35</td>
<td>68.9</td>
</tr>
</tbody>
</table>

TABLE THREE

Example Five

[0044] The composition of the starting materials were the same for Example Four. The sintering time/temperature profile is shown in FIG. 7, where the coating was sintered at 1430°C for 120 minutes (2 hours).

[0045] Five crystal phases were found in the x-ray diffraction of the glass-ceramic coating structure. The coating layer included YOF and Nd₂O₃. There was a transition area between the coating and the aluminum oxide substrate which was Nd₃Al₂O₉, Nd₃Al₂O₉, NdAl₂O₉, and Al₂O₃, followed by Al₂O₃ adjacent to the substrate. There was no amorphous phase indicated. This means that the amorphous phase content is lower than 1% by weight and X-ray diffraction cannot detect a presence. The presence of one Nd—Al—O phase (Nd₃Al₂O₉) with one Nd—Y—Al—O phase (Nd₃Al₂O₉, Nd₃Al₂O₉, and Al₂O₃) in the transition area between the glass-ceramic coating and the substrate provided particularly strong binding between the coating and the substrate. The surface of the coating remains impervious to erosion despite the fact that X-ray diffraction cannot detect an amorphous phase, as there is still a low content of amorphous phase which makes up the grain boundaries between crystals.

Example Six

[0046] In Example Six, the substrate was also Al₂O₃, but one of skill in the art will recognize that the substrate could be either aluminum oxide or aluminum nitride. The ceramic powder used to produce the coating was a mixture of 90% by weight YF₃ and 10% by weight NdF₃. The YF₃ powder had an average powder size of about 100 nm. The NdF₃ powder had an average powder size of about 100 nm. The powders were suspended in an ethanol suspension media, where the weight % of the powder mixture was about 30%, and the ethanol in the suspension was about 70 weight %. The coating was applied over an aluminum oxide substrate using a dipping technique, to produce an unsintered coating thickness over the substrate of about 100 μm. The sintering process was carried out in flowing argon protective gas at atmospheric pressure using a sintering profile as shown in FIG. 7, where the sintering temperature was 1430°C for a time period of 120 minutes.

[0047] Six crystal phases were found in the x-ray diffraction of the glass-ceramic coating structure. The upper portion of the coating is YOF and Nd₂O₃ (or Nd₂O₃). The transition layer is composed of Nd₃Al₂O₉, Nd₃Al₂O₉, Nd₃Al₂O₉, and Al₂O₃, with an Al₂O₃ phase being present near the surface of the Al₂O₃ substrate. There is about 4 molar % of amorphous Y—Nd—Al—O—F phase present between crystalline grains. The presence of one Na—Al—O phase (Nd₃Al₂O₉) with one Nd—Y—Al—O phase (Nd₃Al₂O₉, Nd₃Al₂O₉, and Al₂O₃) in the transition area between the glass-ceramic coating and the substrate provides particularly strong binding between the coating and the substrate. The Phase Composition and Grain Size analyzed by XRD for the coating structure are shown below in Table Four.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Phase Composition</th>
<th>Grain Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous Y—Nd—Al—O—F</td>
<td>4.48</td>
<td></td>
</tr>
<tr>
<td>YOF</td>
<td>11.14</td>
<td>7.1</td>
</tr>
<tr>
<td>Nd₃Al₂O₉</td>
<td>1.64</td>
<td>&gt;1100</td>
</tr>
<tr>
<td>NdAlO₃</td>
<td>10.49</td>
<td>77.1</td>
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<td>Nd₃Al₂O₉</td>
<td>49.58</td>
<td>2.4</td>
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<tr>
<td>Al₂O₃</td>
<td>4.47</td>
<td>47</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.2</td>
<td>&gt;1100</td>
</tr>
</tbody>
</table>

TABLE FOUR

Example Seven

[0049] FIGS. 3A and 3B illustrate the coating structure obtained for a coating of the kind produced as described in Example Six. FIG. 3A shows a photomicrograph of the structure 300, with the Al₂O₃ substrate 302, the transition area 304, and the coating 306 having phases of crystalline...
A substrate protected by a coating in accordance with claim 1, wherein additional crystalline phase compounds are present, and wherein said additional crystalline phase compounds were formed during sintering of said composition due to the presence of a dopant selected from the group consisting of: an oxide, fluoride, or oxyfluoride of neodymium, cerium, samarium, erbium, aluminium, scandium, lanthanum, hafnium, niobium, zirconium, ytterbium, hafnium, and combinations of an oxide, or fluoride or oxyfluoride of at least one of these elements.

A coating combination in accordance with claim 2, wherein said crystalline portion of said coating composition ranges from about 70% by weight to about 100% by weight.

A coating in accordance with claim 3, wherein said crystalline portion of said coating composition ranges from about 70% by weight to about 100% by weight.

A component of a semiconductor processing apparatus, where a surface of the apparatus is exposed to a halogen-comprising reactive plasma, the component comprising:

- a ceramic or glass substrate with a melting point higher than about 1600°C; and
- a protective coating applied over at least one surface of said substrate, said coating including at least one yttrium-based fluoride crystal phase, or at least one yttrium-based oxyfluoride crystal phase, or at least one amorphous phase, or a combination thereof, wherein said amorphous phase comprises yttrium and fluorine.

A structure in accordance with claim 6, wherein said substrate is selected from aluminium oxide, aluminium nitride, quartz, silicon carbide, silicon nitride, and combinations thereof.

A structure in accordance with claim 6, wherein said protective coating comprises a matrix area near an upper surface of said coating which matrix area contains crystal grains selected from the group consisting of: an oxide, fluoride, or oxyfluoride of neodymium, cerium, samarium, erbium, aluminium, scandium, lanthanum, hafnium, niobium, zirconium, ytterbium, hafnium, and combinations of an oxide, fluoride or oxyfluoride of at least one of these elements.

A structure in accordance with claim 8, wherein said crystal grains are present at a concentration ranging from about 70 weight % to about 100 weight %.

A structure in accordance with claim 7, wherein a transition matrix area is present between said matrix area near the upper surface of said coating and said substrate, and wherein said transition matrix area comprises aluminium fluoride.

A component of a semiconductor processing apparatus, where a surface of the apparatus is exposed to a halogen-comprising reactive plasma, the structure comprising:

- a solid structure having an overall uniform composition, wherein said composition comprises: crystal grains selected from the group consisting of yttrium oxide, yttrium fluoride, yttrium oxyfluoride, and at least one additional compound selected from the group consisting of: an oxide, fluoride, or oxyfluoride of neodymium, cerium, samarium, erbium, aluminium, scandium, lanthanum, hafnium, niobium, zirconium, ytterbium, hafnium, and combinations of an oxide, fluoride or oxyfluoride of at least one of these elements.
12. A structure in accordance with claim 11, wherein said solid structure also comprises an amorphous phase including yttrium and fluorine.

13. A method of forming a protective coating comprising yttrium fluoride, yttrium oxyfluoride, or a combination thereof upon at least one surface of a substrate, comprising:
   a) applying a slurry comprising a powder in suspension over at least one surface of a substrate, to provide a coating over said at least one surface, wherein said powder comprises yttrium fluoride, and said substrate is selected to have a melting point higher than about 1600° C.; and
   b) sintering said coating present on said substrate surface to produce a sintered coating comprising yttrium fluoride, or yttrium oxyfluoride, or a combination thereof in an argon environment.

14.-24. (canceled)