A corrosion-resistant member used in a corrosive environment includes a substrate, and a ceramic sprayed film, which covers a part or all of the substrate surface and has relative density of 80% or greater. Maximum diameter of voids existing in the ceramic sprayed film surface is 25 μm or less. This corrosion-resistant member is obtained by using Y₂O₃ as a material having a bulk density of at least 1.5 g/cm³ and dried to a moisture content of 1 mass percent or less and spraying plasma on the substrate with an output power of 40 to 110 kW by a spraying device including two anode torches.
FIG. 2
CORROSION-RESISTANT MEMBER AND
METHOD FOR MANUFACTURE THEREOF

TECHNICAL FIELD

[0001] The present invention relates to a corrosion-resistant member used in a corrosive atmosphere such as a corrosive plasma gas environment, and a method for manufacture thereof. More specifically, it relates to a corrosion-resistant member having excellent resistance to halogen plasma gas or halogen corrosive gas used in a semiconductor device manufacturing process or a liquid crystal device manufacturing process, for example, and a method for manufacture thereof.

BACKGROUND ART

[0002] In manufacture of semiconductor devices or liquid crystal devices, silica glass and a ceramic have been often used in the past as material for members such as chambers, susceptors, and clamp rings used in a highly chemically corrosive environment.

[0003] In recent years, the size of substrates for manufacturing semiconductor devices or liquid crystal devices has been increased in view of cost reduction. For example, it has been required to accommodate a wafer of 12 inch size for semiconductor wafers, or a substrate of larger than 1 m square size for liquid crystal devices. As a result, enlargement of manufacturing apparatus is also required. However, there are limits to use of conventional silica glass or ceramic for large sized parts in terms of strength and rigidity. Therefore, a member including a metal substrate covered by a film of a corrosion-resistant material such as a ceramic has come into use.

[0004] A technology for allowing formation of a larger corrosion-resistant member has been proposed (e.g., Japanese Patent Gazette No. 3510993, Japanese Patent Application Laid-open No. 2004-10981). According to the technology, a film is formed through thermal spraying using a corrosion-resistant material such as alumina or a rare-earth oxide such as Y₂O₃, for example.

[0005] When forming a corrosion-resistant film by spraying, generation of voids in the film is unavoidable, and the voids tend to become larger than in a bulk ceramic. Particularly, a Y₂O₃ sprayed film has higher corrosion resistance than other sprayed films such as an Al₂O₃ sprayed film. However, since the melting point of Y₂O₃ or material is high and is thus difficult to melt, the voids in a sprayed film composition will be larger than in the Al₂O₃ sprayed film.

[0006] Even before now, voids on a sprayed film surface are considered a contributing factor to reducing corrosion resistance of the sprayed film. However, according to study by the present inventors, it is revealed that size of each void greatly contributes to corrosion resistance more than the existence of voids in the sprayed film surface.

[0007] In other words, when a sprayed film including large voids is exposed to halogen plasma gas or halogen corrosive gas, the voids serve as starting points for void corrosion, resulting in easy development of corrosion. Furthermore, where voids are larger than a certain size, locally low adhesive strength regions are easily generated at an interface between the substrate and the sprayed film, so handling of such a member during manufacture such as mounting of the member becomes difficult, and film peeling also occurs easily. However, according to conventional spraying technology, voids in the sprayed film surface are given attention, but there is no consideration given to controlling the size thereof.

DISCLOSURE OF INVENTION

[0008] An objective of the present invention is to provide a corrosion-resistant member having voids controlled in size and also having excellent corrosion resistance and adhesiveness to a substrate, and a method for manufacture thereof.

[0009] In view of the aforementioned actual condition, through devoted research, the inventors have concentrated on developing a material that has small voids existing in a sprayed film surface, excellent resistance to halogen plasma gas or halogen corrosive gas, and excellent adhesive strength between a substrate and a sprayed film. As a result, it has been found that size of voids in the sprayed film depends on manufacturing conditions thereof, and that void size can be controlled to be less than a certain size through selection of the manufacturing conditions, thereby providing a sprayed film with excellent corrosion resistance and adhesiveness to a substrate. The present invention has been made on the basis of the findings.

[0010] According to a first aspect of the present invention, there is provided a corrosion-resistant member used in a corrosive environment including a substrate and a ceramic sprayed film, which covers a part or all of the substrate surface and has relative density of 80% or greater. The ceramic sprayed film has a thickness of 50 to 500 μm, and a surface prepared such that voids existing therein have a maximum diameter of 25 μm or less.

[0011] Furthermore, the ceramic sprayed film may be a film made of Y₂O₃, and have an etching rate of 5 nm/min or less when plasma etching is performed under conditions of a flow rate of 50 mL/min, output power of 1,000 W, and a pressure of 6.7 Pa using a mixed gas made of 80% CF₄ and 20% O₂ by a parallel plate type RIE apparatus with inter-electrode gap of 100 mm. In this case, the corrosion-resistant member is obtained by using Y₂O₃ having a bulk density of at least 1.5 g/cm³ and a moisture content of 1 mass percent or less as material for the ceramic sprayed film and spraying plasma on the substrate with an output power of 40 to 110 kW by a spraying device including two anode torches.

[0012] Alternatively, the ceramic sprayed film may be a film made of Al₂O₃, and have an etching rate of 20 nm/min or less when plasma etching is performed under conditions of a flow rate of 50 mL/min, output power of 1,000 W, and a pressure of 6.7 Pa using a mixed gas made of 80% CF₄ and 20% O₂ by a parallel plate type RIE apparatus with inter-electrode gap of 100 mm. In this case, the corrosion-resistant member is obtained by using Al₂O₃ having a bulk density of at least 1.0 g/cm³ and a moisture content of 1 mass percent or less as material for the ceramic sprayed film and spraying plasma on the substrate with an output power of 40 to 110 kW by a spraying device including two anode torches.

[0013] According to a second aspect of the present invention, there is provided a method for manufacture of corrosion-resistant member by covering a substrate surface with a Y₂O₃ film through plasma thermal spraying. The method includes: a drying step of drying material having a bulk
density of at least 1.5 g/cm³ until a moisture content is 1 percent or less by mass; and a plasma thermal spraying step of spraying the material after drying on a substrate surface with an output power of 40 to 110 kW by a spraying device including two anode torches, and forming a Y₂O₃ film having a relative density of 80% or greater, a thickness of 50 to 500 µm, and a surface prepared such that voids existing therein have a maximum diameter of 25 µm or less.

[0014] According to a third aspect of the present invention, there is provided a method for manufacture of corrosion-resistant member by covering a substrate surface with an Al₂O₃ film through plasma thermal spraying. The method includes: a drying step of drying material having a bulk density of at least 1.0 g/cm³ until a moisture content is 1 percent or less by mass; and a plasma thermal spraying step of spraying the material after drying on a substrate surface with an output power of 40 to 110 kW by a spraying device including two anode torches, and forming an Al₂O₃ film having a relative density of 80% or greater, a thickness of 50 to 500 µm, and a surface prepared such that voids existing therein have a maximum diameter of 25 µm or less.

[0015] According to the present invention, since the sprayed film obtained by adjusting moisture content and bulk density of the material and spraying with output power of 40 to 110 kW by a spraying device including two anode torches separated from one another is controlled such that the maximum diameter of voids (hereafter referred to as "maximum void diameter") existing in the surface is 25 µm or less, starting points for corrosion decrease, and etching rate at the time of plasma exposure is low.

[0016] Furthermore, by keeping the maximum void diameter in the sprayed film surface at 25 µm or less, locally low adhesive strength regions decrease at the interface with the substrate, allowing adhesive strength degradation before and after plasma irradiation and adhesive strength degradation due to purified water ultrasonic cleaning after plasma irradiation to be under 30%. Therefore, use of the corrosion-resistant member according to the present invention as a member within a chamber or the like in semiconductor manufacturing processes and liquid crystal manufacturing processes allows prevention of particle generation due to corrosion, and extension of the lifetime of the member. Furthermore, this allows reduction in manufacturing costs for semiconductor devices and liquid crystal devices, and improvement in productivity due to reduction in frequency of part replacement.

BRIEF DESCRIPTION OF DRAWINGS

[0017] FIG. 1 is a cross sectional view schematically showing a device for forming a sprayed film on a corrosion-resistant member of the present invention; and

[0018] FIG. 2 is a cross sectional view schematically showing a configuration of a RIE apparatus used for etching the corrosion-resistant member.

BEST MODE FOR CARRYING OUT THE INVENTION

[0019] A preferred embodiment according to the present invention is described forthwith.

[0020] A corrosion-resistant member according to the present invention is used in a corrosive environment for a plasma process or the like using a corrosive gas. For example, it may be used as materials for a chamber of a plasma apparatus used during film formation or etching of a semiconductor wafer or a substrate for liquid crystal devices. Further, it may be used as materials for a gas distributor, a liner, a susceptor, a clamp ring, a sleeve, or a door, which are members within the chamber.

[0021] The corrosion-resistant member includes at least a substrate and a ceramic sprayed film, which covers a part or all of the substrate. While material of the substrate is not limited, it may be formed of a metal such as stainless steel or aluminum, glass, a ceramic, or a ceramic composite, for example. The ceramic sprayed film is a film covering the surface of the substrate and at least a region exposed to a corrosive atmosphere. The film has a relative density of 80% or greater, and a maximum void diameter of 25 µm or less in the film surface.

[0022] Where the relative density of the ceramic sprayed film is low, corrosion resistance and plasma resistance decrease, degasification from the corrosion-resistant member increases, and degree of vacuum in the chamber does not increase, thereby raising running cost. Accordingly, relative density is preferably 80% or greater, and in order to prevent reduction in chip yield due to particle generation, relative density of 85% or greater is more preferable.

[0023] Where void diameter in the ceramic sprayed film surface becomes large, irregular portions in which plasma easily gathers increase, and thus local plasma corrosion becomes easy to develop. It can be considered that void size (void diameter) more than number or gross area of voids profoundly contributes to the tendency to bring about plasma corrosion. In other words, as an extremely simplified example, rather than a case where many small voids exist in the sprayed film surface, a case where a single or few voids larger than a certain size exist is greater cause for significant reduction in plasma resistance of the sprayed film. According to the inventors’ knowledge, maximum diameter of voids existing in the sprayed film surface has important implications in terms of affecting plasma resistance. As shown in working examples and comparative examples to be described later, it is confirmed that voids with a diameter of 25 µm or greater compared to voids with a diameter of 25 µm or less reduce adhesiveness to the sprayed film, easily cause corrosion, and further cause particle contamination.

[0024] According to the conventional sprayed films, maximum void diameter in the sprayed film surface is given attention, but there is no consideration given to control thereof. However, where the maximum void diameter exceeds 25 µm, depth of the voids also deepens in compliance with the diameter. Therefore, locally low adhesive strength regions are generated at the interface with the substrate.

[0025] Furthermore, where the maximum void diameter is large, edges thereof are also formed long in compliance with the diameter. Since regions closer to void edges are shaved off and detached more easily in a plasma environment, voids greater than 25 µm in diameter with long edges and a high depth ratio to film thickness easily cause detachment in the plasma environment and tend to generate particles.

[0026] Moreover, when repeatedly exposed to the plasma environment, the voids gradually enlarge and depth thereof
also increases. Ultimately, in this case, deficient regions may develop locally in the sprayed film, resulting in an exposed substrate surface, which may give rise to corrosion.

[0027] Because of this, a sprayed film including even a single void greater than 25 μm in diameter in the surface significantly reduces in corrosion resistance.

[0028] On the other hand, where the maximum void diameter is 25 μm or less, there is hardly any influence on adhesive strength of the sprayed film, and the voids do not become large enough such that deficiencies are generated in the sprayed film under normal use conditions, so the corrosion resistance can be maintained.

[0029] Furthermore, since particles having gotten into the voids are difficult to remove through cleaning, this contaminates the chamber during processes, and may lead to reduction in chip yield. However, if the maximum void diameter is 15 μm or less, probability of particles getting into the voids may significantly lower, thereby preventing particle contamination emanating from intrusion of particles into the voids.

[0030] Therefore, a maximum void diameter of 25 μm or less is preferable, 15 μm or less is even more preferable. Note that “maximum void diameter” may be determined based on the diameter of the largest void on the surface in which ten fields of view are observed using a scanning microscope at a 500-fold magnification after the sprayed film surface has been polished.

[0031] Thickness of the sprayed film of the corrosion-resistant member is preferably 50 to 500 μm, more preferably 100 to 300 μm, for example. Where the film is too thick, thermal history increases due to repeated film formation, and micro cracks developing on the interface between the substrate and the sprayed film increase, thereby facilitating detachment of the sprayed film. Where the film is too thin, since through-holes in the sprayed film increase, the interface between the substrate and the sprayed film is easy to corrode, thereby facilitating detachment of the sprayed film.

[0032] Furthermore, by keeping the maximum void diameter at 25 μm or less, reduction in number of through-holes is possible even where the film is relatively thin. Corrosion at the interface between the substrate and the sprayed film is prevented, and detachment of the sprayed film is suppressed from occurring, thereby allowing improved durability. In other words, suppression of the maximum void diameter to 25 μm or less allows formation of a sprayed film having sufficient durability even with a thickness of 50 μm, for example.

[0033] In the case where the ceramic sprayed film including voids with a maximum diameter of 25 μm or less is a Y₂O₃ film, it has an etching resistance property of an etching rate of 5 nm/min or less when it has been subjected to plasma etching under predetermined conditions such as a flow rate of 50 mL/min, power of 1,000 W, and pressure of 6.7 Pa (50 mTorr) using a mixed gas made of 80% CF₄ and 20% O₂, for example, by a parallel plate type RIE apparatus with inter-electrode gap of 100 mm. Since the Y₂O₃ film having an etching rate of 5 nm/min in the above-mentioned conditions is barely etched even through plasma irradiation, particle contamination can be prevented from occurring, lifetime of the corrosion-resistant member extends, and frequency of member replacement reduces, thereby improving productivity of semiconductor devices and liquid crystal devices.

[0034] Furthermore, in the case where the ceramic sprayed film including voids with a maximum diameter of 25 μm or less is an Al₂O₃ film, it has an etching resistance property of an etching rate of 20 nm/min or less when it has been subjected to plasma etching under predetermined conditions such as a flow rate of 50 mL/min, power of 1,000 W, and pressure of 6.7 Pa (50 mTorr) using a mixed gas made of 80% CF₄ and 20% O₂, for example, by a parallel plate type RIE apparatus with inter-electrode gap of 100 mm. Since the Al₂O₃ film having an etching rate of 20 nm/min in the above-mentioned conditions is only slightly etched through plasma irradiation, particle contamination is prevented from occurring, and a sufficient lifetime of the corrosion-resistant member is provided, thereby contributing to high productivity of semiconductor devices and liquid crystal devices.

[0035] A manufacturing method for the corrosion-resistant member according to the present invention is described forthwith while referencing the drawings.

[0036] In order to form a sprayed film as described above, a spraying device including a cathode torch and two anode torches separated from one another is used with the present invention. Since use of two such separated anode torches allows introduction of material to a plasma arc, which is at a very high temperature, ceramic material may be completely melted, thereby achieving a desired sprayed film. An anode integrated spraying device has difficulty in complete melting a ceramic material, because it cannot introduce the material to the plasma arc, structurally.

[0037] When spraying a ceramic material, use of an oxygen (O) contained plasma gas is preferable. Oxygen contained plasma gas may be formed by supplying oxygen gas (O₂), air, or a mixed gas thereof, for example. Use of such an oxygen contained plasma gas in this manner prevents defects and coloration from occurring through reduction of a ceramic when melting the ceramic at a high temperature.

[0038] A specific structure of the spraying device including a cathode torch and two anode torches separated from one another will be described now. FIG. 1 is a cross sectional view schematically showing an example of such a spraying device. This spraying device includes a device main unit 1 having a spray particle outlet 1a, a cathode torch 2 provided on the opposite side to the spray particle outlet 1a of the device main unit 1, and two anode torches 3a and 3b respectively supported by supporting members 4a and 4b on both sides of the device main unit 1.

[0039] Ar gas is supplied to the tip of the cathode torch 2 via an Ar gas supply pipe 11 and an Ar gas lead-in path 11a, generating an arc while preventing oxidation of the torch (electrode). An accelerator nozzle 5 is provided on the downstream side of the cathode torch 2, and the arc generated at the cathode torch 2 accelerates to generate a plasma arc 40. Air or oxygen gas from an air supply pipe 12 via an air lead-in path 12a is supplied to an arc generated at the cathode torch 2, and the plasma arc 40 generated from the accelerator nozzle 5 becomes oxygen contained plasma gas.

[0040] Ceramic powder or spray material powder is introduced into the plasma arc 40 generating region from a material feed hopper not shown in the drawing via a material
supply pipe 13, and this material powder is completely melted to form spray particles. While complete melting of the material powder is possible in the same way even if the material powder is supplied to the tip of the plasma arc 40, it is preferable to supply the powder to the plasma arc 40 generating region since it is at a higher temperature.

[0041] Ar gas is supplied to the tip of the anode arc 3a via an Ar gas supply pipe 21a and Ar gas lead-in paths 22a and 23a, an arc is generated while preventing oxidation of the torch (electrode), and a plasma arc 41a extends perpendicular to the plasma arc 40 projected out from the cathode torch 2.

[0042] Ar gas is also supplied to the tip of the anode arc 3b via an Ar gas supply pipe 21b and Ar gas lead-in paths 22b and 23b, resulting in generation of an arc while preventing oxidation of the torch (electrode), and a plasma arc 41b extends perpendicular to the plasma arc 40 projected out from the cathode torch 2. A plasma jet 40a develops at the confluence of the plasma arcs 40, 41a, and 41b. In the vicinity of the spray particle outlet 1a of the device main unit 1, air is supplied to the plasma jet 40a from air pipes 24a and 24b via respective air lead-in paths 25a and 25b and heat not contributing to melting in the plasma jet 40a is removed.

[0043] Auxiliary power supplies 32a and 32b functioning as high-frequency starters for starting arc generation, and DC main power supplies 31a and 31b functioning as energy resources for sustaining arcs are connected to the cathode torch 2 and the anode torches 3a and 3b, respectively. Note that the auxiliary power supplies 32a and 32b and the DC main power supplies 31a and 31b are controlled by a control unit not shown in the drawing.

[0044] A cooling jacket 14 is provided to surround the cathode torch 2 and the accelerator nozzle 5 for protecting them from high temperatures, and cooling jackets 26a and 26b are provided to surround the anode torches 3a and 3b.

[0045] In such a spraying device, spray particles 51 carried by the plasma jet 40a hit a substrate 53, thereby forming a sprayed film 52.

[0046] Where spray output power is too low, melting of the material does not progress, thereby increasing the maximum void diameter. On the other hand, where spray output power is too high, defects are generated through ceramic reduction. Accordingly, it is preferable to make the spray output power 40 kW or greater and 110 kW or less.

[0047] As an advantage of using an anode separated plasma thermal spray device as shown in FIG. 1, this device is capable of completely melting the ceramic of a sprayed film material, since the material is put into a plasma arc generating region, which is at a very high temperature. On the other hand, with the anode integrated spraying device, since material cannot be supplied to the plasma arc generating region structurally, melting of the material may be insufficient.

[0048] Furthermore, in the case of the anode separated plasma thermal spray device having separated anodes, output power for a single anode may be reduced, and high output power is possible. Accordingly, it facilitates uniform melting of the material, and improves denseness of the sprayed film, thereby providing voids having a reduced maximum diameter. However, with the anode integrated spraying device, where the output power for the anode is great, there is fear of the spraying device being damaged since it cannot endure high output power.

[0049] Furthermore, in the case of a flame spraying device, melting of the material does not progress due to a low flame temperature, and formation of a sprayed film having uniform, fine, small voids is difficult.

[0050] It is preferable that the ceramic material to be sprayed is a powder or granular having a fixed bulk density. Where the bulk density of the material is low, the material has a light weight. Therefore, the material cannot get into the plasma flame and a film is insufficiently melted and formed, resulting in difficult formation of a dense film as well as difficult control of void diameter. Furthermore, where material density is low and pores exist in the material, they enter the sprayed film and make it difficult to form a dense sprayed film. Therefore, the bulk density of the material for Y2O3 is preferably 1.5 g/cm3 or greater, more preferably 1.8 g/cm3 or greater, with a desired upper limit of 3.0 g/cm3. Furthermore, the bulk density for Al2O3 is preferably 1.0 g/cm3 or greater, more preferably 1.2 g/cm3 or greater, with a desired upper limit of 2.4 g/cm3.

[0051] When drying of the ceramic material used for spraying is insufficient, the material may be clogged in a material feeder due to moisture adsorbed to the material, supply becomes unstable, and melting of the material also becomes insufficient, thereby facilitating generation of large voids in the film. Therefore, it is preferable to use material that is pre-dried until moisture content is approximately 1 percent or less by mass. Furthermore, since probability of voids being generated during spraying is high due to moisture evaporation from the material, moisture content of the material is preferably approximately 5 percent or less by mass. Heating at a temperature of 70°C or higher, for example, for 12 hours or more as a guide for when drying the material allows reduction in the moisture content down to approximately 1 percent or less by mass. Heating at a temperature of 250°C or higher for 12 hours or more allows reduction in the moisture content down to approximately 0.5% mass or less.

[0052] It should be noted that an ordinary commercially available powder material may be used on the condition that bulk density and dryness are set to the above given conditions. As needed, the material may be granulated so as to improve flowability of the powder.

[0053] The substrate 53 may be subjected to surface processing such as blasting. It is preferable that the blasted substrate is sufficiently cleaned to completely remove blast materials, shavings, and the like deposited on the surface. Adhesion of the film decreases when such debris is left on the substrate surface, and is thus unfavorable.

[0054] As described above, by adjusting bulk density and moisture content of the material and completely melting the ceramic material when spraying in such a spraying device as shown in FIG. 1, a film having a relative density of 98% or higher, a maximum void diameter of 25 μm or less, few remaining pores, excellent adhesion and mechanical resistance to the substrate, and high etching resistance can be formed.

[0055] Working examples and comparative examples are given hereafter to further describe the present invention in detail. However, the present invention is not limited thereto.
WORKING EXAMPLES 1 TO 8,
COMPARATIVE EXAMPLES 1 TO 9

[0056] An Al substrate (JIS 6061) surface roughened to a surface roughness Ra greater than 4 µm was prepared, different types of spraying devices were used, and a Y2O3 sprayed film was formed as a test plate. A spraying device including two separated anode torches (see FIG. 1), a spraying device having an integrated anode torch, and a high velocity oxygen fuel thermal spraying (HVOF) device were used as the spraying devices.

[0057] Sprayed film manufacturing conditions: drying temperature, drying time, moisture content, and bulk density of material (granular), and sprayed film thickness and spray output power (15 to 110 kW), were varied as shown in Tables 1 and 2, and were called Working Examples 1 to 8 and Comparative Examples 1 to 9. In the respective working examples and comparative examples, film formation property, relative density, porosity, maximum void diameter, etching rate, adhesive strength degradation due to plasma irradiation, and adhesive strength degradation due to purified water ultrasonic cleaning after plasma irradiation were respectively evaluated by the following methods. Results thereof are shown in Tables 1 and 2 collectively.

[Film Formation Property]

[0058] Film formation property was evaluated by confirming film peeling after spraying. Samples with no film peeling after spraying were denoted by “O”, samples with partial film peeling by “△” and samples with complete film peeling after spraying by “×”.

[Relative Density]

[0059] Relative density was evaluated by peeling off just the sprayed film from the substrate and measuring bulk density using the Archimedes method and was then provided by (bulk density)+(theoretical density). Porosity was calculated based on the relative density.

[Maximum Void Size]

[0060] Maximum void diameter was defined by the diameter of the largest void found when ten fields of view in the surface were observed using a scanning microscope at a 500-fold magnification after the sprayed film surface was polished.

[Etching Rate]

[0061] Etching rate was calculated by polishing the surface of the test plate, masking a part of the polished surface with polyimide tape, conducting reactive ion etching (RIE), and then measuring difference in height of regions covered by the mask and regions not covered by the mask.

[0062] A structure of a RIE apparatus used in this etching test is schematically shown in FIG. 2. This RIE apparatus 101 is configured as a parallel plate type RIE apparatus in which a pair of electrode plates faces each other vertically. The RIE apparatus 101 has a susceptor 103, which is a mounting table for a test plate TP within a chamber 102 and functions as a lower electrode. In this test, the susceptor 103 having a length L2 of 480 mm was used.

[0063] A showerhead 105 functioning as an upper electrode facing the susceptor 103 in parallel is provided over the susceptor 103. Interval (inter-electrode gap L1) between the susceptor 103 and the showerhead 105 is adjustable by a lifting mechanism not shown in the drawing. A gas supply pipe 108 is connected to the showerhead 105, and the gas supply pipe 108 is split on the upstream side of a valve 109 and connected to a CF4 gas supply source 110 and an O2 gas supply source 111. Pipes from these gas supply sources are respectively provided with a flow adjustment means not shown in the drawing, which is structured capable of adjusting flow of CF4 gas and O2 gas as etching gases. The etching gases reach a gas supply chamber 107 via the gas supply pipe 108, and are then discharged evenly from gas discharge openings 106.

[0064] A high-frequency power source 112 is connected to the susceptor 103, which functions as a lower electrode, via a converter not shown in the drawing, and this high-frequency power source 112 may supply high-frequency power of 13.56 MHz, for example, to the susceptor 103.

[0065] An exhaust outlet 104 is formed at the bottom of the chamber 102, and is structured capable of evacuating the chamber 102 to a predetermined reduced-pressure atmosphere using a vacuum pump not shown in the drawing.

[0066] With the RIE apparatus 101, the arc power supply 109 was connected to the susceptor 103, the inter-electrode gap L1 was adjusted to 100 mm, and the chamber 102 was evacuated to create a high vacuum state of 6.7 Pa (50 mTorr). Afterwards, the etching gases were supplied to the chamber 102 in a mixing ratio of CF4:O2=80:20 while maintaining a flow of 50 mL/min (scm). In this state, a high-frequency electric field was generated by applying high-frequency power of 1,000 W to the susceptor 103 as a lower electrode, the etching gases were transformed into plasma, and the surface of the test plate was then etched. Etching was conducted for two hours.

[Adhesive Strength Degradation]

[0067] Adhesive strength before and after performing plasma processing under the aforementioned conditions was measured for five test pieces (φ25 mm) at a pulling rate of 1 mm/min. The average value thereof was calculated, and adhesive strength degradation due to plasma irradiation was then calculated by the following equation:

\[
(\%)(adhesive \ strength \ before \ plasma \ irradiation)(adhesive \ strength \ before \ plasma \ irradiation)\times100
\]

[0068] This adhesive strength degradation due to plasma irradiation is preferably no greater than 30% since there is a possibility that the sprayed film will peel off during the process where the value thereof is high.

[0069] Adhesive strength after performing plasma processing under the aforementioned conditions and before and after cleaning using purified water ultrasonic waves was measured for five test pieces (φ25 mm) at a pulling rate of 1 mm/min. The average value thereof was calculated, and adhesive strength degradation due to the purified water ultrasonic waves was then calculated by the following equation:

\[
(\%)(adhesive \ strength \ before \ purified \ water \ ultrasonic \ cleaning)(adhesive \ strength \ before \ purified \ water \ ultrasonic \ cleaning)\times100
\]

[0070] This adhesive strength degradation due to the purified water ultrasonic waves is preferably no greater than 30% since there is a possibility that the sprayed film will peel off during the process where the value thereof is high.
### TABLE 1

<table>
<thead>
<tr>
<th>No</th>
<th>Spraying Device</th>
<th>Output Power (kW)</th>
<th>Material Drying Temperature (°C)</th>
<th>Material Drying Time (h)</th>
<th>Material Moisture Content (%)</th>
<th>Material Bulk Density (g/cm³)</th>
<th>Film Thickness (μm)</th>
<th>Film Formation Property x³</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Anode Separated-Type</td>
<td>110</td>
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<td>14</td>
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<td>O</td>
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<td>O</td>
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<tr>
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<td>100</td>
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<td>0.3</td>
<td>1.8</td>
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<td>2.1</td>
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<td>O</td>
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<td>O</td>
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<td>14</td>
<td>0.4</td>
<td>1.6</td>
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</table>

### Adhesive Strength Degradation (%)

<table>
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<tr>
<th>No</th>
<th>Relative Density (%)</th>
<th>Maximum Void Diameter (μm) x²</th>
<th>Etching Rate x³ (μm/min)</th>
<th>After Plasma Irradiation x⁴</th>
<th>After Purified Water Ultrasonic Cleaning x⁵</th>
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</table>

x³ Sample allowing film formation is denoted by O, sample with partial peeling during film formation by Δ, and sample with no film formation by X.

x² Maximum void diameter when ten fields of view in the sprayed surface were observed after polishing.

x³ Gas: CF₄ + 20% O₂, Output power: 1,000 kW, gas flow: 50 mL/min (sccm), pressure: 6.7 Pa (50 mTorr), processing time: 2 hours.

x⁴ Adhesive strength degradation after etching was conducted under plasma conditions in X³.

x⁵ Adhesive strength degradation after step of drying at 70°C for 1 hour was repeated thirty times after cleaning at 40 kHz for 10 min.

### TABLE 2

<table>
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<tr>
<th>No</th>
<th>Spraying Device</th>
<th>Output Power (kW)</th>
<th>Material Drying Temperature (°C)</th>
<th>Material Drying Time (h)</th>
<th>Material Moisture Content (%)</th>
<th>Material Bulk Density (g/cm³)</th>
<th>Film Thickness (μm)</th>
<th>Film Formation Property x³</th>
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</table>
As is evident from Tables 1 and 2, with the Y_{2}O_{3} sprayed film sprayed by the spraying device including two separated anode torches in Working Examples 1 to 8, relative density was 80% or greater and maximum void diameter was 25 μm or less in all cases. From this, it was confirmed that starting points for corrosion due to plasma decreased, and the etching rate using CF_{4}+O_{2} plasma was 5 μm/min or less.

[0073] Particularly, in Working Examples 1 to 5, a sprayed film having a thickness of 100 to 300 μm was formed by heating material having a bulk density of 1.8 g/cm^{3} or greater at a temperature of 100° C. or higher for at least twelve hours, drying it until the moisture content was 0.5 percent or less by mass, and spraying it with an output power of 40 kW to 110 kW using the spraying device including two anode torches. Consequently, it was confirmed that melting of the material progressed, so relative density was 90% or greater, maximum void diameter was 15 μm or less, and etching rate was 3 μm/min or less.

[0074] Furthermore, in Working Examples 1 to 5, since voids 25 μm or greater in diameter, which became starting points for corrosion due to plasma, did not exist, adhesive strength degradation before and after plasma irradiation was below 20% without generation of locally low adhesive strength regions between the sprayed film and the substrate. Furthermore, it was confirmed that there was little corrosion at the interface between the substrate and the sprayed film after plasma irradiation, and adhesive strength degradation by purified water ultrasonic cleaning after plasma irradiation was also below 20%.

[0075] Meanwhile, in Comparative Examples 1 and 2 where material drying was not performed, maximum void diameter exceeded 25 μm, etching rate was high, and adhesive strength degradation was prominent.

[0076] Furthermore, in Comparative Example 3 using a material having a low bulk density, maximum void diameter was large, etching rate was high, adhesive strength degradation was prominent, and film peeling occurred during an adhesive strength test after purified water ultrasonic cleaning. In Comparative Example 4 where spray output power was low, film formation property was poor, and etching rate was high.

[0077] In Comparative Examples 5 to 7 using the anode integrated spraying device, maximum void diameter was large, etching rate was high, and adhesive strength degradation was prominent. In Comparative Example 8 using the anode integrated spraying device and using material having low spray output power and high bulk density, film formation was impossible.
In Comparative Example 9 using the HVOF (high velocity oxygen fuel thermal spraying) device, maximum void diameter was small, relative density was low, and etching rate was high.

**WORKING EXAMPLES 9 TO 16, COMPARATIVE EXAMPLES 10 TO 18**

An Al substrate (JIS 6061) surface roughened to a surface roughness Ra greater than 4 μm was prepared, different types of spraying devices were used, and an Al₂O₃ sprayed film was formed and used as a test plate. The same spraying devices as mentioned above were used.

Film manufacturing conditions: drying temperature, drying time, moisture content, bulk density of material (granular), sprayed film thickness, and spray output (15 to 110 kW), were varied as shown in Tables 3 and 4, and were called Working Examples 9 to 16 and Comparative Examples 10 to 18. In the respective working examples and comparative examples, film formation property, porosity, relative density, maximum void diameter, etching rate, adhesive strength degradation due to plasma irradiation, and adhesive strength degradation due to purifed water ultrasonic cleaning after plasma irradiation were respectively evaluated by the same standards as in Working Example 1 and the other examples by the following methods. Results thereof are shown in Tables 3 and 4 collectively.

As is evident from Tables 3 and 4, with the Al₂O₃ sprayed film sprayed by the spraying device including two separated anode torches in Working Examples 9 to 16, relative density was 80% or greater and maximum void diameter was 25 μm or less in all cases. From this, it was confirmed that starting points for plasma corrosion decreased, and the etching rate using CF₄+O₂ plasma was 20 μm/min or less.

Particularly, in Working Examples 9 to 13, a sprayed film having a thickness of 100 to 300 μm was formed by heating material having a bulk density of 1.2 g/cm³ or greater at a temperature of 100°C. or higher for at least twelve hours, drying it until the moisture content was 0.5 percent or less by mass, and spraying it with output power of 40 kW to 110 kW using the spraying device including two anode torches. Consequently, it was confirmed that melting of the material progressed, relative density was 90% or greater, maximum void diameter was 15 μm or less, and etching rate was 15 μm/min or less.

Furthermore, in Working Examples 9 to 13, since voids 25 μm or greater in diameter, which became starting points for corrosion due to plasma, did not exist, adhesive strength degradation before and after plasma irradiation was below 20% without generation of locally low adhesive strength regions between the sprayed film and the substrate. Furthermore, it was confirmed that there was little corrosion at the interface between the substrate and the sprayed film after plasma irradiation, and adhesive strength degradation after purifed water ultrasonic cleaning after plasma irradiation was also below 20%.

Meanwhile, in Comparative Examples 10 and 11 where material drying was not performed, etching rate was high and adhesive strength degradation was prominent.

Furthermore, in Comparative Example 12 using a material having a low bulk density, maximum void diameter was large, etching rate was high, adhesive strength degradation was prominent, and film peeling occurred during an adhesive strength test after purifed water ultrasonic cleaning. In Comparative Example 13 where spray output power was low, film formation property was poor, and etching rate was high.

In Comparative Examples 14 and 15 using the anode integrated spraying device, maximum void diameter was large, etching rate was high, and adhesive strength degradation was prominent. In Comparative Examples 16 and 17 using the anode integrated spraying device and using material having relatively low spray output power and high bulk density, film formation was impossible. In Comparative Example 18 using the HVOF (high velocity oxygen fuel thermal spraying) device, maximum void diameter was small and etching rate was high.

**TABLE 3**

<table>
<thead>
<tr>
<th>No</th>
<th>Spraying Device</th>
<th>Output Power (kW)</th>
<th>Material Drying Temperature (°C.)</th>
<th>Material Drying Time (h)</th>
<th>Material Moisture Content (%)</th>
<th>Material Bulk Density (g/cm³)</th>
<th>Film Thickness (μm)</th>
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TABLE 3-continued

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</table>

X5: Sample allowing film formation is denoted by ○, sample with partial peeling during film formation by Δ, and sample with no film formation by X.
X3: Maximum void diameter when ten fields of view in the sprayed surface were observed after polishing
X4: Adhesive strength degradation after etching was conducted under plasma conditions in X3
X6: Adhesive strength degradation after step of drying at 70° C. for 1 hour was repeated thirty times after cleaning at 40 kHz for 10 min

[0087]

TABLE 4

<table>
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<tr>
<th>No</th>
<th>Spraying Device</th>
<th>Output Power (kW)</th>
<th>Material Drying Temperature (°C)</th>
<th>Material Drying Time (h)</th>
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### TABLE 4-continued

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<th>Maximum Void Diameter (μm)</th>
<th>Etching Rate (nm/min)</th>
<th>Adhesive Strength Degradation (%) After Plasma Irradiation</th>
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**Notes:**
- Sample allowing film formation is denoted by ○, sample with partial peeling during film formation by Δ, and sample with no film formation by X.
- Maximum void diameter when ten fields of view in the sprayed surface were observed after polishing.
- Etching: CF₄ + 20% O₂, Output power: 1,000 kW, gas flow: 50 mL/min(eccm), pressure: 6.7 Pa(50 mTorr), processing time: 2 hours.
- Adhesive strength degradation after etching was conducted under plasma conditions in X³³
- Adhesive strength degradation after step of drying at 70°C for 1 hour was repeated thirty times after cleaning at 40 kHz for 10 min.

### INDUSTRIAL APPLICABILITY

[00088] The corrosion-resistant member according to the present invention is applicable preferably in manufacturing processes for semiconductor devices and liquid crystal devices, for example.

1. A corrosion-resistant member used in a corrosive environment, the corrosion-resistant member comprising a substrate and a ceramic sprayed film, which covers a part or all of the substrate surface and has a relative density of 80% or greater, wherein the ceramic sprayed film has a thickness of 50 to 500 μm, and a surface prepared such that voids existing therein have a maximum diameter of 25 μm or less.

2. The corrosion-resistant member of claim 1, wherein the ceramic sprayed film is a film made of Y₂O₃, and has an etching rate of 5 nm/min or less when plasma etching is performed under conditions of a flow rate of 50 mL/min, an output power of 1,000 W, and a pressure of 6.7 Pa using a mixed gas made of 80% CF₄ and 20% O₂ by a parallel plate type RIE apparatus with inter-electrode gap of 100 mm.

3. The corrosion-resistant member of claim 2, wherein the corrosion-resistant member is obtained by using Y₂O₃ having a bulk density of at least 1.5 g/cm³ and a moisture content of 1 mass percent or less as material for the ceramic sprayed film and spraying plasma on the substrate with an output power of 40 to 110 kW by a spraying device including two anode torches.

4. The corrosion-resistant member of claim 1, wherein the ceramic sprayed film is a film made of Al₂O₃, and has an etching rate of 20 nm/min or less when plasma etching is performed under conditions of a flow rate of 50 mL/min, an output power of 1,000 W, and a pressure of 6.7 Pa using a mixed gas made of 80% CF₄ and 20% O₂ by a parallel plate type RIE apparatus with inter-electrode gap of 100 mm.

5. The corrosion-resistant member of claim 4, wherein the corrosion-resistant member is obtained by using Al₂O₃ having a bulk density of at least 1.0 g/cm³ and a moisture content of 1 mass percent or less as material for the ceramic sprayed film and spraying plasma on the substrate with an output power of 40 to 110 kW by a spraying device including two anode torches.

6. A method for manufacture of a corrosion-resistant member by covering a substrate surface with a Y₂O₃ film through plasma thermal spraying, the method comprising:
   - a drying step of drying material having a bulk density of at least 1.5 g/cm³ until a moisture content is 1 percent or less by mass; and
   - a plasma thermal spraying step of spraying the material after drying on a substrate surface with an output power of 40 to 110 kW by a spraying device including two anode torches, and forming a Y₂O₃ film having a relative density of 80% or greater, a thickness of 50 to 500 μm, and a surface prepared such that voids existing therein have a maximum diameter of 25 μm or less.

7. A method for manufacture of a corrosion-resistant member by covering a substrate surface with an Al₂O₃ film through plasma thermal spraying, the method comprising:
   - a drying step of drying material having a bulk density of at least 1.0 g/cm³ until a moisture content is 1 percent or less by mass; and
   - a plasma thermal spraying step of spraying the material after drying on a substrate surface with an output power of 40 to 110 kW by a spraying-device including two anode torches, and forming an Al₂O₃ film having a relative density of 80% or greater, a thickness of 50 to 500 μm, and a surface prepared such that voids existing therein have a maximum diameter of 25 μm or less.

* * * * *