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(54) **METHOD OF MANUFACTURING PLASMA-RESISTANT COATING FILM**

(71) Applicant: **KOMICO LTD.**, Anseong-si (KR)

(72) Inventors: **Dong Hun Jeong**, Anseong-si (KR); **Seong Sik Bang**, Anseong-si (KR); **Jae Im Jeong**, Anseong-si (KR); **Dae Sung Kim**, Anseong-si (KR)

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CPC ***C23C 4/11*** (2016.01); ***C23C 6/00*** (2013.01); ***C23C 4/134*** (2016.01)

(57) **ABSTRACT**

Disclosed herein is a method of manufacturing a plasma-resistant coating film. The method includes (1) forming a lower coating layer through a thermal spray process, on a base member, from a first rare earth metal compound powder including 90 to 99.9 wt % of first rare earth metal compound particles and 0.1 to 10 wt % of silica (SiO_2) particles, (2) processing the surface of the lower coating layer formed in step (1) to have an average surface roughness of 1 to 6 μm, and (3) forming an upper coating layer through a suspension plasma spray process, on the lower coating layer which is surface-treated in step (2), from second rare earth metal compound particles, to obtain a structurally dense and chemically stable plasma-resistant coating film with improved plasma resistance.

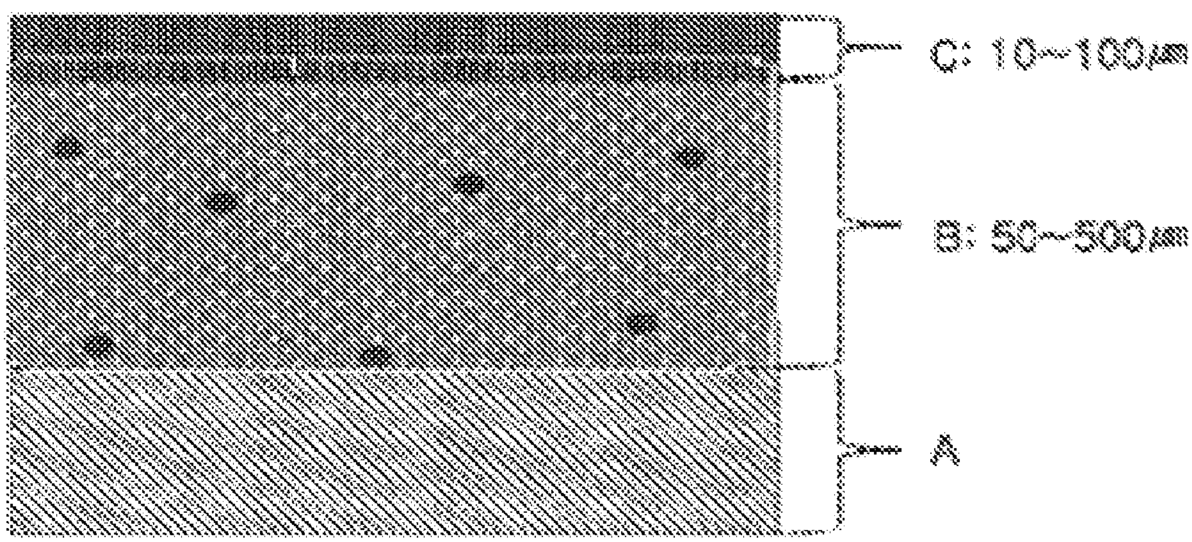


FIG. 1

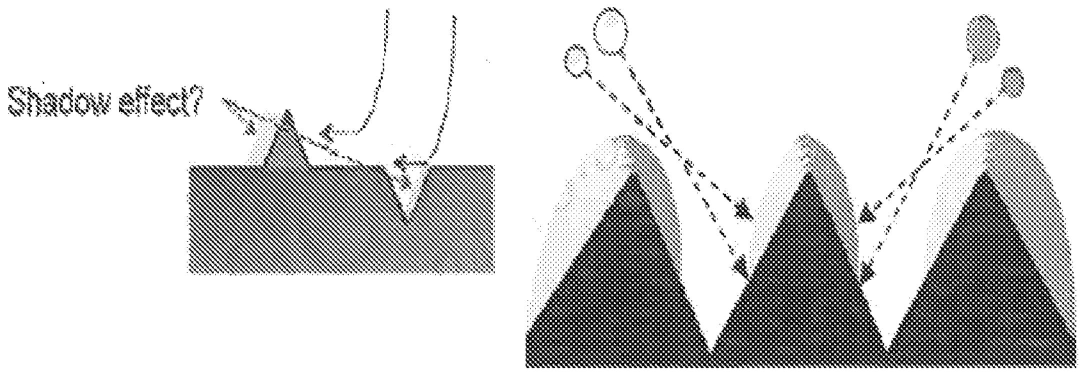


FIG. 2

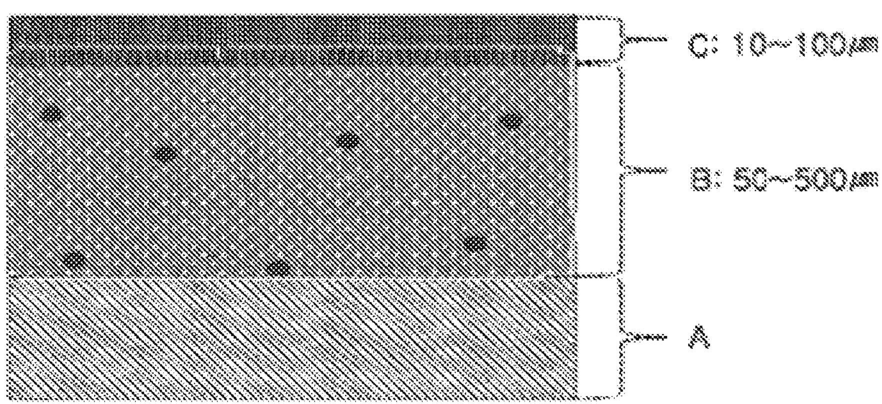


FIG. 3(A)

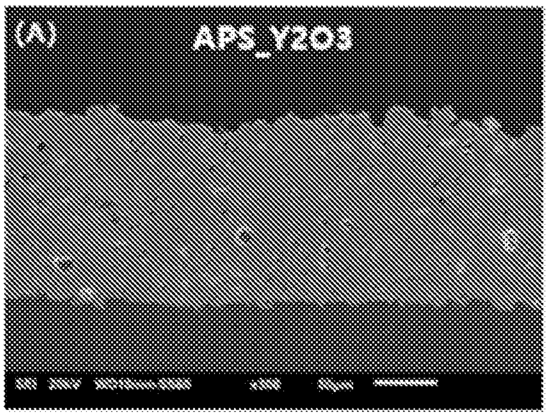


FIG. 3(B)

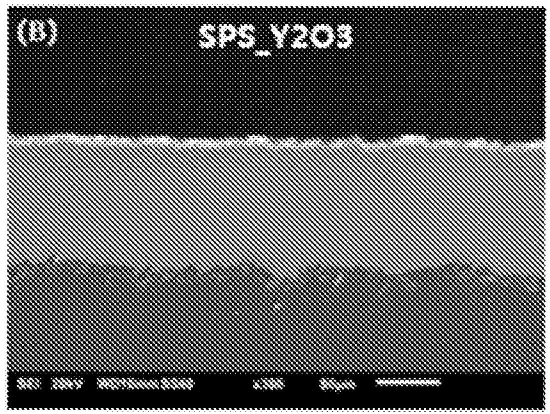


FIG. 3(C)

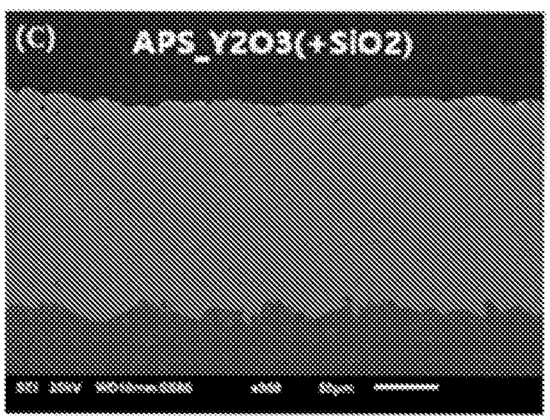


FIG. 3(D)

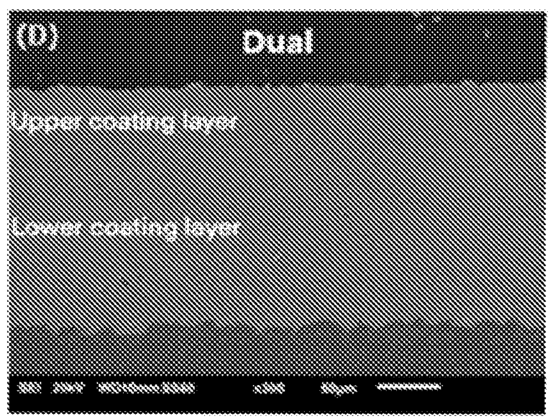


FIG. 4 (A)

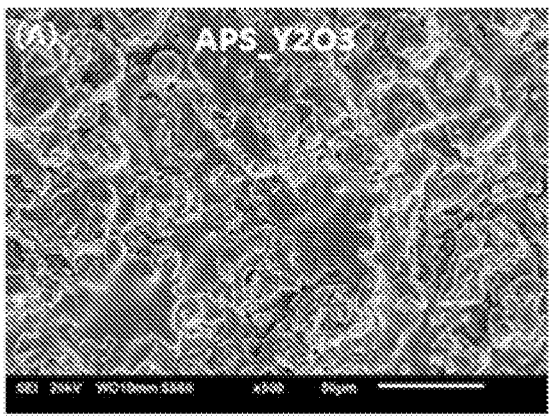


FIG. 4(B)

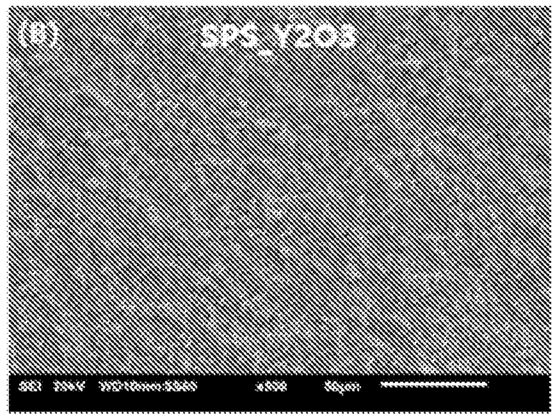


FIG. 4(C)

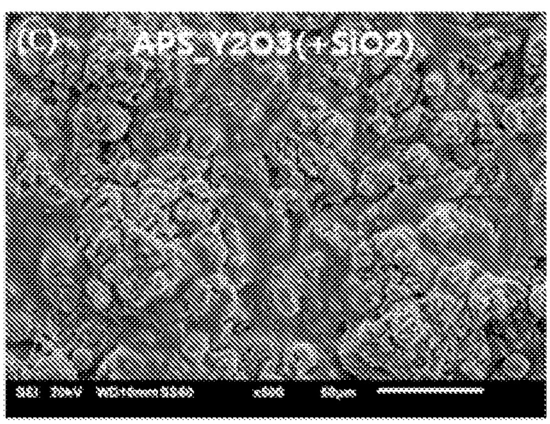
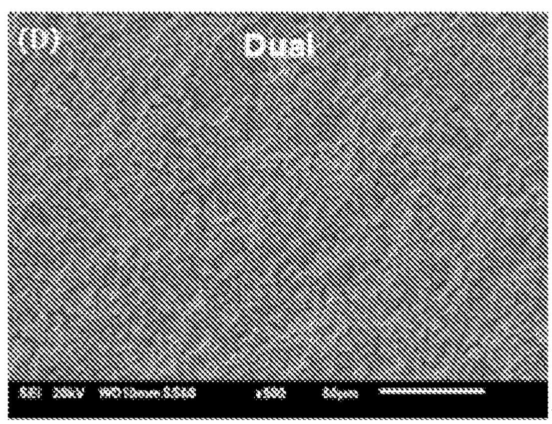


FIG. 4(D)



METHOD OF MANUFACTURING PLASMA-RESISTANT COATING FILM

CROSS-REFERENCE TO RELATED APPLICATION

[0001] The present application claims priority to Korean Patent Application No. 10-2021-0111370 filed on Aug. 24, 2021, the entire contents of which is incorporated herein for all purposes by this reference.

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0002] The present invention relates to a method of manufacturing a plasma-resistant coating film and, more particularly, to a method of manufacturing a plasma-resistant coating film applicable to a semiconductor manufacturing process involving semiconductor etching equipment.

2. Description of the Related Art

[0003] Typically, a process chamber in a semiconductor manufacturing facility is made of anodized aluminum alloy or a ceramic bulk such as alumina for insulation.

[0004] Recently, as to chambers used in semiconductor manufacturing facilities such as deposition facility for chemical vapor deposition or the like and etching facility for plasma etching, the need for corrosion resistance to highly corrosive gas or plasma, etc. increases. For this reason, the chambers used in semiconductor manufacturing processes have been manufactured by forming a ceramic coating layer on aluminum alloy or alumina through plasma spray or thermal spray so that the chambers have high corrosion resistance.

[0005] In addition, since most of the semiconductor manufacturing processes are high-temperature processes such as heat treatment, chemical vapor deposition, etc., the chambers are required to have thermal resistance as well as corrosion resistance. In addition, a component of a semiconductor manufacturing facility such as a chamber requires insulation, heat resistance, corrosion resistance. In addition, it is necessary for a coating layer to have high adhesion to a base member to prevent the coating layer from being peeled off, resulting in prevention of occurrence of particles and of contamination of wafers during the manufacturing processes.

[0006] For this purpose, a chemical vapor deposition method, a physical vapor deposition method, a sputtering method, etc. have been typically used. However, these methods are to form a thin film, there is a problem in that it takes a long time to form a thick film with a sufficient thickness to satisfy the corrosion resistance requirement, resulting in low economic feasibility, and it is difficult to obtain strong adhesion between the base member and the coating layer.

[0007] On the other hand, a method of forming a thick coating film with a thickness of 100 μm or more through plasma spray is disclosed in Korean patent No. 10-100454987. However, there is a problem in that it is difficult to form a dense coating film when the thick film is coated through plasma spray.

[0008] Aerosol deposition can overcome the above problems and provide a dense thick film. However, but in the case of using a rare earth metal compound, there is a problem in that it is difficult to form a dense thick film of 100 μm or more. In the case of aerosol deposition, which is being researched recently, it is technically possible to form a 10-μm thick film, but problems such as peeling may occur during long-term use due to the low adhesive strength formed by mechanical engagement between the film and the surface. In addition, the film is etched by CF_4 plasma ions and radicals used in a dry etching process, resulting in particles, which may contaminate the wafer.

[0009] In addition, as a conventional art, Korean patent application publication No. 10-2017-0080123 (Jul. 10, 2017) discloses securing chemical resistance characteristics and a technology of manufacturing a dense rare-earth metal coating film by minimizing open channel and open pore of the coating layer by double sealing through aerosol deposition and hydration treatment after thermal spraying a first rare earth metal compound.

[0010] In addition, Korean patent application publication No. 10-2013-0123821 (Nov. 13, 2013) discloses a multi-layer plasma-resistant coating film technology in which a second coating film having a higher density and plasma resistance than those of a first coating film due to aerosol deposition after manufacturing an amorphous first coating film formed by plasma thermal spray coating a thermal coating powder mixed with 30 to 50% by weight of aluminum oxide and 50 to 70% by weight of yttrium oxide on the base member to be coated.

[0011] However, in the literature, as the coating layer manufactured by atmospheric plasma spray generates tensile stress due to volume contraction accompanied by the melting-solidification process and the coating layer manufactured by aerosol deposition generates compression stress due to mechanical collision, when atmospheric plasma spray and aerosol coating layer are simultaneously applied when manufacturing a multi-layer coating layer, peeling and destruction of the coating layer may be induced due to the stress difference between coating layers.

[0012] Therefore, in the plasma-resistant coating film formed of the multi-layered coating layer, peeling and particle generation problems that may occur due to a decrease in adhesive strength between the coating layers still remain, and the technology of manufacturing a plasma-resistant coating film having durability and long life characteristics is required.

[0013] Meanwhile, suspension plasma spray (SPS) has emerged as a means for depositing finer particles. It is an advanced technology of plasma thermal spray technology that stably provides thermal spray powder in a plasma frame after preparing a suspension by mixing thermal spray powder of several micrometers with a liquid such as water or ethanol.

[0014] However, since suspension plasma spray supplies with plasma energy high enough to volatilize water or ethanol, it is difficult to form a thick coating layer of 150 μm or more by thermal shock, and particles may occur by peeling of the coating layer. In addition, the concentration of the thermal spray powder in the suspension is limited to a level of 50% or less, so the film formation speed is slow. Such film formation speed causes fatal problems in decreasing the manufacturing speed and increasing the manufacturing costs.

[0015] In addition, as illustrated in FIG. **1** below, since the size of powder used is small, the suspension plasma spray may have a shadow effect that does not cover the entire surface roughness and causes some defects, resulting in problems such as high surface roughness, low adhesive strength, low density, etc.

[0016] Therefore, in order to improve the suspension plasma spray method, the inventors have repeatedly studied a method of manufacturing a high dense plasma-resistant coating film having excellent breakdown voltage characteristics while optimizing bonding force between coating layers, resulting in the present invention.

DOCUMENT OF RELATED ART

[0017] Patent Document

[0018] Patent Document 1: Korean patent No. 10-0454987

[0019] Patent Document 2: Korean patent application publication No. 10-2017-0080123

[0020] Patent Document 3: Korean patent application publication No. 10-2013-0123821

SUMMARY OF THE INVENTION

[0021] An objective of the present invention is to provide a method of manufacturing a plasma-resistant thin coating film having excellent adhesion to a base member, having high density, and improved breakdown voltage characteristics.

[0022] Another objective of the present invention is also to provide a plasma-resistant member with a plasma-resistant thin coating film with improved plasma resistance and improved breakdown voltage characteristics, the coating film manufactured by using the plasma-resistant thin coating film manufacturing method.

[0023] In order to accomplish the above objectives, in one aspect of the present invention, there is provided a method of manufacturing a plasma-resistant coating film, the method including: (1) forming a lower coating layer on a base member to be coated from a first rare earth metal compound powder including 90 to 99.9 wt % of first rare earth metal compound particles and 0.1 to 10 wt % of silica (SiO_2) particles through a thermal spray process; (2) processing the surface of the lower coating layer formed in step (1) to have an average surface roughness of 1 to 6 μm; and (3) forming an upper coating layer on the lower coating layer which is surface-treated in step (2) from second rare earth metal compound particles through a suspension plasma spray process.

[0024] In a preferred embodiment of the present invention, the first rare earth metal compound powder may include 95 to 99.9 wt % of first rare earth metal compound particles and 0.1 to 5 wt % of silica (SiO_2) particles.

[0025] In a preferred embodiment of the present invention, the first rare earth metal compound powder may have a particle size of 10 to 60 μm, and the lower coating layer may have a thickness of 50 to 500 μm.

[0026] In a preferred embodiment of the present invention, the second rare earth metal compound may have a particle size of 0.1 to 10 μm, and the upper coating layer may have a thickness of 50 to 150 μm.

[0027] In a preferred embodiment of the present invention, the lower coating layer may have a porosity of less than 2 vol %, and the upper coating layer may have a porosity of less than 1 vol %.

[0028] In a preferred embodiment of the present invention, each of the first rare earth metal compound and the second rare earth metal compound may be selected from the group consisting of yttria (Y_2O_3), yttrium fluoride (YF), and yttrium oxyfluoride (YOF).

[0029] In a preferred embodiment of the present invention, the first rare earth metal compound may be yttria (Y_2O_3).

[0030] In a preferred embodiment of the present invention, the thermal spray process in step (1) may be atmospheric plasma spray.

[0031] In a preferred embodiment of the present invention, the surface processing in step (2) may be performed by polishing using a diamond pad.

[0032] In another aspect of the present invention, there is provided a plasma-resistant member manufactured by the manufacturing method described above.

[0033] In a further aspect of the present invention, there is provided a plasma-resistant coating film including: a lower coating layer formed on a base member to be coated and made from a first rare earth metal powder including 90 to 99.9 wt % of first rare earth metal compound particles and 0.1 to 10 wt % of silica (SiO_2) particles through a thermal spray process, the lower coating layer having an adhesive strength of 20 MPa or more with respect to the base member; and an upper coating layer formed on the lower coating layer and made from second rare earth metal compound particles through a suspension plasma spray process, in which the plasma-resistant coating film has a porosity of less than 1 vol %.

[0034] In a preferred embodiment of the present invention, each of the first rare earth metal compound and the second rare earth metal compound may be selected from the group consisting of yttria (Y_2O_3), yttrium fluoride (YF), and yttrium oxyfluoride (YOF).

[0035] In a preferred embodiment of the present invention, the first rare earth metal compound may be yttria (Y_2O_3).

[0036] In a preferred embodiment of the present invention, the lower coating layer may have a porosity of less than 2 vol %, and the upper coating layer may have a porosity of less than 1 vol %.

[0037] In a preferred embodiment of the present invention, the lower coating layer may have a thickness of 50 to 500 μm and the upper coating layer may have a thickness of 50 to 150 μm.

[0038] The plasma-resistant coating film manufacturing method according to the present invention uses the suspension plasma spray process causing high thermal stress when forming the upper coating layer from the second rare earth metal compound, thereby giving the annealing effect and the thermal diffusion effect on the lower coating layer made from the first rare earth metal compound, thereby forming a structurally dense and chemically stable thin coating film. In addition, due to the structurally dense upper coating layer made from the second rare earth metal compound through the suspension plasma spray, the thin coating film also has plasma resistance and improved breakdown voltage characteristics.

[0039] In addition, since the upper coating layer formed by the suspension plasma spray and the lower coating layer formed by the thermal spray exhibit almost the same tension stress, the upper and lower coating layers provide stable adhesion, thereby preventing the coating film from being peeled and minimizing the generation of particles.

[0040] In addition, the present invention can provide a reasonable process time by solving the problem of the slow film formation speed of the suspension plasma spray, by using the thermal spray to form the lower coating layer.

BRIEF DESCRIPTION OF THE DRAWINGS

[0041] FIG. **1** is a schematic diagram for explaining a shadow effect that occurs during thermal spray coating;

[0042] FIG. **2** is a schematic diagram for explaining the structure of a plasma-resistant coating film including a first rare earth metal compound coating layer and a second rare earth metal compound coating layer of the present invention;

[0043] FIG. **3**(A). FIG. **3**(B), FIG. **3**(C), FIG. **3**(D) show scanning electron microscope (SEM) images, in which FIG. **3**(A) and FIG. **3**(B) show coating films manufactured according to Comparative Example 1 and Comparative Example 4, respectively, FIG. **3**(C) shows a lower coating film of a plasma-resistant coating film of the present invention, and FIG. **3**(D) shows a side surface of a plasma-resistant coating film manufactured according to Example 1; and

[0044] FIG. **4**(A), FIG. **4**(B), FIG. **4**(C), FIG. **4**(D) show SEM images in which FIG. **4**(A) and FIG. **4**(B) show coating films manufactured according to Comparative Example 1 and Comparative Example 4, respectively, FIG. **4**(C) shows a lower coating film of a plasma-resistant coating film according to the present invention, and FIG. **4**(D) shows a surface of a plasma-resistant coating film manufactured according to Example 1.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0045] Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by experts skilled in the art to which the present invention pertains. In general, the nomenclature used herein is well known and commonly used in the art.

[0046] Throughout the present specification, when a part "includes" a certain component, this means that it may further include other components rather than excluding other components, unless specifically stated to the contrary.

[0047] In one aspect of the present invention, there is provided a method of manufacturing a plasma-resistant coating film, the method including:

[0048] (1) forming a lower coating layer on a base member to be coated from a first rare earth metal compound powder including 90 to 99.9 wt % of first rare earth metal compound particles and 0.1 to 10 wt % of silica (SiO_2) particles through a thermal spray process; and

[0049] (2) processing the surface of the lower coating layer formed in step (1) to have an average surface roughness of 1 to 6 μm; and

[0050] (3) forming an upper coating layer on the lower coating layer which is surface-treated in step (2) from a second rare earth metal compound particles through a suspension plasma spray process.

[0051] More specifically, as illustrated in FIG. **2**, a method of manufacturing a plasma-resistant coating film according to the present invention forms a lower coating layer (B) on a base member to be coated (A) from a first rare earth metal compound powder including 0.1 to 10 wt % of silica (SiO_2) particles through a thermal spray process. After processing the surface of the lower coating layer (B) to have an average surface roughness of 1 to 6 μm, an upper coating layer (C) from a second rare earth metal compound is formed on the lower coating layer (B) which is surface-treated through a suspension plasma spray (SPS) process having a high coating density to obtain a high dense plasma-resistant coating film having excellent adhesive strength between layers, plasma-resistant and breakdown voltage.

[0052] A method of manufacturing a plasma-resistant coating film according to the present invention, first, forms a lower coating layer on a base member to be coated from a first rare earth metal compound powder including 90 to 99.9 wt % of first rare earth metal compound particles and 0.1 to 10 wt % of silica (SiO_2) particles through a thermal spray process [Step (1)].

[0053] The base member to be coated may be a plasma device part such as electrostatic chuck applied inside the plasma device, a heater, a chamber liner, a shower head, a boat for CVD, a focus ring, a wall liner, etc., the material of the base member to be coated may be metal such as iron, magnesium, aluminum or ally thereof; ceramic such as SiO_2, MgO, CaCO3, alumina, etc.; and polymer such as polyethylene terephthalate, polyethylene naphthalate, polypropylene adipate, polyisocyanate, etc., but is not limited thereto.

[0054] In addition, by sanding the surface of the base member to be coated to provide a certain surface roughness, the adhesive characteristics of the lower coating layer including the base member to be coated and the first rare earth metal compound to be formed thereafter can be improved.

[0055] In the present embodiment, the base member to be coated may be sanded to have a surface roughness having an average center roughness value of about 1 to 6 μm. When the surface roughness of the base member to be coated is less than 1 μm, the adhesive characteristics of the lower coating layer including the first rare earth metal compound and the silica compound formed thereafter and the base member to be coated are lowered, there may be a problem that the lower coating layer may be easily peeled off from the base member to be coated by an external impact. On the other hand, when the surface roughness of the base member to be coated exceeds 6 μm due to the sanding, it may affect the surface roughness of the lower coating layer formed thereafter and thus, there may be a problem that the upper coating layer including the second rare earth metal compound formed on the lower coating layer may not be formed in a uniform thickness.

[0056] Meanwhile, as illustrated in Table 1 below, when a coating film is manufactured using a rare earth metal compound powder including a small amount of silica component as a thermal spray material in addition to the rare earth metal compound particles, there is an effect of improving the adhesive strength of the coating layer.

TABLE 1

Classification	Coating method	Kind of coating film	Adhesive strength (MPa)
1	APS	YF3	10.0
2	APS	YOF	8.0
3	APS	Y2O3 (+SiO_2 0.1~10 wt. %)	20.0

[0057] Therefore, in manufacturing a plasma-resistant coating layer according to the present invention, in order to improve the adhesive strength of the lower coating layer, the first rare earth metal compound powder may include 90 to

99.9 wt % of the first rare earth metal compound particles and 0.1 to 10 wt % of silica (SiO_2) particles, thereby further improving the adhesive characteristics of the lower coating layer, and more preferably, 95 to 99.9 wt % of the first rare earth metal compound particles and 0.1 to 5 wt % of silica (SiO_2) particles.

[0058] In this case, the first rare earth metal compound may be selected from the group consisting of yttria (Y_2O_3), yttrium fluoride (YF), and yttrium oxyfluride (YOF), and specifically, yttria (Y_2O_3), is preferable.

[0059] In step (1), the lower coating layer is a coating layer formed on a base member to be coated from a first rare earth metal compound powder including a first rare earth metal compound and silica through a thermal spray process. It is preferable to manufacture it by using the first rare earth metal compound powder having a particle size of 10 to 60 μm, and more preferably, 20 to 40 μm. When the first rare earth metal compound powder is less than 10 μm, the granular powders may agglomerate with each other due to electrostatic attraction between the granular powders, making it practically difficult to transfer in the atmosphere, or due to low mass after transfer of the granular powder, it is highly possible that the transfer to the central frame of the thermal spray gun may not performed and deviate from the target position. When it exceeds 60 μm, the size of the droplet increases and the size of the defect is formed relatively large in the process of solidification of the droplet, resulting in a decrease in density, such that the surface roughness of the first rare earth metal compound coating layer cannot form a uniform thin film.

[0060] In addition, it is preferably that the first rare earth metal compound coating layer has a thickness of 50 to 500 μm, and more preferably, 100 to 200 μm. When the first rare earth metal compound coating layer has a thickness of less than 50 μm, the effect of improving the entire film formation speed is reduced, and when it exceeds 500 μm, the process time is increased, thereby reducing productivity.

[0061] In addition, it is preferable that the porosity of the lower coating layer formed by thermal spraying the first rare earth metal compound powder has a porosity of less than 2 vol %.

[0062] The thermal spray in step (1) may be applied without limitation as long as it is a thermal spray coating capable of forming a coating layer that satisfies the requirements such as strong bonding force and corrosion resistance between the base member to be coated and the lower coating layer, etc., and preferably in terms of high hardness and high electrical resistance of the coating layer, plasma thermal coating may be applied.

[0063] Specifically, the thermal spraying in step (1) may be performed by a plasma spray method, and the plasma spray method may be a form of atmospheric plasma spraying (APS) performed in the atmosphere, low pressure plasma spraying (LSP) performed spraying at a pressure lower than atmospheric pressure, and high pressure plasma spraying performed in a pressurized container at higher than atmospheric pressure.

[0064] According to such plasma spray, for example, a coating layer may be manufactured by generating plasma under condition of a voltage of 80.0V and a current of 600 A using, for example, argon gas 40NLPM and hydrogen gas 8NLPM.

[0065] In addition, thermal spray of the present invention may be performed by atmospheric pressure plasma spray. In this case, the plasma gas is not particularly limited, and may be appropriately selected, and for example, nitrogen/hydrogen, argon/hydrogen, argon/helium, argon/nitrogen, etc. may be used, and in the present invention, it is desirable that argon/hydrogen is sprayed.

[0066] In addition, as a specific example of plasma spray, in the case of argon/hydrogen plasma spray, atmospheric pressure plasma spray using a mixed gas of argon and hydrogen in an atmospheric atmosphere is mentioned. The thermal spray conditions such as a thermal spray distance, a current value, a voltage value, an argon gas supply amount, a hydrogen gas supply amount, etc. are set according to the use of the thermal spray member, etc. An amount of thermal spray material is filled in a powder supply device, and powder is supplied to the front end of the plasma spray gun by a carrier gas (argon) through a powder hose. By continuously supplying the powder in the plasma flame, the thermal spray material is melted and liquefied, and is liquid-framed with the force of the plasma jet. When liquid frame touches the substrate, the molten powder adheres, solidifies, and is deposited, thereby forming the first rare earth metal compound coating layer.

[0067] Subsequently, step (2) is a step of processing the surface of the lower coating layer including the first rare earth metal compound and the silica component to have an average surface roughness of 1 to 6 μm.

[0068] In the method of manufacturing a plasma-resistant coating film according to the present invention, step (2) is a step of processing the surface of the lower coating layer formed in step (1) to have an average surface roughness of 1 to 6 μm, and after grinding to have a uniform thickness, the surface of the lower coating layer is roughly processed to have an average surface roughness of 1 to 6 μm.

[0069] In this case, the surface processing may be performed by polishing using a diamond pad but is not limited thereto. In addition to polishing using a diamond pad, it may be polished using chemical mechanical polishing (CMP) or other polishing procedures.

[0070] Through the surface processing, the surface of the lower coating layer formed in step (1) may be roughened to have an average surface roughness of 1 to 6 μm, thereby improving adhesive strength between the lower coating layer and the upper coating layer. When the surface of the lower coating layer has an average surface roughness of 6 μm or more, the surface roughness is excessively high and thus coating is not properly performed, thereby causing peeling of the upper coating layer.

[0071] Subsequently, step (3) is a step of forming an upper coating layer by depositing a second rare earth metal compound by suspension plasma spray to form a denser coating layer on the lower coating layer.

[0072] Meanwhile, in forming the double coating layer, an upper layer may be formed by aerosol deposition on a lower coating layer manufactured by atmospheric plasma spray as disclosed in the prior literature. In addition, as in the present invention, after forming the lower coating layer by atmospheric plasma spray, the upper coating layer may be formed by aerosol suspension plasma spray deposition.

[0073] In this case, as illustrated in Table below, as the coating layer manufactured by atmospheric plasma spray generates tensile stress, and the coating layer formed by aerosol deposition generates compressive stress due to mechanical collision, when the atmospheric plasma spray and the aerosol deposition are simultaneously applied, peeling and breaking of the coating layer may be induced due to the stress difference between the coating layers, whereas as the same tensile stress is generated in the coating layer manufactured by atmospheric plasma spray and the coating layer manufactured by suspension plasma spray, peeling between coating layers due to the stress difference does not occur.

TABLE 2

	APS	SPS	Aerosol Deposition
Coating stress (MPa)	−3.0 ± 6.0	−3.0 ± 6.0	−195.9 ± 49.9
Base metal stress (MPa)	−26.9 ± 13.9	−30 ± 15.8	−63.9 ± 17.1
Base metal stress-coating stress (MPa)	−10~−43.8	−10~−55.8	99.2~199
Stress	Tensile stress	Tensile stress	Compressive stress

[0074] Therefore, in forming the plasma-resistant coating film of the present invention, in order to improve adhesive strength between the lower coating layer and the upper coating layer manufactured by atmospheric plasma spray, an upper coating layer including a second rare earth compound was formed using a suspension plasma spray method.

[0075] As an embodiment, a second rare earth metal compound suspension composition for forming an upper coating layer including a second rare earth metal compound will be described.

[0076] As an embodiment, the second rare earth metal compound powder is ball milled in the range of 100 to 140 revolution per minute (RPM) for 3 hours or more to manufacture solid contents and then distilled water is mixed. A slurry composition is prepared by adding a dispersant, etc. as an additive. In this case, the content of the second rare earth metal compound powder may be contained in an amount of 10 to 50 parts by weight based on 100 parts by weight of distilled water.

[0077] In this case, it is preferable for the second rare metal compound to use a powder having a particle size of 0.1 to 10 μm, and more preferably, 1 to 5 μm. When the second rare earth metal compounder powder is less than 0.1 μm, it is difficult to agglomerate and disperse the powder of the second rare earth metal compound powder in the solvent, and when it exceeds 10 μm, it is difficult to achieve the object of the present invention by increasing the surface roughness and porosity of the second rare earth metal compound coating layer.

[0078] According to such suspension plasma spray, for example, the plasma generation condition may be supplied at a flow rate of argon gas 340SCFH, nitrogen gas 100SCFH, and hydrogen gas 80SCFH to generate plasma under a condition of voltage 285.0V and current 380 A to form a coating player.

[0079] In this case, the upper coating layer including the second rare earth metal compound may be formed by repeatedly laminating the second rare earth metal compound twice or more using the suspension plasma spray method.

[0080] In addition, it is preferable that the upper coating layer including the second rare metal compound has a thickness of 50 to 150 μm. When the second rare earth metal compound coating layer has a thickness of less than 50 μm, it is difficult to secure plasma resistance because the thickness of the chemically stable and dense second rare earth metal compound coating layer is not sufficient. When it exceeds 150 μm, peeling may occur due to residual stress of the coating layer and a phenomenon in which breakdown voltage characteristics deteriorate occurs.

[0081] As illustrated in Table 3 below, the coating layer formed by the suspension plasma spray of yttria (Y_2O_3) solution exhibits an effect of improving the breakdown voltage characteristics as the thickness of the coating layer increases in the range of 150 μm or less, whereas when the thickness of the coating layer exceeds 150 μm, the breakdown voltage characteristics rather deteriorate as the thickness of the coating layer increases.

TABLE 3

classification	Coating method	Kind of coating film	Thickness of coating film	Breakdown voltage (V)
1	SPS	Y2O3 coating film	50	2,384
2	SPS	Y2O3 coating film	100	2,453
3	SPS	Y2O3 coating film	150	2,173
4	SPS	Y2O3 coating film	200	1,987

[0082] In this case, it is preferable that the upper coating layer including the second rare earth metal compound has a low porosity and is dense in order to secure the mechanical strength and electrical characteristics of the plasma-resistant coating film.

[0083] Therefore, the upper coating layer including the second rare earth metal compound formed by the suspension plasma spray coating has a porosity of less than 1 vol %, and it is preferable to indicate a value lower than 2 vol %, which is the porosity of the lower coating layer including the first rare earth metal compound and the silica compound.

[0084] As an embodiment, it is more preferably that the upper coating layer including the second rare earth metal compound has a porosity less than 40% or less of the porosity of the lower coating layer including the first rare earth metal compound and the silica compound to form a chemically stable coating film with improved plasma resistance.

[0085] In addition, the second rare earth metal compound may be selected from the group consisting of yttria (Y_2O_3), yttrium fluoride (YF), and yttrium oxyfluoride, and preferably, yttria is desirable. More preferably, when the first rare earth metal compound and the second rare earth metal compound are the same compound, the adhesive strength between the first rare earth metal compound coating layer (lower coating layer) and the second rare earth metal compound coating layer (upper coating layer) is improved, thereby minimize peeling of the coating film, generation of particles during the manufacturing process and contamination of the wafer therefrom.

[0086] In another aspect of the present invention, there is provided a plasma-resistant member manufactured by the method of manufacturing a plasma-resistant coating film, the method including:

[0087] (1) forming a lower coating layer on a base member to be coated from a first rare earth metal compound powder including 90 to 99.9 wt % of first rare earth metal compound particles and 0.1 to 10 wt % of silica (SiO_2) particles through a thermal spray process;

[0088] (2) processing the surface of the first rare earth metal compound coating layer formed in step (1) to have an average surface roughness of 1 to 6 μm; and

[0089] (3) forming an upper coating layer on the first rare earth metal compound coating layer which is surface-treated in step (2) from a second rare earth metal compound particles through a suspension plasma spray process.

[0090] In further another aspect of the present invention, there is provided a plasma-resistant coating film including:

[0091] a lower coating layer formed on a base member to be coated and made from a first rare earth metal powder including 90 to 99.9 wt % of first rare earth metal compound particles and 0.1 to 10 wt % of silica (SiO_2) particles through a thermal spray process, the lower coating layer having an adhesive strength of 20 MPa or more with respect to the base member; and

[0092] an upper coating layer formed on the lower coating layer and made from second rare earth metal compound particles through a suspension plasma spray process,

[0093] in which the plasma-resistant coating film has a porosity of less than 1 vol %.

[0094] In this case, each of the first rare earth metal compound and the second rare earth metal compound may be selected from the group consisting of yttria (Y_2O_3), yttrium fluoride (YF), and yttrium oxyfluoride (YOF), and preferably, the first rare earth metal compound may be yttria (Y_2O_3).

[0095] In addition, the lower coating layer may have a porosity of less than 2 vol %, the upper coating layer may have a porosity of less than 1 vol %, the lower coating layer may have a thickness of 50 to 500 μm and the upper coating layer may have a thickness of 50 to 150 μm.

[0096] Hereinafter, the present invention will be described in more detail with reference to the examples. The following examples are intended to illustrate the present invention, but the present invention is not limited by the following examples.

Comparative Example 1 to 3

[0097] It was performed using an atmospheric plasma spray device (Oerlikon Metco, F4 MB), and using argon gas 40 NLPM and hydrogen gas 8 NLPM, plasma was generated under the condition of voltage 80.0V and current 600 A to form a coating layer with Y_2O_3, YF_3 or YOF thermal spray coating powder to a thickness of 150 μm.

Comparative Example 4 to 6

[0098] It was performed using a suspension plasma thermal spray device (Progressive, 100HE), and using a flow rate of argon gas 340SCFH, nitrogen gas 100SCFH, and hydrogen gas 80SCFH, plasma was generated under the condition of voltage 285.0V and current 380 A to form a Y_2O_3, YF_3 or YOF coating layer to a thickness of 100 μm.

TABLE 4

Classification	Material	Coating method	Hardness (Hv)	Porosity (%)	Surface roughness	Adhesive strength
Comparative example 1	Y2O3	APS	415	4.5	4.5±0.4	10.0
Comparative example 2	YF3	APS	272	1.7	5.1±0.8	10.0
Comparative example 3	YOF	APS	377	4.4	4.6±0.5	8.0
Comparative example 4	Y2O3	SPS	524	0.6	2.0±0.5	15.0
Comparative example 5	YF3	SPS	466	0.8	2.2±0.4	13.0
Comparative example 6	YOF	SPS	497	0.8	1.7±0.2	10.0

Examples 1 to 3

[0099] 1-1: Forming Lower Coating Layer

[0100] It was performed using an atmospheric plasma spraying device (Oerlikon Metco, F4 MB), and using argon gas 40 NLPM and hydrogen gas 8 NLPM, plasma was generated under the condition of voltage 80.0V and current 600 A to form a coating layer with an average thickness of 200 μm. Then, surface polishing was performed so that the surface roughness of the coating layer was 1 to 3 μm and the thickness of the coating layer was 150 μm.

[0101] 1-2: Forming Upper Coating Layer

[0102] It was performed using a suspension plasma thermal spray device (Progressive, 100HE), and using a flow rate of argon gas 340SCFH, nitrogen gas 100SCFH, and hydrogen gas 80SCFH, plasma was generated under the condition of voltage 285.0V and current 380 A to form a Y_2O_3, YF_3 or YOF coating layer to a thickness of 50 μm.

TABLE 5

	Lower coating layer		Upper coating layer					
classification	Material	Coating method	Material	Coating method	Hardness (Hv)	Porosity (%)	Surface roughness	Adhesive strength
Example 1	Y2O3 + 1 wt % SiO_2	APS	Y2O3	SPS	542, 531	0.8	1.8 ± 0.2	20.0
Example 2	Y2O3 + 1 wt % SiO_2	APS	YF3	SPS	554, 458	0.9	1.9 ± 0.3	20.0
Example 3	Y2O3 + 1 wt % SiO_2	APS	YOF	SPS	548, 487	0.9	1.8 ± 0.3	20.0

[0103] As illustrated in Table 4, it was confirmed that the plasma-resistant coating films according to Examples 1 to 3 not only have better adhesive strength than the coating films according to Comparative Examples 1 to 3, but also have excellent mechanical properties and form a dense thin film.

[0104] In addition, as illustrated in FIGS. **3**(D) and **4**(D) below, it was confirmed that the high-density upper coating layer in the plasma-resistant coating film manufactured by Example 1 forms a coating layer of a very dense structure compared to the lower coating layer.

DESCRIPTION OF LETTER IN DRAWINGS

[0105] A: base member to be coated

[0106] B: first rare earth metal compound coating layer (lower coating layer)

[0107] C: second rare earth metal compound coating layer (upper coating layer)

What is claimed is:

1. A method of manufacturing a plasma-resistant coating film, the method comprising:

(1) forming a lower coating layer on a base member to be coated from a first rare earth metal compound powder comprising 90 to 99.9 wt % of first rare earth metal compound particles and 0.1 to 10 wt % of silica (SiO_2) particles through a thermal spray process;

(2) processing a surface of the lower coating layer formed in step (1) to have an average surface roughness of 1 to 6 μm; and

(3) forming an upper coating layer on the lower coating layer that is surface-treated in step (2), through a suspension plasma spray process from a second rare earth metal compound powder.

2. The method of claim **1**, wherein the first rare earth metal compound powder comprises 95 to 99.9 wt % of rare earth metal compound particles and 0.1 to 5 wt % of silica (SiO_2) particles.

3. The method of claim **1**, wherein the first rare earth metal compound powder has a particle size of 10 to 60 μm, and the lower coating layer has a thickness of 50 to 500 μm.

4. The method of claim **1**, wherein the second rare earth metal compound has a particle size of 0.1 to 10 μm, and the upper coating layer has a thickness of 50 to 150 μm.

5. The method of claim **1**, wherein the lower coating layer has a porosity of less than 2 vol % and the upper coating layer has a porosity of less than 1 vol %.

6. The method of claim **1**, wherein each of the first rare earth metal compound and the second rare earth metal compound is selected from the group consisting of yttria (Y_2O_3), yttrium fluoride (YF), and yttrium oxyfluoride (YOF).

7. The method as set forth in claim **1**, wherein the first rare earth metal compound is yttria (Y_2O_3).

8. The method of claim **1**, wherein the thermal spray process in step (1) is atmospheric plasma spray.

9. The method of claim **1**, wherein the surface process in step (2) is performed by polishing using a diamond pad.

10. A plasma-resistant member manufactured by the method of claim **1**.

11. A plasma-resistant coating film comprising:

a lower coating layer formed on a base member to be coated and made from a first rare earth metal compound powder comprising 90 to 99.9 wt % of first rare earth metal compound particles and 0.1 to 10 wt % of silica (SiO_2) particles through a thermal spray process, the lower coating layer having an adhesive strength of 20 MPa or more with respect to the base member; and

an upper coating layer formed on the lower coating layer and made from a second rare earth metal compound particles through a suspension plasma spray process,

wherein the plasma-resistant coating film has a porosity of less than 1 vol %.

12. The film of claim **11**, wherein each of the first rare earth metal compound and the second rare earth metal compound is selected from the group consisting of yttria (Y_2O_3), yttrium fluoride (YF), and yttrium oxyfluoride (YOF).

13. The film of claim **11**, wherein the first rare earth metal compound is yttria (Y_2O_3).

14. The film of claim **11**, wherein the lower coating layer has a porosity of less than 2 vol % and the upper coating layer has a porosity of less than 1 vol %.

15. The film of claim **11**, wherein the lower coating layer has a thickness of 50 to 500 μm and the upper coating layer has a thickness of 50 to 150 μm.

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