

### (19) United States

### (12) Patent Application Publication (10) Pub. No.: US 2025/0257441 A1 JEONG et al.

Aug. 14, 2025 (43) Pub. Date:

(54) METHOD FOR MANUFACTURING HIGH-DENSITY YTTRIA FILM BY ATMOSPHERIC PLASMA SPRAYING METHOD AND YTTRIA THERMAL-SPRAYED FILM MANUFACTURED USING SAME

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(21) Appl. No.: 19/101,915 (22) PCT Filed: Jan. 4, 2024

(86) PCT No.: PCT/KR2024/000154

§ 371 (c)(1),

(2) Date: Feb. 7, 2025 (30)Foreign Application Priority Data

Jan. 10, 2023 (KR) ...... 10-2023-0003705

#### **Publication Classification**

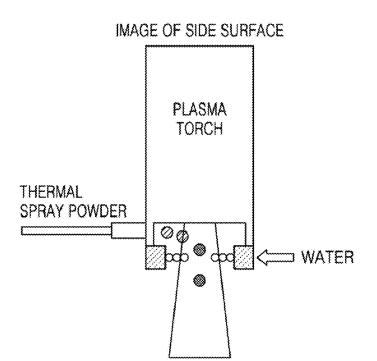
(51) Int. Cl. C23C 4/134 (2016.01)C23C 4/11 (2016.01)

(52) U.S. Cl. CPC ...... C23C 4/134 (2016.01); C23C 4/11 (2016.01)

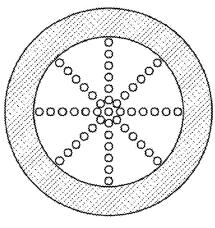
#### (57)ABSTRACT

Provided is a method of manufacturing an yttria thermal spray coating having low porosity, high density, and excellent plasma resistance, including arranging a spray unit at a distance of 50 to 130 mm from a base material, subjecting Y<sub>2</sub>O<sub>3</sub> thermal spray powder to atmospheric plasma spraying to form an yttria thermal spray coating on the base material, and supplying water at a rate of 50 to 400 ml/min together with the Y<sub>2</sub>O<sub>3</sub> thermal spray powder.

THERMAL SPRAY POWDER MELTED POWDER WATER 0



### **IMAGE OF LOWER SURFACE**



THERMAL SPRAY POWDER	0
MELTED POWDER	0
WATER	0

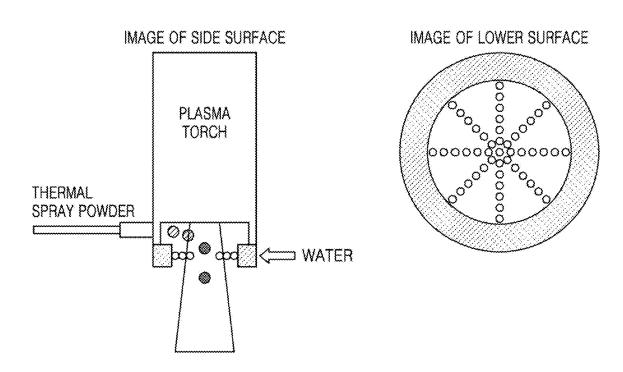


FIG. 1

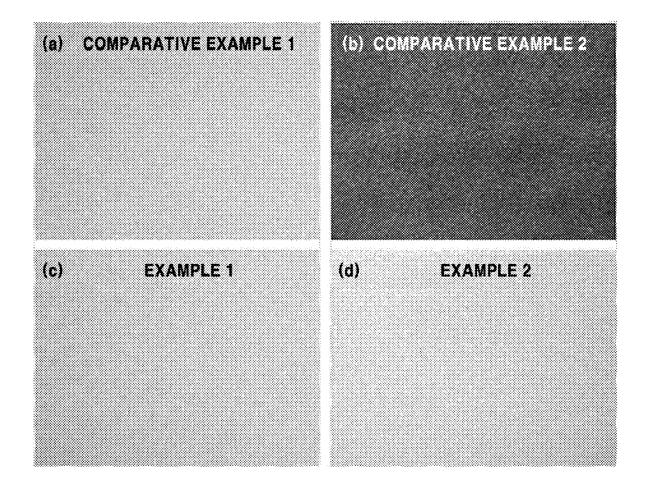


FIG. 2

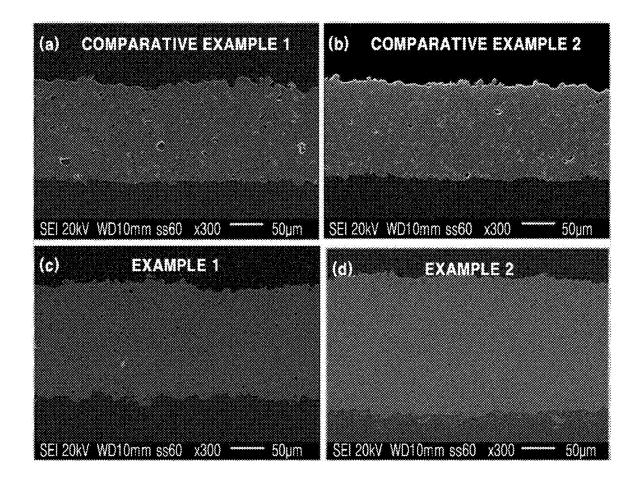


FIG. 3

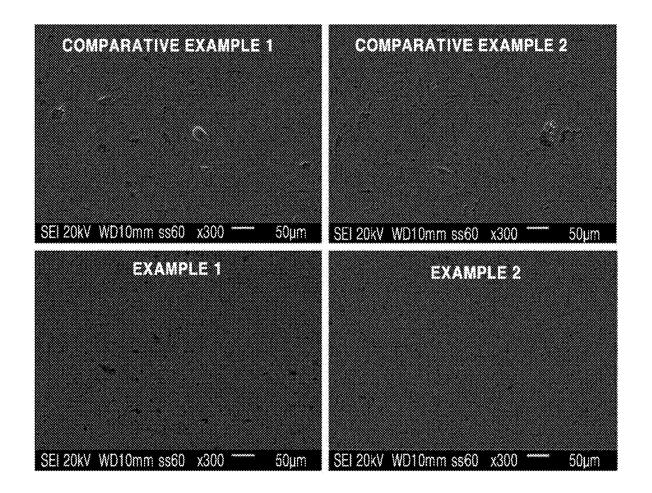
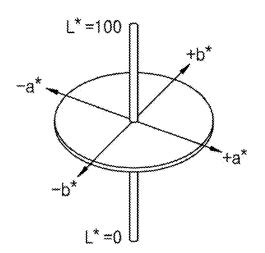


FIG. 4



AXIS	CO	REMARKS	
	+	-	
L	BRIGHT	DARK	BRIGHTNESS
a	RED	GREEN	CHROMA
b	YELLOW	BLUE	CONUMA

FIG. 5

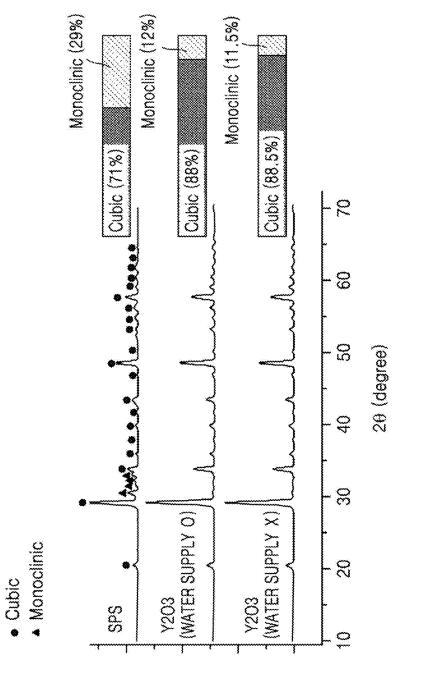
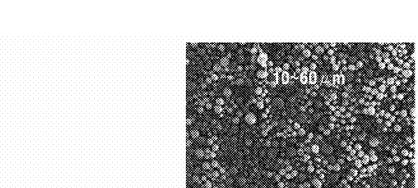
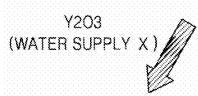
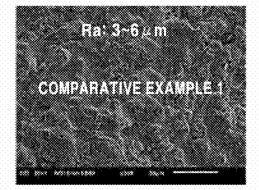
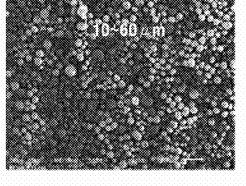


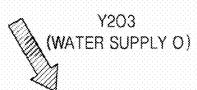
FIG. 6

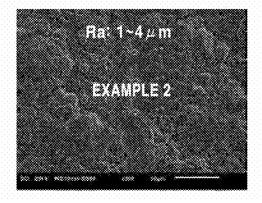












**FIG.** 7

#### METHOD FOR MANUFACTURING HIGH-DENSITY YTTRIA FILM BY ATMOSPHERIC PLASMA SPRAYING METHOD AND YTTRIA THERMAL-SPRAYED FILM MANUFACTURED USING SAME

#### TECHNICAL FIELD

[0001] The present disclosure relates to a method of manufacturing a high-density yttria thermal spray coating by using a  $\rm Y_2O_3$  thermal spray powder through an atmospheric plasma spraying method.

#### BACKGROUND ART

[0002] The importance of plasma dry etching processes is increasingly growing for micro-processing to achieve high integration of substrate circuits such as silicon wafers in semiconductor manufacturing processes.

[0003] For use in such environments, materials with excellent plasma resistance have been proposed as chamber components, or methods have been suggested to extend component life by forming films of materials with superior plasma resistance on surfaces of such components.

[0004] Among these, the technology of imparting new functionality by coating the surfaces of base materials with various materials has been used in many fields traditionally. As one of these surface coating technologies, for example, a thermal spraying method of forming a thermal spray coating is known, where spray particles made of materials such as ceramics are sprayed onto the base material surface in a softened or molten state by using combustion or electrical energy.

[0005] Generally, thermal spray coating is performed by heating fine powders to melt them and spraying the molten powders toward the surface to be coated of the base material. As the sprayed molten powder rapidly cools and solidifies, it is primarily layered on the coating target surface through mechanical bonding forces.

[0006] Among thermal spray coatings, plasma spray coating, which uses high-temperature plasma flames to melt these powders, is essential for coating metals with high melting points such as tungsten and molybdenum, as well as ceramics. This thermal spray coating is not only advantageous for manufacturing high-functional materials that exhibit wear resistance, corrosion resistance, heat resistance and thermal barrier properties, super-hardness, oxidation resistance, insulation, friction characteristics, heat dissipation, biological function, and radiation resistance while maintaining the material characteristics of the base material, but it can also coat large areas quickly compared to other coating methods such as chemical vapor deposition or physical vapor deposition.

[0007] In the field of semiconductor device manufacturing, dry etching using plasma of halogen gases such as fluorine, chlorine, and bromine is generally performed for micro-processing on the surface of a semiconductor substrate. Additionally, after dry etching, the chamber (vacuum vessel) interior is cleaned using oxygen gas plasma after removing the semiconductor substrate. At this time, components exposed to highly reactive oxygen gas plasma or halogen gas plasma inside the chamber may become corroded. In case that corroded (eroded) portions detach as particles from these components, these particles can adhere

to the semiconductor substrate and become foreign matter (hereinafter referred to as particles) that causes circuit defects.

[0008] Therefore, in semiconductor device manufacturing equipment of the related art, thermal spray coatings of ceramics with plasma erosion resistance have been applied to components exposed to oxygen gas or halogen gas plasma to reduce particle generation.

[0009] Factors contributing to particle generation include not only the peeling of reaction products adhered inside the vacuum chamber but also chamber degradation due to the use of halogen gas plasma or oxygen gas plasma. Additionally, according to the inventors' investigation, the number and size of particles generated from thermal spray coatings under dry etching conditions are known to be caused by the strength of bonding between particles constituting the thermal spray coating, the presence of unmelted particles, or high porosity.

[0010] Particularly, as the density within ceramic thermal spray coatings increases, the absorption of CFx-series process gases due to defects such as pores during dry etching processes decreases, reducing etching by plasma ion collision.

[0011] Generally, suspension plasma spray (SPS) is used as a coating method for forming high-density thermal spray coatings, but compared to atmospheric plasma spraying (APS), SPS has more complex manufacturing processes and higher manufacturing costs.

[0012] SPS technology involves relatively high process temperatures during coating of the inside of the semiconductor chamber due to higher heat sources, which can cause product deformation, and as particle size decreases, the particle travel distance becomes shorter, requiring the plasma equipment to be closer to the base material to be coated, which partially restricts operation. Additionally, since SPS technology uses a suspension state where particles are dispersed in water, the coating formation rate is lower for the same volume injection, resulting in additional process time and higher manufacturing costs.

[0013] Furthermore, as semiconductor process conditions become more severe, the formation of a stable thick film having a thickness of 150  $\mu m$  or more is needed in RF plasma high-power equipment, but when forming films having the thickness of 150  $\mu m$  or more using SPS technology, delamination occurs due to internal cracks or residual stress, making it technically challenging to achieve coating thicknesses of several hundred  $\mu m$ .

[0014] Therefore, there is a need to develop a technology that can create a high-density thermal spray coating using the atmospheric plasma spraying (APS) method of the related art.

[0015] In conventional APS spray methods, the powder of a thermal spray material typically consists of primary particles of several  $\mu m$  forming granulated powder of 20  $\mu m$  to 40  $\mu m$ , and methods have been proposed to increase thermal spray coating density by making the primary powder particles constituting such spray materials smaller than 1  $\mu m$ . However, with this method, as the specific surface area of the granulated powder increases, heat is not uniformly transferred to the primary powder inside the particles, resulting in the formation of coatings containing unmelted or re-melted states on the surface or inside of the thermal spray coating, which becomes a source of particle generation in dry etching processes.

[0016] In addition, in case that the secondary particles formed from the granular powder become too small, the particles may clump together due to electrostatic attraction between the granular powders, making transport in air practically difficult, or after particle transport, due to low particle mass, they are likely to scatter elsewhere instead of being transported to the central flame.

[0017] Another method for constructing high-density coating layers is coating with a close standoff distance (distance between the base material and plasma). This enables relatively high-density coating formation due to the large kinetic energy of the molten particles, i.e., thermal spray powder, and short cooling time.

[0018] However, due to the close standoff distance, the travel distance of the molten thermal spray powder becomes short, causing deoxidation, which results in partial or complete blackening of the thermal spray coating surface, and this different coating color from the original can cause the following problems.

[0019] When the thermal spray coating is black, it becomes difficult to distinguish from contaminants after semiconductor processing, making it hard to predict cleaning and recoating cycles, and changes in coating color alter emissivity, necessitating changes in semiconductor process conditions.

[0020] To solve these problems, blackened thermal spray coatings can be restored to white through heat treatment in an atmospheric (oxygen-containing) environment, but additional heat treatment processes lead to decreased production speed and increased manufacturing costs, and additionally, since most semiconductor chambers are made of metal materials, thermal damage to the base material can occur during the heat treatment process.

[0021] As prior art, Korean patent application publication no. 10-2016-0131918 (Nov. 16, 2016) discloses spray material containing rare earth element oxohalides (RE-O—X) including rare earth elements (RE), oxygen (O), and halogen elements (X) as constituent elements, where the molar ratio of halogen elements to rare earth elements (X/RE) is 1.1 or greater, resulting in improved plasma resistance and improved characteristics such as porosity and hardness.

[0022] As described above, despite proposals for technologies to manufacture yttrium oxyfluoride thermal spray materials with improved properties such as porosity and hardness to overcome the physical limitations of conventional yttrium oxide spray materials, there remains a continuous industrial demand for technology development to produce dense thermal spray coatings for improved plasma resistance.

#### **DISCLOSURE**

#### Technical Problem

[0023] Provided is a method of manufacturing dense yttrium oxide thermal spray coating in which water (distilled water) is supplied along with  $Y_2O_3$  thermal spray powder to prevent deoxidation of yttrium oxide and prevent color changes in the thermal spray coating, while a spray unit is positioned at a relatively close standoff distance (distance between the base material and plasma) to utilize the large kinetic energy of the thermal spray powder.

#### Technical Solution

[0024] According to an aspect of an embodiment, a method of manufacturing an yttria thermal spray coating includes arranging a spray unit at a distance of 50 to 130 mm from a base material, subjecting  $Y_2O_3$  thermal spray powder to atmospheric plasma spraying to form an yttria thermal spray coating on the base material, and supplying water at a rate of 50 to 400 ml/min together with the  $Y_2O_3$  thermal spray powder.

[0025] In an embodiment of the present disclosure, during the atmospheric plasma spraying, the spray unit may be arranged at a distance of 80 to 120 mm with respect to the base material.

[0026] In an embodiment of the present disclosure, water may be supplied at a rate of 200 to 350 ml/min together with the  $Y_2O_3$  thermal spray powder.

[0027] In an embodiment of the present disclosure, the location at which the water is supplied may be at a distance of 2:8 to 8:2 between the plasma forming nozzle and the base material.

**[0028]** In an embodiment of the present disclosure, the location at which the water is supplied may be at a distance of 3:7 to 5:5 between a plasma forming nozzle and the base material.

[0029] In an embodiment of the present disclosure, the location at which the water is supplied may be 25 to 50 mm from the plasma forming nozzle.

[0030] In an embodiment of the present disclosure, four water supply nozzles through which water is supplied may be arranged at 90° intervals from each other to allow water to be supplied from four directions.

[0031] In an embodiment of the present disclosure, eight water supply nozzles through which water is supplied are arranged at 45° intervals from each other to allow water to be supplied from eight directions.

[0032] In an embodiment of the present disclosure, the orifice used in the water supply nozzle has a circular shape, and the size of the orifice may be 0.007 to 0.011 inches.

[0033] In an embodiment of the present disclosure, the average particle size of the  $\rm Y_2O_3$  thermal spray powder may be 5 to 60  $\mu m$ .

[0034] In an embodiment of the present disclosure, the thickness of the yttria thermal spray coating may be 100 to 300  $\mu m$ .

[0035] In an embodiment of the present disclosure, the present disclosure provides an yttria thermal spray coating formed by the method of manufacturing an yttria thermal spray coating.

[0036] In an embodiment of the present disclosure, the colorimetric measurement value L of the yttria thermal spray coating may be 85 or more.

[0037] In an embodiment of the present disclosure, the porosity of the yttria thermal spray coating may be less than 2.6%.

[0038] In an embodiment of the present disclosure, the porosity of the yttria thermal spray coating may be less than 1.0%.

#### Advantageous Effects

**[0039]** Yttria thermal spray coatings manufactured according to the present disclosure form high-density white thermal spray coating layers with 1.5% or less porosity, which reduces the etching rate by process gases in dry

etching processes, providing excellent durability when used as coating materials for components in semiconductor chambers, and suppresses the delamination of coating materials due to etching phenomena, thereby contributing to improved semiconductor wafer yield.

[0040] Furthermore, the manufacturing method of yttria thermal spray coatings according to the present disclosure provides reasonable processing time by whitening the coating layer surface during the manufacturing process, and can provide high-quality thermal spray coating layers without additional cost increases.

#### DESCRIPTION OF DRAWINGS

[0041] FIG. 1 shows a schematic diagram of supplying water (distilled water) in a method of manufacturing an yttria thermal spray coating according to the present disclosure.

[0042] FIG. 2 shows scanning electron microscope (SEM) images of the surface of a thermal spray coating according to (a) Comparative Example 1, (b) Comparative Example 2, (c) Example 1, and (d) Example 2 of the present disclosure. [0043] FIG. 3 shows low-magnification scanning electron microscope (SEM) images of a side surface of a thermal spray coating according to (a) Comparative Example 1, (b) Comparative Example 2, (c) Example 1, and (d) Example 2 of the present disclosure.

[0044] FIG. 4 shows high-magnification SEM images of a side surface of a thermal spray coating according to (a) Comparative Example 1, (b) Comparative Example 2, (c) Example 1, and (d) Example 2 of the present disclosure.

[0045] FIG. 5 shows what the values along the axis of the colorimeter indicate.

[0046] FIG. 6 shows the results of X-ray diffraction (XRD) analysis of the thermal spray coating film according to yttria, SPS coating film, Comparative Example 1, and Example 2.

[0047] FIG. 7 shows a SEM image of the surface of the thermal spray coating according to Comparative Example 1 and Example 2.

### BEST MODE

[0048] Unless otherwise defined, all technical and scientific terms used in the present specification have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. In general, the nomenclature used in the present specification is well known and commonly used in the art.

[0049] Throughout this specification, when a portion is described as "including" a component, it means that, unless specifically stated otherwise, it does not exclude other components but may further include other components.

[0050] In semiconductor manufacturing processes, gate etcher devices, insulating film etcher devices, resist film etcher devices, sputtering devices, CVD devices, and the like are used. Meanwhile, in liquid crystal manufacturing processes, etcher devices for forming thin film transistors and the like are used. Furthermore, these manufacturing devices are configured with plasma generation mechanisms for purposes such as high integration through fine processing

[0051] In these manufacturing processes, halogen-based corrosive gases such as fluorine and chlorine are used as treatment gases in these devices due to their high reactivity.

Fluorine gases include SF<sub>6</sub>, CF<sub>4</sub>, CHF<sub>3</sub>, CIF<sub>3</sub>, HF, NF<sub>3</sub>, etc., and chlorine gases include Cl<sub>2</sub>, BCl<sub>3</sub>, HCl, CCl<sub>4</sub>, SiCl<sub>4</sub>, etc., and when microwaves or high frequency are introduced into the atmosphere containing these gases, these gases become plasma. Device components exposed to these halogen gases or plasma thereof are required to have very little metal other than the material components on their surfaces and also to have high corrosion resistance.

[0052] Accordingly, the present disclosure aims to provide a method of manufacturing a thermal spray coating having excellent plasma resistance for coating a member for a plasma etcher device.

[0053] The method of manufacturing an yttria thermal spray coating according to the present disclosure includes arranging a spray unit at a distance of 50 to 200 mm on a base material, subjecting  $Y_2\mathrm{O}_3$  thermal spray powder to atmospheric plasma spraying to form an yttria thermal spray coating on the base material, and supplying water at a rate of 50 to 400 ml/min together with the  $Y_2\mathrm{O}_3$  thermal spray powder.

[0054] In the atmospheric plasma spraying method of manufacturing the coating film of the present disclosure, there is a method of coating by keeping the distance between the base material (object to be coated) and the plasma unit close to form a high-density coating layer.

[0055] However, due to the short standoff distance, the travel distance of the molten thermal spray powder is reduced, causing deoxidation, which results in the thermal spray coating surface turning black. The coating color being different from the conventional one makes it difficult to distinguish from contaminants after used in a semiconductor process and to predict cleaning and recoating cycle timing. Furthermore, the change in the thermal spray coating color causes a need for change in emissivity to modify the semiconductor process conditions.

[0056] Therefore, according to the method of manufacturing an yttria thermal spray coating according to the present disclosure, an yttria thermal spray coating having low porosity and high density may be formed by arranging the spray unit at a relatively close distance (50 to 130 mm) on the base material while simultaneously supplying water (distilled water) at a rate of 50 to 400 ml/min along with  $Y_2O_3$  thermal spray powder to prevent deoxidation of the yttria component.

[0057] A spray gun in the atmospheric plasma spray coating melts the coating material using a plasma flame and sprays the molten coating material onto the base material. For example, the plasma flame may be formed by dissociation of a portion of a plasma gas including argon gas (Ar), nitrogen gas (N<sub>2</sub>), hydrogen gas (H<sub>2</sub>), helium gas (He), etc. [0058] The atmospheric plasma spray coating may have, as spray process variables, a flow rate of inert gas of 320 SCFH to 420 SCFH, a flow rate of nitrogen gas of 120 SCFH to 160 SCFH, and a flow rate of hydrogen gas of 120 SCFH to 160 SCFH.

[0059] In some embodiments, the atmospheric plasma spray coating may have a plasma generation current of 360 to 460 A, for example, 380 to 440 A.

[0060] The plasma spray coating may be applied by arranging the spray unit at a distance of 50 to 130 mm with respect to the base material, for example, at a distance of 80 to 120 mm with respect to the base material.

[0061] When the distance between the spray unit and the base material surface is smaller than about 50 mm, the base

material becomes deformed due to the plasma being too close to the base material, and there exists a risk of coating-layer delamination due to high thermal energy. When the distance is greater than 130 mm, as the travel distance of the yttria powder increases, solidification of the molten granular powder progresses upon reaching the base material, and due to reduced kinetic energy, pores form within the coating, resulting in the formation of a coating with low density.

[0062] In this regard, by supplying water together with the  $Y_2O_3$  thermal spray powder to prevent deoxidation of the yttria component, a white yttria thermal spray coating may be formed.

[0063] At this time, water (distilled water) may be supplied at a rate of 50 to 400 ml/min together with the  $\rm Y_2O_3$  thermal spray powder, and for example, water (distilled water) may be supplied at a rate of 200 to 350 ml/min together with the  $\rm Y_2O_3$  thermal spray powder.

[0064] In some embodiments, the position at which the water is supplied may be at a distance of 2:8 to 8:2 between a plasma forming nozzle and the base material, and for example, the position at which the water is supplied may be at a distance of 3:7 to 5:5 between the plasma forming nozzle and the base material.

[0065] In an embodiment, when the distance between the plasma forming nozzle and the base material surface is 100 mm, the position at which water is supplied may be 20 to 80 mm from the plasma forming nozzle, and for example, the position at which water is supplied may be 30 to 50 mm from the plasma forming nozzle.

[0066] In an embodiment, when the distance between the plasma forming nozzle and the base material surface is 50 mm, the position at which water is supplied may be 10 to 40 mm from the plasma forming nozzle, and for example, the position at which water is supplied may be 15 to 25 mm from the plasma forming nozzle.

[0067] In an embodiment, the location at which water is supplied may be 25 to 50 mm from the plasma forming nozzle, and for example, the location at which water is supplied may be 35 to 45 mm from the plasma forming nozzle

[0068] In addition, a plurality of water supply nozzles through which water is supplied may be arranged irregularly or regularly, and in an embodiment, four water supply nozzles may be arranged at 90° intervals from each other so that water may be supplied from four directions, and for example, as illustrated in FIG. 1 below, eight water supply nozzles through which water is supplied may be arranged at  $45^{\circ}$  intervals from each other so that water may be supplied from eight directions, thereby evenly supplying water (distilled water) to the  $\rm Y_2O_3$  thermal spray powder and effectively preventing the deoxidation phenomenon of yttria.

**[0069]** The orifice used in the water supply nozzle may have any shape. In some embodiments, the orifice may be a circular orifice. The size of the orifice is not limited. In some embodiments, the size of the orifice may be 0.007 to 0.011 inches

[0070] In the plasma spray coating method, the yttria thermal spray coating may have a thickness of 50 to 500  $\mu m,$  and for example, a thickness of 100 to 300  $\mu m.$ 

[0071] In this regard, the average particle size of the  $Y_2\mathrm{O}_3$  thermal spray powder may be 5 to 60  $\mu m$ , for example, 10 to 40  $\mu m$ , or 15 to 30  $\mu m$ .

[0072] In case that the size of the  $Y_2O_3$  thermal spray powder is less than 5  $\mu$ m, the flowability of the powder is

low during thermal spray coating, making it difficult to implement a uniform film, and the powder is oxidized before being delivered to the flame or is not delivered to the center of a flame, making it difficult to satisfy the droplet ejection speed and heat quantity required to form a dense film, resulting in the formation of a film with high pores or low hardness. In case that the average diameter of the  $Y_2 O_3$  thermal spray powder exceeds 60  $\mu m$ , the melting specific surface area of the granular powder decreases, resulting in incomplete melting, which causes unmelted portions within the coating film, making it difficult to satisfy the thermal spray coating quality required by the present disclosure.

[0073] In addition, in the present disclosure, the base material on which the thermal spray coating is coated is not particularly limited. For example, the component or shape of the base material is not limited as long as the base material includes a material that provides a desired level of resistance when supplied to spraying of a spray material. A material constituting such a base material to be subjected to spraying may be selected from at least one or more combinations of aluminum, nickel, chromium, zinc and alloys thereof, alumina, aluminum nitride, silicon nitride, silicon carbide and quartz glass, which constitute components for semiconductor manufacturing devices, for example.

[0074] Such a base material may be, for example, a component constituting a semiconductor device manufacturing device, and may be a component exposed to highly reactive oxygen gas plasma or halogen gas plasma.

[0075] The surface of the base material may be treated in accordance with the ceramic spraying work standard specified in JIS H 9302 before plasma spraying. For example, after removing rust or grease from the surface of the base material, the surface is roughened by spraying abrasive particles such as  $\mathrm{Al_2O_3}$  and  $\mathrm{SiC}$ , and the pretreatment is performed thereon so that the spray granule powder easily adheres.

[0076] Yttria spray films of the related art have a high porosity within a coating layer. However, according to the present disclosure, a spray unit is placed at a distance of 50 to 130 mm from a base material, and  $\rm Y_2O_3$  thermal spray powder is sprayed by atmospheric plasma to form a high-density yttria thermal spray coating on the base material, and further, water is supplied at a rate of 50 to 400 ml/min at a position of 25 to 50 mm from a plasma forming nozzle together with the  $\rm Y_2O_3$  thermal spray powder to suppress the deoxidation phenomenon of yttria at a short distance, thereby manufacturing a white, high-density yttria thermal spray coating.

[0077] Therefore, the yttria thermal spray coating manufactured by the method shows excellent durability when applied to semiconductor chambers used in existing etcher processes due to its superior porosity level compared to conventional thermal spray coatings, and suppresses the detachment of the coating material by etching gas.

[0078] In an embodiment, the colorimetric measurement value L of the yttria sprayed film formed by the method of manufacturing the yttria thermal spray coating may be 85 or more.

[0079] In an embodiment, the yttria thermal spray coating formed by the method of manufacturing the yttria thermal spray coating may have a porosity of less than 2.6%, for example, less than 1.5%, or less than 1%.

[0080] Hereinafter, the present disclosure will be described in more detail through examples. However, the

following examples are only intended to illustrate the present disclosure, and the present disclosure is not limited to the following examples.

## Comparative Examples 1 and 2 and Examples 1 and 2

[0081] Using the  $\rm Y_2O_3$  spray material and a plasma gun, a coating film was formed on the base material by melting the source powder using plasma generated at 80-120 kW power while moving the spray gun and flowing argon, nitrogen, and hydrogen gases as heat source gases. The thickness of the coating film was 150  $\mu$ m to 250  $\mu$ m and the experimental conditions are shown in Table 1 below. In addition, a charge-coupled device (CCD) image of the surface of the manufactured thermal spray coating is shown in FIG. 2, and scanning electron microscope (SEM) images of the side surface of the manufactured thermal spray coating are shown in FIGS. 3 and 4.

(XRD) using a SEM and confirmed that the cubic crystal structure, known as a high-density coating, existed at a higher ratio than the monoclinic structure.

Experimental Example 3: Hardness Measurement

[0086] The "Hardness" column in Table 1 above shows the measurement results of the Vickers hardness of each thermal spray coating. The Vickers hardness is measured using a microhardness tester, and is the Vickers hardness (Hv0.2) obtained when a test force of 294.2 mN is applied by a diamond indenter with a face angle of 136°.

**[0087]** As shown in Table 1 above, it was confirmed that the hardness of the thermal spray coatings of Examples 1 and 2 was in a similar range to that of the thermal spray coatings of Comparative Examples 1 and 2.

Experimental Example 4: Roughness Measurement **[0088]** The surface roughness  $(\mu m)$  of the coating films manufactured in Example 2 and Comparative Example 1 of

TABLE 1

No.	Water supply Use or not	Separation distance	Porosity (%)	Hardness (Hv)	L	a	ь
Comparative Example 1	X	160	4.32	450	91.17	-0.22	0.18
Comparative Example 2	X	100	2.33	525	41.89	-0.43	-0.62
Example 1	0	160	2.54	512	91.57	-0.33	0.17
Example 2	0	100	0.85	535	91.18	-0.32	0.19

## Experimental Example 1: Observation of Thermal Spray Coating

[0082] FIGS. 3 and 4 show SEM images of the surfaces and side surfaces of the thermal spray coatings according to Comparative Examples 1 and 2 and Examples 1 and 2 according to the present disclosure. From SEM images of the side surfaces of the thermal spray coatings in FIGS. 3 and 4, it was confirmed that a dense thin film with low porosity was formed in the thermal spray coating according to Example 2.

[0083] In addition, the measurement of porosity was performed as follows. That is, the thermal spray coating was cut perpendicular to the surface of abase material, and the obtained cross-section was embedded in resin and polished. Then, the cross-sectional image was captured using an electron microscope (JEOL, JS-6010) (FIGS. 3 and 4). The image was analyzed using image analysis software (MEDIA CYBERNETICS, Image Pro) to identify the area of pores in the cross-sectional image. The porosity was calculated by determining the ratio of the pore area to the total cross-sectional area. The porosity (%) of the thermal spray coating obtained through this analysis of pores in the cross-sectional image is shown in Table 1.

[0084] Examples 1 and 2 showed a porosity of less than 2.6%, indicating that the density of the yttria thermal spray coating according to the present disclosure increased compared to the thermal spray coating of a conventional method. In addition, the colorimetric L value was 85 or higher, confirming that a white yttria thermal spray coating was formed.

# Experimental Example 2: Crystal Structure Analysis

[0085] As illustrated in FIG. 6, the thermal spray coating according to Example 2 was analyzed by X-ray diffraction

the present disclosure was measured using a roughness meter (SJ-201). Results are shown in FIG. 7.

[0089] As shown in FIG. 7, when a thermal spray coating was formed using powder having a size of 10 to 60  $\mu m$ , it was confirmed that the thermal spray coating according to Comparative Example 1 exhibited a surface roughness of 3  $\mu m$  to 6  $\mu m$ , whereas the thermal spray coating according to Example 2 exhibited a surface roughness of 1  $\mu m$  to 4  $\mu m$ . This was confirmed that roughness was reduced through the use of water.

## Experimental Example 5: Colorimetric Measurement of Surface of Thermal Spray Coating

[0090] FIG. 2 shows CCD images of the surfaces of the thermal spray coatings according to Comparative Examples 1 and 2 and Examples 1 and 2 according to the present disclosure. It was confirmed that among Comparative Example 2 and Example 2 with the same standoff distance, Example 2 using water exhibited a white color.

[0091] In Table 1, L, a, and b represent the colorimetric measurement results of the surface of the thermal spray coating. Among these, the L value represents brightness, with higher values indicating brighter appearance, and between Comparative Example 2 and Example 2 which have the same standoff distance, Example 2 using water showed a higher value, confirming that it exhibits white color.

[0092] While specific portions of the present disclosure have been described in detail above, it will be apparent to those skilled in the art that such specific descriptions are merely preferred embodiments and that the scope of the present disclosure is not limited thereby. Accordingly, the substantial scope of the present disclosure will be defined by the appended claims and their equivalents.

- $1.\,\mathrm{A}\,\mathrm{method}$  of manufacturing an yttria thermal spray film, the method comprising:
  - arranging a spray unit at a distance of 50 to 130 mm from a base material;
  - subjecting Y2O3 thermal spray powder to atmospheric plasma spraying to form an yttria thermal spray film on the base material; and
  - supplying water at a rate of 50 to 400 ml/min together with the Y2O3 thermal spray powder,
  - wherein a water supply location corresponds to a distance of 2:8 to 8:2 between a plasma forming nozzle and the base material
- 2. The method of claim 1, wherein in the atmospheric plasma spraying, the spray unit is arranged at a distance of 80 to 120 mm with respect to the base material.
- 3. The method of claim 1, wherein water is supplied at a rate of 200 to 350 ml/min together with the Y2O3 thermal spray powder.
  - 4. (canceled)
- 5. The method of claim 1, wherein the water supply location corresponds to a distance of 3:7 to 5:5 between the plasma forming nozzle and the base material.
- **6**. The method of claim **1**, wherein the water supply location corresponds to 25 to 50 mm from a plasma forming nozzle.

- 7. The method of claim 1, wherein four water supply nozzles through which water is supplied are arranged at  $90^{\circ}$  intervals from each other and thus water is supplied from four directions.
- **8**. The method of claim **1**, wherein eight water supply nozzles through which water is supplied are arranged at 45° intervals from each other and thus water is supplied from eight directions.
- 9. The method of claim 1, wherein an orifice used in a water supply nozzle is circular in shape, and a size of the orifice is 0.007 to 0.011 inches.
- 10. The method of claim 1, wherein an average particle size of the Y2O3 thermal spray powder is 5 to 60  $\mu$ m.
- 11. The method of claim 1, wherein a thickness of the yttria thermal spray coating film is 100 to 300  $\mu$ m.
- 12. An yttria thermal spray coating formed by the method of manufacturing an yttria thermal spray coating according to claim 1.
- 13. The yttria thermal spray coating of claim 12, wherein a colorimetric measurement value  $\rm L$  of the yttria thermal spray coating is 85 or more.
- **14**. The yttria thermal spray coating of claim **12**, wherein a porosity of the yttria thermal spray coating is less than 2.6%.
- 15. The yttria thermal spray coating of claim 12, wherein a porosity of the yttria thermal spray coating is less than 1.0%.

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