

TITLE OF THE INVENTION

Sprayed Film, Method for Forming Same, and Sprayed Member

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TECHNICAL FIELD

The present invention relates to a sprayed film that is excellent as, for example, a corrosion-resistant film of a member for a semiconductor manufacturing apparatus, a method for forming the sprayed film, and a sprayed member in which a sprayed film is formed on
10 a substrate.

BACKGROUND ART

As a corrosion-resistant film of a member for a semiconductor manufacturing apparatus, a sprayed film is used. In recent years, densification of semiconductors has
15 proceeded, a minimum width required for the line width of a circuit pattern formed on a wafer by dry etching using gas plasma has been becoming as small as 10 nm or less, and reduction of particles (foreign matter) generated in a semiconductor manufacturing process has been desired. With respect to particle resistance performance required as a corrosion-resistant film of a member for a semiconductor manufacturing apparatus,
20 studies of a rare earth element oxyhalide film made by atmospheric plasma spraying have heretofore proceeded. For example, JP-A 2020-056115 (Patent Document 1) discloses a sprayed film containing, as a principal component, a rare earth element oxyhalide containing a rare earth element, oxygen and a halogen element (X) as constituent elements.

Development of a dense rare earth element oxyfluoride film made by suspension
25 plasma spraying, which is expected to have improved particle resistance performance, has also proceeded. For example, JP-A 2018-080401 (Patent Document 2) discloses a film containing a rare earth element oxyfluoride as a main phase.

In the formation of a film by spraying, molten particles, upon collision with a substrate, are rapidly cooled to form splats, and the splats are stacked to form a spray film,
30 but cracks may be formed in the splats by rapid-cooling solidification in formation of the splats. If the film is excessively densified, the residual stress between the splats may be released, resulting in formation of cracks. In dry etching using gas plasma, gas plasma

is known to preferentially etch crack portions of a sprayed film, and existence of cracks causes generation of particles even in a dense film.

Citation List

Patent Document 1: JP-A 2020-056115

5 Patent Document 2: JP-A 2018-080401

SUMMARY OF THE INVENTION

The present invention has been made in view of the above circumstances, and it is an object of the present invention to provide a sprayed film having few cracks, and a method
10 for forming the sprayed film, as well as a sprayed member in which a sprayed film having few cracks is formed on a substrate.

The present inventors have conducted intensive studies to solve the above problems, and resultantly found that a sprayed film having a film surface in which in measurement of a shape of the film surface by a non-contact process using a laser, a value of an area ratio S/A obtained by dividing a surface area S (μm^2) of a measurement surface (S-L surface) of the
15 film surface by an area A (μm^2) of a reference surface of the measurement surface (S-L surface) is 1.75 or more and 3 or less, and a surface roughness Sa of the measurement surface (S-L surface) is $0.4\ \mu\text{m}$ or more and $8\ \mu\text{m}$ or less hardly undergoes generation of particles which is caused by cracks of the sprayed film in dry etching with gas plasma
20 using the sprayed film as a corrosion-resistant film. In this way, the present invention has been completed.

Accordingly, the present invention provides the following sprayed film, sprayed member, and method for forming sprayed film.

1. A sprayed film including a film surface in which in measurement of a shape of the
25 film surface by a non-contact process using a laser, a value of an area ratio S/A obtained by dividing a surface area S (μm^2) of a portion of the measurement surface (S-L surface) of the film surface within one evaluation region by an area A (μm^2) of a portion of a reference surface forming a plane located at an arithmetic average height of the measurement surface (S-L surface), which is within the evaluation region is 1.75 or more and 3 or less, and a
30 surface roughness Sa of a portion of the measurement surface (S-L surface) within the evaluation region is $0.4\ \mu\text{m}$ or more and $8\ \mu\text{m}$ or less.

2. The sprayed film according to 1, including a rare earth element oxyfluoride.
3. The sprayed film according to 2, wherein the rare earth element oxyfluoride is one or more selected from ROF, $R_5O_4F_7$, $R_6O_5F_8$ and $R_7O_6F_9$ (wherein R represents one or more selected from rare earth elements including Sc and Y).
- 5 4. The sprayed film according to any one of 1 to 3, including a rare earth element oxyfluoride of ROF (wherein R represents one or more selected from rare earth elements including Sc and Y), wherein in X-ray diffraction using a Cu-K α ray as a characteristic X-ray, a diffraction peak having the largest integrated intensity, among diffraction peaks detected within a diffraction angle range of $2\theta = 10^\circ$ to 70° , is a diffraction peak derived
- 10 from the ROF.
5. The sprayed film according to any one of 1 to 4, including oxygen, wherein an oxygen content is 5 atom% or more and 55 atom% or less.
6. The sprayed film according to any one of 1 to 5, wherein a thickness is 10 μm or more and 500 μm or less.
- 15 7. A sprayed member comprising a substrate, and the sprayed film of any one of 1 to 6 formed on the substrate.
8. The sprayed member according to 7, which is a member for a semiconductor manufacturing apparatus.
9. A method for forming the sprayed film of any one of 1 to 6, including a step of
- 20 performing suspension plasma spraying of a slurry, in which a spray material in a form of particles with a mean particle size D50 of 1 μm or more and 9 μm or less is dispersed in a dispersion medium, by supplying the slurry containing the spray material to plasma produced by setting a current value C to 450 A or more and 1,000 A or less, a voltage value V to 20 V or more and 235 V or less, a value of C/V obtained by dividing the current value C by the
- 25 voltage value V to 1.92 or more and 30 or less, and an applied power value P to 20 kW or more and 120 kW or less.
10. The method according to 9, wherein the spray material contains a rare earth element oxyfluoride, or a rare earth element oxyfluoride and a rare earth element fluoride.

30 ADVANTAGEOUS EFFECTS OF THE INVENTION

In the sprayed film and the sprayed member of the present invention, generation of particles which is caused by cracks of the sprayed film can be reduced when dry etching

using gas plasma is performed with a semiconductor manufacturing apparatus or the like using the sprayed film as a corrosion-resistant film.

BRIEF DESCRIPTION OF DRAWINGS

5 FIG. 1 is an image obtained by performing whitening treatment on a scanning electron microscope image on a film surface of a sprayed film from Example 1 to whiten cracks;

 FIG. 2 is an image obtained by performing whitening treatment on a scanning electron microscope image on a film surface of a sprayed film from Example 3 to whiten cracks;

 FIG. 3 is an image obtained by performing whitening treatment on a scanning electron
10 microscope image on a film surface of a sprayed film from Comparative Example 1 to whiten cracks; and

 FIG. 4 is an image obtained by performing whitening treatment on a scanning electron microscope image on a film surface of a sprayed film from Comparative Example 2 to whiten cracks.

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DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention is described in more detail below.

 A sprayed film of the present invention has a film surface in which in measurement of the shape of the film surface by a non-contact process using a laser, the value of an area
20 ratio S/A obtained by dividing a surface area S (μm^2) of a portion of a measurement surface (S-L surface) of the film surface within an evaluation region by an area A (μm^2) of a portion of a reference surface within the evaluation region is preferably 1.75 or more.

 The risk of generation of cracks in a splat becomes higher as the flatness of the splat in the sprayed film increases, with the formed splat having a larger diameter. When the
25 size of the spray material for use in formation of a sprayed film is within the normal range, the value of the area ratio S/A becomes larger as the flatness of the splat decreases, with the formed splat having a smaller diameter. When the value of the area ratio S/A is 1.75 or more, generation of cracks in the splat is effectively suppressed. The value of the area ratio S/A is more preferably 1.77 or more, still more preferably 1.79 or more, and
30 particularly preferably 1.8 or more. On the other hand, the upper limit of the value of the area ratio S/A is preferably 3 or less, more preferably 2.8 or less, still more preferably 2.6 or less, and particularly preferably 2.4 or less.

The measurement of the shape of the film surface of the sprayed film by a non-contact process using a laser can be performed according to ISO 25178-2: 2021. The measurement of the shape can be performed using, for example, a laser microscope. In the present invention, the film surface is typically a surface (principal surface) that is substantially orthogonal to the thickness direction of the film.

In the present invention, the measurement surface (S-L surface), the reference surface and the evaluation region correspond to a measurement surface (S-L surface), a reference surface and the evaluation region defined in ISO 25178-2: 2021, respectively. The S-L surface is a surface obtained by applying an L-filter (a filter for removing a large-scale shape component (e.g., a wavy shape)) to a basic surface obtained by applying an S-filter (a filter for removing a small-scale shape component (e.g., a measurement noise)). As the filter, for example, a Gaussian filter can be applied. The reference surface corresponds to, for example, a plane located at an arithmetic average height of the measurement surface (S-L surface). The surface area S, the area A, and the surface roughness Sa described later are evaluated using the same evaluation region (one evaluation region).

The surface area S represents an actual area of the film surface of the sprayed film. The surface of the sprayed film includes irregularities and fine texture, and therefore is not a flat surface. The surface area S is an area of a surface including irregularities and fine texture of the surface, and is different from an area of a flat surface. On the other hand, the area A is an area of a plane, and measurement regions of the same size are identical in value of the area A.

In the present invention, when a laser microscope is used for measuring the shape of the film surface of the sprayed film by a non-contact method using a laser, the magnification can be set according to a size of a spray material for use in formation of the sprayed film, and a size of a splat in the sprayed film formed from the spray material. For example, when the size of the splat in the sprayed film is in the normal range, the shape of the film surface can be appropriately evaluated preferably by setting the object lens magnification to 50 times, and more preferably by setting the total magnification to 1,200 times. For setting the S-filter and the L-filter, the settings of respective laser microscopes which are appropriate to an object lens magnification can be applied to the extent of conforming to ISO 25178-2:2021. On the other hand, setting the evaluation region so that the area A is

50,000 μm^2 or more enables evaluation. The evaluation region is typically set so that the area A is 60,000 μm^2 or less.

The sprayed film of the present invention has a film surface in which in measurement of the shape of the film surface by a non-contact process using a laser, the surface roughness Sa of a portion of a measurement surface (S-L surface) of the film surface within the evaluation region is preferably 8 μm or less. In the sprayed film having a film surface whose surface roughness S is within a predetermined range, generation of cracks in the splat is effectively suppressed when the sprayed film has a film surface whose area ratio S/A is within a predetermined range. The surface roughness Sa of the sprayed film is more preferably 6 μm or less, still more preferably 4 μm or less, and particularly preferably 3 μm or less. On the other hand, the lower limit of the surface roughness Sa of the sprayed film is preferably 0.4 μm or more, more preferably 0.6 μm or more, still more preferably 0.8 μm or more, and particularly preferably 1 μm or more.

The sprayed film of the present invention preferably contains a rare earth element oxyfluoride. The sprayed film of the present invention may contain one or both of a rare earth element oxide and a rare earth element fluoride. In particular, when the sprayed film contains a rare earth element fluoride, the sprayed film preferably contains the rare earth element fluoride together with a rare earth element oxyfluoride.

In the present invention, the rare earth element oxyfluoride is preferably crystalline. Examples of the rare earth element oxyfluoride include $\text{ROF}(\text{R}_1\text{O}_1\text{F}_1)$, $\text{R}_4\text{O}_3\text{F}_6$, $\text{R}_5\text{O}_4\text{F}_7$, $\text{R}_6\text{O}_5\text{F}_8$, $\text{R}_7\text{O}_6\text{F}_9$, $\text{R}_{17}\text{O}_{14}\text{F}_{23}$, RO_2F and ROF_2 (wherein R represents one or more selected from rare earth elements including Sc and Y (the same applies hereinafter)). The rare earth element oxyfluorides may be used alone, or as a mixture of two or more thereof. The rare earth elements (R) may be the same for some or all rare earth element oxyfluorides, or different for each rare earth element oxyfluoride.

In the present invention, the rare earth element oxide is preferably crystalline. Examples of the rare earth element oxide include RO and R_2O_3 . The rare earth element oxides may be used alone, or as a mixture of two or more thereof. The rare earth elements (R) may be the same for some or all rare earth element oxides, or different for each rare earth element oxide.

In the present invention, the rare earth element fluoride is preferably crystalline. Examples of the rare earth element fluoride include RF_2 and RF_3 . The rare earth element

fluorides may be used alone, or as a mixture of two or more thereof. The rare earth elements (R) may be the same for some or all rare earth element fluorides, or different for each rare earth element fluoride.

In the present invention, the rare earth element (R) includes scandium (Sc), yttrium (Y), and lanthanoids (elements of atomic numbers 57 to 71). As the rare earth element (R), yttrium (Y), scandium (Sc) and ytterbium (Yb) are particularly preferred.

The sprayed film of the present invention preferably contains one or more ROF, $R_5O_4F_7$, $R_6O_5F_8$ and $R_7O_6F_9$ selected from as the rare earth element oxyfluoride, and particularly preferably contains ROF, as the rare earth element oxyfluoride. When the sprayed film contains ROF, it is preferred that in X-ray diffraction using a Cu-K α ray as a characteristic X-ray, a diffraction peak having the largest integrated intensity, among diffraction peaks detected within a diffraction angle range of $2\theta = 10^\circ$ to 70° , is a diffraction peak derived from ROF.

In a plasma etching apparatus, fluorination proceeds near the surface of the sprayed film in etching with fluorine-based gas plasma containing CF_4 or the like. Oxidation proceeds near the surface of the sprayed film in etching with oxygen-based gas plasma that contains O_2 or the like, and is used in ashing for removal of a photoresist on a wafer which remains after etching. When the diffraction peak having the largest integrated intensity, among the diffraction peaks, is a diffraction peak derived from ROF, both fluorination of the sprayed film by etching with fluorine-based gas plasma and oxidation of the sprayed film by etching with oxygen-based gas plasma can be suppressed, which is advantageous in that the composition of the sprayed film hardly changes, and particle resistance performance and process stability are improved.

For example, assume that the rare earth element (R) is yttrium (Y). When the characteristic X-ray is a Cu-K α ray, the maximum peak of the rhombohedral crystal system of yttrium oxyfluoride (YOF) is not limited, but is typically a diffraction peak derived from the (012) plane of the crystal lattice. The diffraction peak is normally detected around $2\theta = 28.7^\circ$.

The maximum peak of the orthorhombic crystal system of yttrium oxyfluoride ($Y_5O_4F_7$) is not limited, but is typically a diffraction derived from the (151) plane of the crystal lattice. The diffraction peak is normally detected around $2\theta = 28.1^\circ$.

The maximum peak of the orthorhombic crystal system of yttrium oxyfluoride ($\text{Y}_6\text{O}_5\text{F}_8$) is not limited, but is typically a diffraction derived from the (161) plane of the crystal lattice. The diffraction peak is normally detected around $2\theta = 28.1^\circ$.

The maximum peak of the orthorhombic crystal system of yttrium oxyfluoride ($\text{Y}_7\text{O}_6\text{F}_9$) is not limited, but is typically a diffraction derived from the (171) plane of the crystal lattice. The diffraction peak is normally detected around $2\theta = 28.1^\circ$.

The maximum peak of the cubic system of yttrium oxyfluoride (Y_2O_3) is not limited, but is typically a diffraction derived from the (222) plane of the crystal lattice. The diffraction peak is normally detected around $2\theta = 29.2^\circ$.

The maximum peak of the orthorhombic crystal system of yttrium fluoride (YF_3) is not limited, but is typically a diffraction derived from the (111) plane of the crystal lattice. The diffraction peak is normally detected around $2\theta = 27.9^\circ$.

The sprayed film of the present invention preferably contains oxygen. The sprayed film of the present invention preferably has an oxygen content of 5 atom% or more.

Since the rare-earth element fluoride has cleavability, a sprayed film containing a rare earth element fluoride becomes a sprayed film in which cracks are easily generated depending on spray conditions, but when the oxygen content is 5 atom% or more, the amount of the rare earth element fluoride contained in the sprayed film becomes relatively small, so that generation of cracks is suppressed. The oxygen content is more preferably 15 atom% or more, still more preferably 20 atom% or more, and particularly preferably 25 atom% or more.

On the other hand, the oxygen content is preferably 55 atom% or less. Fluorination of the rare earth element oxide proceeds during etching with fluorine-based gas plasma, so that a rare earth fluoride or a rare earth oxyfluoride is formed. Particles may be generated in formation of a rare earth fluoride or a rare earth oxyfluoride, but when the oxygen content is 55 wt% or less, the amount of the rare earth fluoride or the rare earth oxyfluoride formed becomes relatively small, so that generation of particles is suppressed. The oxygen content is more preferably 52 atom% or less, still more preferably 49 atom% or less, and particularly preferably 46 atom% or less.

The oxygen content of the sprayed film can be adjusted by appropriately adjusting the oxygen content of the spray material, the spray atmosphere in spraying, the plasma gas flow rate, the current, the voltage, the power, the spray distance, the raw material supply rate, and the like.

The thickness of the sprayed film of the present invention is preferably 10 μm or more, more preferably 20 μm or more, still more preferably 30 μm or more, and particularly preferably 40 μm or more, and preferably 500 μm or less, more preferably 400 μm or less, still more preferably 300 μm or less, and particularly preferably 200 μm or less.

5 In the sprayed film of the present invention, it is preferable that the uniformity of the composition of elements contained in the sprayed film, in particular, the uniformity of the composition in the plane of the film is preferably high. When the uniformity of the composition of the sprayed film is high, the number of positions that are preferentially etched by gas plasma is small, and generation of particles is suppressed. Therefore, for elements,
10 preferably all elements, contained in the sprayed film, the standard deviation σ of the content in the sprayed film, in particular, the standard deviation σ of the content in the plane of the film is preferably less than 14. The standard deviation σ is preferably 13 or less, more preferably 12 or less, and still more preferably 11 or less. When the sprayed film of the present invention contains a rare earth element oxyfluoride, in particular, a rare earth element
15 oxyfluoride as a main phase, the standard deviation σ of the content in the sprayed film is relatively small even if the oxygen content of the sprayed film is relatively high (e.g., the oxygen content is 25 atom% or more), which is advantageous.

The sprayed film of the present invention preferably has a crack area ratio of less than 1.1%. When the crack area ratio is low, it is possible to suppress generation of
20 particles, which starts from cracks, and occurs in plasma etching. The crack area ratio is preferably 1% or less, more preferably 0.9% or less, and still more preferably 0.8% or less. The crack area ratio can be evaluated by, for example, identifying cracks using a scanning electron microscope (SEM) observation image of a film surface of a sprayed film, measuring the area of cracks in the observation image, and determining a ratio (percentage) of the area
25 of cracks to the area of the entire observation image. For measuring the area of cracks, image analysis software can be used.

The sprayed member of the present invention comprises a substrate, and a sprayed film formed on the substrate. The sprayed film and the sprayed member of the present invention are preferred as members for a semiconductor manufacturing apparatus. A
30 substrate formed from a known material as a substrate for a sprayed member can be used. A material of the substrate is selected from stainless steel, aluminum, nickel, chromium, zinc alloys thereof, alumina, aluminum nitride, silicon nitride, silicon carbide, quartz glass,

and the like, and a material preferred as a sprayed member, for example, a sprayed member for a semiconductor manufacturing apparatus is selected.

In the sprayed member, the sprayed film may be formed directly on the substrate, or formed with an underlying film interposed between the substrate and the sprayed film.

5 The underlying film can be formed by spraying. The underlying film preferably contains a rare earth element oxide.

The surface roughness of the underlying film is preferably low. Specifically, in measurement of the shape of the film surface of an underlying film by a non-contact process using a laser, the surface roughness S_a of a portion of a measurement surface (S-L surface) of the film surface of the underlying film within the evaluation region is preferably 3 μm or less. The measurement of the shape of film surface by a non-contact process using a laser, the measurement surface (S-L surface) and the evaluation region for the underlying film by a non-contact method using a laser may be the same as in the measurement of the shape of the film surface of sprayed film of the present invention.

15 In the present invention, the sprayed member can be produced by forming a sprayed film on a substrate. The method for forming the sprayed film of the present invention is not limited, but is preferably plasma spraying. Examples of the plasma spraying include atmospheric plasma spraying, small particle (fine particle) plasma spraying, and suspension plasma spraying, and more preferred is suspension plasma spraying in which a spray material (particles) is dispersed in a dispersion medium and sprayed in the form of a slurry. The spray material (particles) for use in formation of the sprayed film of the present invention preferably contains a rare earth element oxyfluoride, or a rare earth element oxyfluoride and a rare earth element fluoride. When the spray material (particles) contains a rare earth element oxyfluoride, or a rare earth element oxyfluoride and a rare earth element fluoride, 25 the oxygen content of the spray material (particles) is preferably 1 atom% or more, and more preferably 3 atom% or more, and preferably 33 atom% or less, and more preferably 30 atom% or less.

In the case of suspension plasma spraying, the mean particle size D_{50} of the spray material (particles) is preferably 1 μm or more, and more preferably 3 μm or more, and 30 preferably 9 μm or less, and more preferably 7 μm or less. As the dispersion medium, water or an organic solvent (e.g., isopropyl alcohol (IPA)) can be used. The slurry concentration is preferably 10 wt% or more, more preferably 20 wt% or more, and

preferably 60 wt% or less, and more preferably 50 wt% or less. The slurry viscosity is preferably 1 mPa·s or more, and more preferably 3 mPa·s or more, and preferably 15 mPa·s or less, and more preferably 10 mPa·s or less.

In plasma spraying, a spray material or a slurry containing a spray material is supplied
5 to plasma formed. By setting one or more conditions to be applied to formation of the plasma, which are selected from a current value C, a voltage value V, a value of C/V obtained by dividing the current value C by the voltage value V, and an applied power value P, preferably all of the conditions, within a predetermined range, to produce plasma, and performing plasma spraying, the sprayed film of the present invention, in particular, a
10 sprayed film having a film surface in which the value of an area ratio S/A is 1.75 or more can be appropriately formed.

In plasma spraying, the current value C applied to the formation of plasma is preferably 450 A or more, more preferably 455 A or more, and still more preferably 460 A or more, and preferably 1000 A or less, and more preferably 700 A or less.

15 In plasma spraying, the voltage value V applied to the formation of plasma is preferably 20 V or more, more preferably 60 V or more, and still more preferably 100 V or more, and particularly preferably 140 V or more, and preferably 235 V or less, and more preferably 230 V or less.

In plasma spraying, the value of C/V obtained by dividing the current value C
20 applied to the formation of plasma by the voltage value V is preferably 1.92 or more, more preferably 1.95 or more, and still more preferably 1.98 or more, and preferably 30 or less, more preferably 10 or less, and still more preferably 5 or less.

In plasma spraying, the applied power value P applied to the formation of plasma is preferably 20 kW or more, more preferably 60 kW or more, still more preferably 100 kW
25 or more, and particularly preferably 102 kW or more, and preferably 120 kW or less, more preferably 115 kW or less, still more preferably 110 kW or less, and particularly preferably 108 kW or less.

Examples of the plasma gas for use in formation of plasma in plasma spraying include a mixture of two or more gases selected from argon gas, hydrogen gas, helium gas
30 and nitrogen gas, and a mixture of three gases of argon, hydrogen and nitrogen, or a mixture of four gases of argon, hydrogen, helium, and nitrogen is more preferred, but the plasma gas is not limited thereto.

The spray distance in plasma spraying is preferably 150 mm or less. A decreased spray distance leads to an improved formation rate of the sprayed film, and an increased hardness and a decreased porosity of the sprayed film. The spray distance is more preferably 120 mm or less, still more preferably 100 mm or less, and particularly preferably 80 mm or less. On the other hand, since the thermal load on the substrate can be reduced as the spray distance increases, the spray distance is preferably 30 mm or more, more preferably 40 mm or more, still more preferably 50 mm or more, and particularly preferably 60 mm or more.

Other spray conditions such as a supply rate of the spray material and a supply amount of gas in plasma spraying are not limited. Known conditions can be applied. The conditions may be appropriately set according to a substrate, a spray material, and a use of a sprayed member obtained.

In particular, the temperature of the substrate, or the substrate and the underlying film formed on the substrate during spraying is preferably 300°C or lower, more preferably 250°C or lower, and still more preferably 200°C or lower. A lower temperature makes it easier to prevent damage and deformation of the substrate and the underlying film formed on the substrate, which are caused by heat. As the temperature becomes lower, it becomes easier to suppress generation of thermal stress. If the temperature is excessively high, delamination is likely to occur between the substrate and the sprayed film or between the underlying film formed on the substrate and the sprayed film.

On the other hand, the temperature of the substrate, or the substrate and the underlying film formed on the substrate during spraying is preferably 50°C or higher, more preferably 60°C or higher, and still more preferably 80°C or higher. If the temperature is excessively low, the bond between the substrate and the sprayed film or between the underlying film formed on the substrate and the sprayed film may weaken. A higher temperature leads to a stronger bond between splats, and enables formation of a denser sprayed film. The temperature of the substrate or of the substrate and the underlying film formed on the substrate, during spraying, can be achieved by controlling the cooling capacity.

Further, when the sprayed film is directly formed on the surface of the substrate, a sprayed film which is less easily peeled, has a higher hardness, and is denser sprayed film can be formed by increasing the surface roughness of the surface of the substrate on which the sprayed film is formed, and setting the temperature of the substrate during spraying to that described above. In this case, the surface roughness Sa of the sprayed film formed tends to increase. By reducing the surface roughness Sa through surface processing such as mechanical polishing (surface grinding, inner cylinder machining, mirror finishing or the like), blasting using small beads or the like, or hand polishing using a diamond pad, a smooth sprayed film which is less easily peeled, has a higher hardness, is denser, and has lower surface roughness Sa can be obtained.

EXAMPLES

Examples and Comparative Examples are given below to more concretely illustrate the present invention, although the present invention is not limited by these Examples.

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[Examples 1 to 8 and Comparative Examples 1 to 5]

The surface of an A5052 aluminum alloy substrate of 20 mm × 20 mm × 2.5 mm in thickness was degreased with acetone, and one surface of the substrate was roughened by blast polishing with a corundum abrasive of grain size #150. Next, using a slurry obtained by dispersing a spray material (particles) in a dispersion medium, a sprayed film was formed directly on the substrate by suspension plasma spraying to give a sprayed member. Table 1 shows the mean particle size D50, the oxygen (O) content and the ingredients (XRD crystal phase) of the spray material, and the dispersion medium, the concentration and the viscosity of the slurry. IPA as the dispersion medium represents isopropyl alcohol.

Using a plasma spraying apparatus 100 HE (manufactured by Progressive Surface, Inc.) and a spray material supply apparatus Liquifeeder HE (manufactured by Progressive Surface, Inc.), the suspension plasma spraying was performed at ordinary pressure in an air atmosphere using argon gas, hydrogen gas, and nitrogen gas as plasma gas. Table 2 shows conditions for plasma formation (current value C, voltage value V, value of C/V and applied power value P), and the spray distance.

[Example 9]

The surface of an A5052 aluminum alloy substrate of 20 mm × 20 mm × 2.5 mm in thickness was degreased with acetone, and one surface of the substrate was roughened by blast polishing with a corundum abrasive of grain size #150. Next, using a Y₂O₃ spray material (particles) having a mean particle size D50 of 9 μm, an underlying film (thickness: 100 μm) was formed on the substrate by atmospheric plasma spraying.

Using a plasma spraying apparatus F4MB-XL (manufactured by Oerlikon Metco Company) and a spray material supply apparatus TWIN-120 (manufactured by Oerlikon Metco Company), the atmospheric plasma spraying was performed at ordinary pressure in an air atmosphere using argon gas and hydrogen gas as plasma gas. In the plasma formation, the current was 500 A, the voltage was 67 V, the applied power was 34 kW, and the spray distance was 75 mm.

Next, using a slurry obtained by dispersing a spray material (particles) in a dispersion medium, a sprayed film was formed on the underlying film on the substrate by suspension plasma spraying to give a sprayed member. Table 1 shows the mean particle size D50, the oxygen (O) content and the ingredients (XRD crystal phase) of the spray material, and the dispersion medium, the concentration and the viscosity of the slurry.

The suspension plasma spraying was performed in the same manner as in Example 1 except that the conditions for plasma formation (current value C, voltage value V, value of C/V and applied power value P) were changed. Table 2 shows conditions for plasma formation (current value C, voltage value V, value of C/V and applied power value P), and the spray distance.

Table 1

	Spray material			Slurry		
	D50 [μm]	O content [atom%]	Ingredient (XRD crystal phase)	Dispersion medium	Concentration [pbw]	Viscosity [mPa·s]
Example 1	4.9	19	$\text{Y}_5\text{O}_4\text{F}_7$ YF_3	Water	30	4
Example 2	5.0	25	$\text{Y}_5\text{O}_4\text{F}_7$	Water	30	4
Example 3	5.1	5	YF_3 $\text{Y}_5\text{O}_4\text{F}_7$	Water	30	4
Example 4	4.1	23	$\text{Y}_5\text{O}_4\text{F}_7$	Water	30	4
Example 5	5.8	21	$\text{Y}_5\text{O}_4\text{F}_7$ YF_3	Water	30	4
Example 6	4.1	24	ScOF ScF_3	IPA	30	5
Example 7	5.0	25	$\text{Yb}_5\text{O}_4\text{F}_7$	Water	30	4
Example 8	5.0	25	$\text{Y}_5\text{O}_4\text{F}_7$	IPA	30	4
Example 9	6.9	15	$\text{Y}_5\text{O}_4\text{F}_7$ YF_3	Water	30	6
Comparative Example 1	3.6	15	YF_3 Y_2O_3 $\text{NH}_4\text{Y}_2\text{F}_7$	IPA	30	6
Comparative Example 2	3.6	0	YF_3	IPA	30	5
Comparative Example 3	3.9	5	YF_3 Y_2O_3 $\text{NH}_4\text{Y}_2\text{F}_7$	IPA	30	6
Comparative Example 4	3.6	12	Y_2O_3 $\text{NH}_4\text{Y}_2\text{F}_7$ YF_3	IPA	30	5
Comparative Example 5	5.1	24	$\text{Y}_5\text{O}_4\text{F}_7$	IPA	30	5

Table 2

	Plasma formation conditions				Spray distance [mm]
	Current value C [A]	Voltage value V [V]	C/V [A/V]	Applied power value P [kW]	
Example 1	561	189	2.97	106	75
Example 2	539	195	2.76	105	75
Example 3	547	192	2.85	105	75
Example 4	538	195	2.76	105	75
Example 5	571	183	3.12	105	75
Example 6	537	195	2.75	105	75
Example 7	458	228	2.01	105	75
Example 8	483	219	2.21	106	75
Example 9	610	171	3.57	104	75
Comparative Example 1	438	236	1.86	103	75
Comparative Example 2	397	266	1.49	106	75
Comparative Example 3	438	236	1.86	103	75
Comparative Example 4	438	236	1.86	103	75
Comparative Example 5	438	236	1.86	103	75

For the sprayed films obtained, measurement of the shape of the film surface was performed, the surface area S , the area A and the surface roughness S_a were measured, and the value of an area ratio S/A was calculated, by the following method. For the sprayed films obtained, the content of each element contained in the sprayed film was measured, and the uniformity of the composition of the film was evaluated, by the following method. For the sprayed films obtained, X-ray diffraction analysis was performed to obtain an X-ray diffraction profile, ingredients were identified, and evaluation was performed, by the following method. For the sprayed films obtained, the thickness of the sprayed film was measured by the following method. Further, for the sprayed films obtained, the area ratio of cracks on the film surface was evaluated by the following method. Table 3 shows the results.

In Example 9, even for the underlying film obtained, measurement of the shape of the film surface was performed, and the surface roughness S_a was measured, by the following method. The surface roughness S_a of the underlying film was $1.9\text{ }\mu\text{m}$. Further, in Example 9, even for the underlying film obtained, X-ray diffraction analysis was performed to obtain an X-ray diffraction profile, and the ingredients were identified, by the following method. The underlying film contained Y_2O_3 . The measurement and evaluation methods are shown below.

Table 3

		Surface area [μm^2]		S/A	Sa [μm]	Content [atom%]			Composition uniformity (Standard deviation σ)			Ingredient (XRD crystal phase)		Thickness [μm]	Crack area ratio [%]
		S	A			R	O	F	R	O	F	Main phase			
Example	1	127059	57817	2.20	1.4	37	29	33	2.5	6.4	8.4	YOF	Y ₅ O ₄ F ₇ Y ₂ O ₃	100	0.4
	2	117110	57817	2.03	2.1	38	34	28	0.6	6.8	7.3	YOF	Y ₂ O ₃ Y ₇ O ₆ F ₉	100	0.5
	3	113341	57817	1.96	2.4	27	10	63	1.2	4.2	4.5	Y ₅ O ₄ F ₇	Y ₂ O ₃ YF ₃	300	0.8
	4	112329	57817	1.94	1.6	40	38	22	4.6	7.1	7.9	YOF	Y ₂ O ₃ Y ₆ O ₃ F ₈	100	0.7
	5	111586	57817	1.93	1.7	32	31	37	3.1	10.3	12.5	YOF	Y ₂ O ₃ Y ₅ O ₄ F ₇	30	0.6
	6	106742	57817	1.85	1.4	39	45	16	1.9	10.8	11.6	ScOF	Sc ₂ O ₃	100	0.6
	7	106551	57817	1.84	1.3	37	39	24	1.7	6.2	7.6	YbOF	Yb ₂ O ₃ Yb ₅ O ₄ F ₇	100	0.7
	8	106031	57817	1.83	1.6	35	40	25	1.4	5.2	6.5	Y ₂ O ₃	YOF Y ₅ O ₄ F ₇	100	0.8
	9	104031	57817	1.80	2.7	31	27	42	1.5	4.3	5.2	Y ₅ O ₄ F ₇	YOF Y ₂ O ₃	50	0.8
Comparative Example	1	100710	57817	1.74	1.2	36	35	29	2.8	20.6	23.2	Y ₂ O ₃	Y ₅ O ₄ F ₇	100	1.4
	2	98138	57817	1.70	1.0	28	8	64	1.1	3.9	3.9	Y ₅ O ₄ F ₇	YF ₃	100	1.2
	3	97695	57817	1.69	1.2	30	15	55	1.8	7.1	8.5	Y ₅ O ₄ F ₇	Y ₂ O ₃ YF ₃ YOF	100	1.4
	4	97659	57817	1.69	1.5	33	26	41	3.4	14.2	17.6	Y ₂ O ₃	Y ₅ O ₄ F ₇ YF ₃ YOF	100	1.1
	5	97463	57817	1.69	1.6	37	56	7	2.6	6.3	6.1	Y ₂ O ₃	YOF	100	1.5

[Surface area S, area A and surface roughness Sa]

Measurement of the shape of the film surface by a non-contact process using a laser was performed according to ISO 25178-2: 2021. For the measurement, a laser microscope VK-X3000 (manufactured by KEYENCE CORPORATION) was used, and a microscope image was obtained at an object lens magnification of 50 times (total magnification: 1200 times). The obtained microscope image was analyzed with a multfile analysis application accompanying the laser microscope VK-X3000, the surface area S and the area A were measured from the obtained measurement surface (S-L surface) by volume/area measurement with the application, and the area ratio S/A was calculated.

The surface roughness Sa was measured from the obtained measurement surface (S-L surface) by surface roughness measurement with the application. In region setting, the entire region (the entire microscope image (a range corresponding to the area A)) was set. A Gaussian filter was used for both the S-filter and the L-filter. The set value for the S-filter was 0.8 μm and the set value for the L-filter was 0.5 mm.

[Measurement of content of element and evaluation of composition uniformity]

An evaluation sample was prepared by performing mirror polishing so that the surface roughness Sa of a sprayed film was 0.2 μm or less. A 1,000-times magnified SEM image of the evaluation sample was obtained using a desktop scanning electron microscope (SEM) JCM-7000 (manufactured by JEOL Ltd.), and the composition of a rare earth element (R), oxygen (O) and fluorine (F) was analyzed at arbitrarily selected five points on the film surface with an energy dispersive X-ray spectrometer (EDX) accompanying the desktop scanning electron microscope JCM-7000. The content of each element at each point was obtained from the integrated intensity ratio of the peak of a characteristic X-ray unique to the element, and the average value of the five analysis points was calculated as a content of each element in the sprayed film. Further, for evaluating the composition uniformity, the standard deviation σ of the contents at the five analysis points was calculated by the n-1 method.

[X-ray diffraction (identification and evaluation of ingredients)]

An X-ray diffraction profile was obtained using an X-ray diffraction measuring apparatus X'Pert PRO/MPD (manufactured by Malvern Panalytical Ltd), and ingredients (crystal phases) were identified using analysis software HighScore Plus (manufactured by Malvern Panalytical Ltd). The measurement conditions were set to characteristic X-ray: Cu-K α (tube voltage: 45 kV, tube current: 40 mA), scanning range: $2\theta = 10$ to 70° , step size: 0.0167113° , time per step: 13.970 sec, and scanning speed: $0.151921^\circ/\text{sec}$. The integrated intensity of each of the diffraction peaks was calculated. The component (crystal phase) from which a diffraction peak with the largest integrated intensity was derived was a main phase.

[Measurement of thickness]

The thickness was measured using an eddy current thickness meter LH-300J (manufactured by Kett Electric Laboratory Co. Ltd.).

[Measurement of area ratio of cracks]

A 5,000-times magnified reflection electron image of the principal surface of the sprayed film was obtained using a scanning electron microscope (SEM) JSM-IT500HR (manufactured by JEOL Ltd.). Using image processing software Adobe Photoshop Elements 8 (manufactured by Adobe Systems Inc.), whitening treatment was performed on the obtained reflection electron image so that the cracks whitened. Images obtained by performing whitening treatment on the scanning electron microscope images (reflection electron images) of the sprayed films of Examples 1 and 3 and Comparative Examples 1 and 2 to whiten the cracks are shown in FIGS. 1 to 4, respectively. From FIGS. 1 to 4, it can be seen that the sprayed films of Examples (FIGS. 1 and 2) have fewer cracks than those of Comparative Examples (FIGS. 3 and 4). Further, in the obtained image, the area of cracks was quantitated using image analysis software ImageJ (public software from National Institutes of Health), and the percentage of the area of cracks to the area of the entire image was evaluated as an area ratio of cracks.

Specifically, the area ratio of cracks was calculated by the following procedure.

- (1) The surface of the sprayed film obtained is coated with platinum (Pt) by vapor deposition, and a 5,000-times magnified reflection electron image is formed using a SEM.
- (2) Using image processing software Adobe Photoshop Elements 8, whitening treatment
5 is performed on the image so that cracks on the surface of the sprayed film are detected when the thresholds of the image are set as described in (5) below.
- (3) Using image analysis software ImageJ, an area of the photographed surface where image processing is performed is defined, followed by trimming.
- (4) Grayscale transformation of the image is performed.
- 10 (5) The thresholds of the image are set such that the high level side threshold is 255, and the low level side threshold is a numerical value at which all crack portions are red.
- (6) The image is binarized.
- (7) Crack portions are identified.
- (8) The length unit is set to a pixel, and the total area (pixel number) of the crack portions
15 is determined.
- (9) The thresholds of the image are set such that the high level side threshold is 255, and the low level side threshold is 0, and the total area (pixel number) of the image is determined.
- (10) The area ratio of cracks is calculated by dividing the total area (pixel number) of the crack portions by the total area (pixel number) of the image.

CLAIMS:

1. A sprayed film comprising a film surface in which in measurement of a shape of the film surface by a non-contact process using a laser, a value of an area ratio S/A obtained by dividing a surface area S (μm^2) of a portion of the measurement surface (S-L surface) of the film surface within one evaluation region by an area A (μm^2) of a portion of a reference surface forming a plane located at an arithmetic average height of the measurement surface (S-L surface), which is within the evaluation region is 1.75 or more and 3 or less, and a surface roughness Sa of a portion of the measurement surface (S-L surface) within the evaluation region is $0.4\ \mu\text{m}$ or more and $8\ \mu\text{m}$ or less.
2. The sprayed film according to claim 1, comprising a rare earth element oxyfluoride.
3. The sprayed film according to claim 2, wherein the rare earth element oxyfluoride is one or more selected from ROF, $\text{R}_5\text{O}_4\text{F}_7$, $\text{R}_6\text{O}_5\text{F}_8$ and $\text{R}_7\text{O}_6\text{F}_9$ (wherein R represents one or more selected from rare earth elements including Sc and Y).
4. The sprayed film according to any one of claims 1 to 3, comprising a rare earth element oxyfluoride of ROF (wherein R represents one or more selected from rare earth elements including Sc and Y), wherein in X-ray diffraction using a Cu-K α ray as a characteristic X-ray, a diffraction peak having the largest integrated intensity, among diffraction peaks detected within a diffraction angle range of $2\theta = 10^\circ$ to 70° , is a diffraction peak derived from the ROF.
5. The sprayed film according to any one of claims 1 to 4, comprising oxygen, wherein an oxygen content is 5 atom% or more and 55 atom% or less.
6. The sprayed film according to any one of claims 1 to 5, wherein a thickness is $10\ \mu\text{m}$ or more and $500\ \mu\text{m}$ or less.
7. A sprayed member comprising a substrate, and the sprayed film of any one of claims 1 to 6 formed on the substrate.

8. The sprayed member according to claim 7, which is a member for a semiconductor manufacturing apparatus.
9. A method for forming the sprayed film of any one of claims 1 to 6, comprising
5 a step of performing suspension plasma spraying of a slurry, in which a spray material in a form of particles with a mean particle size D50 of 1 μm or more and 9 μm or less is dispersed in a dispersion medium, by supplying the slurry containing the spray material to plasma produced by setting a current value C to 450 A or more and 1,000 A or less, a voltage value V to 20 V or more and 235 V or less, a value of C/V obtained by dividing
10 the current value C by the voltage value V to 1.92 or more and 30 or less, and an applied power value P to 20 kW or more and 120 kW or less.
10. The method according to claim 9, wherein the spray material contains a rare earth element oxyfluoride, or a rare earth element oxyfluoride and a rare earth element fluoride.