(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 4 567 162 A1

(12) EUROPEAN PATENT APPLICATION

published in accordance with Art. 153(4) EPC

(43) Date of publication:
11.06.2025 Bulletin 2025/24

(21) Application number: **23849918.0**

(22) Date of filing: **20.07.2023**

(51) International Patent Classification (IPC):
C25D 9/08 $^{(2006.01)}$ ***C23C 26/00*** $^{(2006.01)}$

(52) Cooperative Patent Classification (CPC):
C23C 26/00; C25D 9/08

(86) International application number:
PCT/JP2023/026615

(87) International publication number:
WO 2024/029363 (08.02.2024 Gazette 2024/06)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
KH MA MD TN

(30) Priority: **05.08.2022 JP 2022125323**

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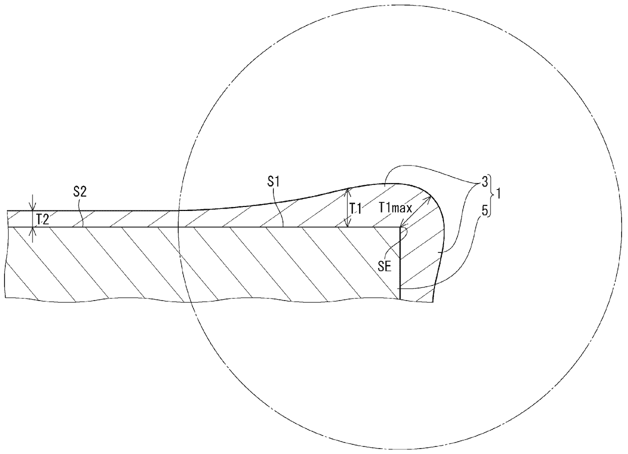
(54) COATED BASE MATERIAL

(57) The present invention provides a novel coated base material which is applicable to various fields, while being able to be mass produced. A coated base material (1) according to the present invention is obtained by covering a base material (5) with a coating film (3). The thickness of the coating film (3) is not less than 1 nm but less than 800 nm. The total elemental percentage of metal elements and oxygen (O) in the coating film (3) is 70 atom% or more as determined by X-ray photoelectron spectroscopy. The coating film (3) has a relative density of 90% or more. This coated base material (1) satisfies at least one of the condition (1) and the condition (2) described below. Condition (1): The maximum thickness of the coating film (3) formed on an edge region of the surface of the base material (5) is larger than the thickness of the coating film (3) formed on an inner region of the surface, the inner region being inside the edge region. Condition (2): The maximum thickness of the coating film (3) formed on a region of the surface of the base material (5), the region having a projection, is larger than the thickness of the coating film (3) formed on another region of the surface, the another region having no projection.

FIG. 1



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Description

TECHNICAL FIELD

[0001] The present disclosure relates to a coated substrate.

BACKGROUND ART

[0002] Patent Literatures 1 to 4 disclose coated substrates having metal oxide films. In Patent Literatures 1 to 4, a wet film-formation method is employed. Meanwhile, in some cases, a dry film-formation method (dry process) has been employed so as to perform thickness control in accordance with complex substrate shapes.

[0003] In consideration of application to various fields and mass production, conventional coated substrates are not necessarily satisfactory, and development of a novel coated substrate has been desired.

CITATION LIST

PATENT LITERATURES

[0004]

Patent Literature 1: JP2011-32521A
Patent Literature 2: JP2009-147192A
Patent Literature 3: JP2015-93821A
Patent Literature 4: JPH9-202606A

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0005] The present disclosure was made in view of the above-described circumstances, and an object is to provide a novel coated substrate which can be applied to various fields and can be mass produced. The present disclosure can be realized as the following modes.

SOLUTION TO PROBLEM

[0006]

[1] A coated substrate in which a substrate is coated with a film, wherein

> the thickness of the film is 1 nm or greater and less than 800 nm,
> x-ray photoelectron spectroscopic measurement of the film shows that the total percent element composition of a metal element and O (oxygen) is 70 atm% or greater,
> the relative density of the film is 90% or greater, and
> at least one of the following conditions (1) and (2) is satisfied;
> condition (1): the maximum thickness of the film formed on an edge region of a surface of the substrate is greater than the thickness of the film formed on an inner region of the surface located inward of the edge region, and
> condition (2): the maximum thickness of the film formed on a convex portion present region of the surface of the substrate is greater than the thickness of the film formed on a convex portion absent region of the surface.

[2] The coated substrate recited in [1], wherein a portion of the substrate where the film is formed is electrically conductive.
[3] The coated substrate recited in [1] or [2], wherein the x-ray photoelectron spectroscopic measurement of the film shows that the percent element composition of C (carbon) is 0.1 atm% or greater and less than 20 atm%.
[4] The coated substrate recited in [1] or [2], wherein the film is amorphous.
[5] The coated substrate recited in [1] or [2], wherein the condition (1) is such that the maximum thickness of the film formed on the edge region is greater than the thickness of the film formed on the inner region by 10% or more of the thickness of the film formed on the inner region.
[6] The coated substrate recited in [1] or [2], wherein the condition (2) is such that the maximum thickness of the film

formed on the convex portion present region is greater than the thickness of the film formed on the convex portion absent region by 10% or more of the thickness of the film formed on the convex portion absent region.

[7] The coated substrate recited in [1] or [2], wherein the condition (1) is such that the thickness of the film decreases toward the inner region from a position where the film formed on the edge region has the maximum thickness.

[8] The coated substrate recited in [1] or [2], wherein the condition (2) is such that the thickness of the film decreases toward the convex portion absent region from a position where the film formed on the convex portion present region has the maximum thickness.

[9] The coated substrate recited in [1] or [2], wherein the metal element is at least one or more metal elements selected from the group consisting of Al (aluminum), Ti (titanium), Mo (molybdenum), Cr (chromium), Mn (manganese), Fe (iron), Co (cobalt), Ni (nickel), Zr (zirconium), V (vanadium), W (tungsten), Ta (tantalum), Nb (niobium), and Sn (tin).

ADVANTAGEOUS EFFECT OF INVENTION

[0007] According to the present disclosure, there is provided a novel coated substrate which can be applied to various fields and can be mass produced.

BRIEF DESCRIPTION OF DRAWINGS

[0008]

[FIG. 1] Schematic view of a cross section of a coated substrate.

[FIG. 2] Schematic view of a cross section of a coated substrate.

[FIG. 3] Schematic view of a film formation apparatus.

[FIG. 4] Graph showing the relation between electrodeposition time and deposition weight (deposition mass).

[FIG. 5] Graph showing the relation between the number of samples experimentally produced and the aluminum element concentration of bath liquid.

DESCRIPTION OF EMBODIMENTS

[0009] The present disclosure will now be described in detail. Notably, in the present specification, in a description in which "-" is used for a numerical range, the numerical range contains its upper and lower limit values, unless otherwise specifically noted. For example, a description of "10 - 20" should be read to contain both "10" (lower limit value) and "20" (upper limit value). Namely, "10 - 20" has the same meaning as "10 or greater and 20 or less." Also, in the present specification, the upper and lower limit values of various numerical ranges may be combined freely.

1. Coated substrate 1

[0010] A coated substrate 1 includes a substrate 5 coated with a film 3. The thickness T of the film 3 is 1 nm or greater and less than 800 nm. X-ray photoelectron spectroscopic measurement of the film 3 shows that the total percent element composition of a metal element and O (oxygen) is 70 atm% or greater. The relative density of the film 3 is 90% or greater. The coated substrate 1 satisfies at least one of the following conditions (1) and (2). The functionality of the coated substrate 1 is enhanced as a result of satisfaction of at least one of the conditions (1) and (2).

[0011] Condition (1): the maximum thickness T1max of the film 3 formed on an edge region S1 of a surface S of the substrate 5 is greater than the thickness T2 of the film 3 formed on an inner region S2 of the surface S located inward of the edge region S1.

[0012] Condition (2): the maximum thickness T3max of the film 3 formed on a convex portion present region S3 of the surface S of the substrate 5 is greater than the thickness T4 of the film 3 formed on a convex portion absent region S4 of the surface S.

[0013] FIG. 1 shows a schematic view of a cross section of one example of the coated substrate 1. Although FIG. 1 shows an example in which the film 3 is formed on one side of the substrate 5, the film 3 may be formed on opposite sides of the substrate 5.

[0014] FIG. 2 shows a schematic view of a cross section of another example of the coated substrate 1. Although FIG. 2 shows an example in which the film 3 is formed on one side of the substrate 5, the film 3 may be formed on opposite sides of the substrate 5.

(1) Substrate 5

[0015] No particular limitation is imposed on the substrate 5. In order to enhance adhesion of the film 3 to the substrate 5, at least a portion (region) of the substrate 5, which portion is to be coated with the film 3, is preferably formed of a material which is electrically conductive and can function as a negative electrode 7 (cathode). In the case where the portion (region) of the substrate 5, which portion is to be coated with the film 3, is electrically conductive and can function as the negative electrode 7 (cathode), the film 3 can be easily formed on that portion by a manufacturing method described below.

[0016] A surface portion of the substrate 5 may be formed of a material which is electrically conductive and can function as the negative electrode 7. The entire substrate 5 may be formed of a material which can function as the negative electrode 7. Examples of preferred materials which can serve as the negative electrode 7 include an iron-based alloy and carbon. An example of preferred iron-based alloys is one or more types of alloys selected from Fe-Ni-Cr alloy (stainless steel), Fe-Ni alloy (permalloy), Fe-Si alloy (silicon iron), Fe-Si-Al alloy (Sendust), Fe-Ni-Mo (supermalloy), Fe-Co alloy (permendur), and Fe-C-B alloy (amorphous).

(2) Film 3

(2.1) Thickness T

[0017] The thickness T of the film 3 is the shortest distance from a point on the surface of the film 3 to the surface S of the substrate 5. From the viewpoint of enabling the film 3 to exhibit a function corresponding to the material of the film 3, the thickness T of the film 3 is 1 nm or greater, preferably 10 nm or greater, more preferably 50 nm or greater. Meanwhile, from the viewpoint of enabling the film 3 to endure stresses generated therein and securing adhesion to the substrate 5, the thickness T of the film 3 is less than 800 nm, preferably 500 nm or less, more preferably 200 nm or less. From theses viewpoints, the thickness T of the film 3 is 1 nm or greater and less than 800 nm, preferably 10 nm or greater and 500 nm or less, more preferably 50 nm or greater and 200 nm or less. Notably, in the case where the thickness T of the film 3 is not uniform, the film 3 satisfies the requirement regarding the thickness T when the thickness T of at least a portion of the film 3 falls within the above-described range. The thickness of the film 3 can be obtained through observation under an FIB-SEM.

(2.2) Condition (1) regarding the thickness T of the film 3

[0018] The condition (1) is such that the maximum thickness T1max of the film 3 formed on the edge region S1 of the surface S of the substrate 5 is greater than the thickness T2 of the film 3 formed on the inner region S2 of the surface S located inward of the edge region S1. The maximum thickness T1max of the film 3 formed on the edge region S1 is the maximum value of the thickness T1 of the film 3 formed on the edge region S1.

[0019] No particular limitation is imposed on the edge region S1 so long as it is an edge portion of the surface S. The edge region S1 is, for example, a region which is located, in a cross sectional view, within a circular region whose center is located an end portion SE of the surface S of the substrate 5 and whose radius is 5 mm. In the example of FIG. 1, the edge region S1 is a region surrounded by a dash-dot line. In the example of FIG. 1, the maximum thickness T1max is the thickness T1 at the end portion SE.

[0020] No particular limitation is imposed on the maximum thickness T1max. The maximum thickness T1max is, for example, preferably 10 nm or greater and 1000 nm or less, more preferably 50 nm or greater and 800 nm or less, further preferably 100 nm or greater and 500 nm or less.

[0021] No particular limitation is imposed on the thickness T2 so long as the thickness T2 is smaller than the maximum thickness T1max. The thickness T2 is, for example, preferably 1 nm or greater and 800 nm or less, more preferably 10 nm or greater and 500 nm or less, further preferably 50 nm or greater and 200 nm or less.

[0022] In the condition (1), from the viewpoint of enhancing the functionality of the coated substrate 1, the maximum thickness T1max of the film 3 formed on the edge region S1 is preferably greater than the thickness T2 of the film 3 formed on the inner region S2 by 10% or more of the thickness T2, more preferably greater than the thickness T2 by 20% or more of the thickness T2, and further preferably greater than the thickness T2 by 30% or more of the thickness T2. In the case where the thickness T2 is not uniform, if the the maximum thickness T1max is greater than the thickness T2 in at least a portion of the inner region S2 by a certain percentage or more of the thickness T2, the above-described relation is satisfied. Although no particular limitation is imposed of the upper limit value of the ratio of the maximum thickness T1max to the thickness T2, it is preferred that, in condition (1), the maximum thickness T1max is equal to or less than 400% of the thickness T2.

[0023] In condition (1), it is preferred that the thickness T of the film 3 decreases toward the inner region S2 from a position where the film 3 formed on the edge region S1 has the maximum thickness T1max. Notably, irregularities whose sizes are equal to or less than 10% of the maximum thickness T1max are not taken into consideration. By virtue of this configuration, the influence of residual stresses occurring at the interface of the substrate 5 can be mitigated in a wide region.

[0024] Notably, determination as to whether or not the condition (1) regarding the thickness T of the film 3 is satisfied is made by observing, under an FIB-SEM, a cross section of the coated substrate 1 which extends perpendicularly to the surface S of the substrate 5.

(2.3) Condition (2) regarding the thickness T of the film 3

[0025] The condition (2) is such that the maximum thickness T3max of the film 3 formed on the convex portion present region S3 of the surface S of the substrate 5 is greater than the thickness T4 of the film 3 formed on the convex portion absent region S4 of the surface S. The maximum thickness T3max of the film 3 formed on the convex portion present region S3 is the maximum value of the thickness T3 of the film 3 formed on the convex portion present region S3. No particular limitation is imposed on the shape, size, number of a convex portion(s) 12. Notably, in the case where a plurality of convex portions 12 are present, the condition (2) regarding the thickness T of the film 3 is satisfied if the condition (2) is satisfied in a combination of the film 3 formed on the convex portion present region S3 associated with one convex portion 12 and the film 3 formed on the convex portion absent region S4 located adjacent thereto. The convex portion 12 may have, for example, a mount-like shape, a protruding shape, a needle-like shape, or a columnar shape. Although no particular limitation is imposed on the maximum height h of the convex portion 12, the maximum height h is, for example, preferably 100 nm or greater and 10 mm or less, more preferably 500 nm or greater and 5 mm or less, further preferably 1000 nm or greater and 2 mm or less. The maximum height h of the convex portion 12 means the height from the surface S of the substrate 5 in the convex portion absent region S4, which surface severs as a reference. Although no particular limitation is imposed on the occupation area of the convex portion 12 as viewed orthogonally from the upper side of the substrate 5, the occupation area is, for example, preferably 10 μm^2 or greater and 100 mm^2 or less, more preferably 100 μm^2 or greater and 10 mm^2 or less, further preferably 500 μm^2 or greater and 1 mm^2 or less.

[0026] No particular limitation is imposed on the maximum thickness T3max. The maximum thickness T3max is, for example, preferably 10 nm or greater and 1000 nm or less, more preferably 50 nm or greater and 800 nm or less, further preferably 100 nm or greater and 500 nm or less.

[0027] No particular limitation is imposed on the thickness T4 so long as the thickness T4 is smaller than the maximum thickness T3max. The thickness T4 is, for example, preferably 1 nm or greater and 800 nm or less, more preferably 10 nm or greater and 500 nm or less, further preferably 50 nm or greater and 200 nm or less.

[0028] In the condition (2), from the viewpoint of enhancing the functionality of the coated substrate 1, the maximum thickness T3max of the film 3 formed on the convex portion present region S3 is preferably greater than the thickness T4 of the film 3 formed on the convex portion absent region S4 by 10% or more of the thickness T4, more preferably greater than the thickness T4 by 20% or more of the thickness T4, and further preferably greater than the thickness T4 by 30% or more of the thickness T4. In the case where the thickness T4 is not uniform, if the the maximum thickness T3max is greater than the thickness T4 in at least a portion of the convex portion absent region S4 by a certain percentage or more of the thickness T4, the above-described relation is satisfied. Although no particular limitation is imposed of the upper limit value of the ratio of the maximum thickness T3max to the thickness T4, it is preferred that, in condition (2), the maximum thickness T3max is equal to or less than 400% of the thickness T4.

[0029] In condition (2), it is preferred that the thickness T of the film 3 decreases toward the convex portion absent region S4 from a position where the film 3 formed on the convex portion present region S3 has the maximum thickness T3max. Notably, irregularities whose sizes are equal to or less than 10% of the maximum thickness T3max are not taken into consideration. By virtue of this configuration, the influence of residual stresses occurring at the interface of the substrate 5 can be mitigated in a wide region.

[0030] Notably, determination as to whether or not the condition (2) regarding the thickness T of the film 3 is satisfied is made by observing, under an FIB-SEM, a cross section of the coated substrate 1 which extends perpendicularly to the surface S of the substrate 5.

(2.4) Percent element composition of C (carbon)

[0031] From the viewpoint of suppressing growth of crystal grains in the film 3 and stabilizing the properties of the film 3, the percent element composition of C (carbon) determined through measurement by x-ray photoelectron spectroscopy (XPS method) is 0.1 atm% or greater, preferably 0.5 atm% or greater, more preferably 1 atm% or greater. Meanwhile, from the viewpoint of enabling the film 3 to sufficiently function as an inorganic film, the percent element composition of C (carbon) is less than 20 atm%, preferably 15 atm% or less, more preferably 10 atm% or less. From these viewpoints, the percent element composition of C (carbon) is 0.1 atm% or greater and less than 20 atm%, preferably 0.5 atm% or greater and 15 atm% or less, more preferably 1 atm% or greater and 10 atm% or less. Notably, in the case where the composition of the film 3 is not uniform, the film 3 satisfies the requirement regarding the percent element composition of C (carbon) when the composition of at least a portion of the film 3 falls within the above-described range.

[0032] The composition analysis by the x-ray photoelectron spectroscopy can be performed by using an x-ray photoelectron spectrometer. The measurement can be performed by scanning a cross section under the following measurement conditions: K-alpha rays of aluminum being used as an x-ray source, the beam diameter being set to 100 μm, and the x-ray incident angle in relation to a surface to be analyzed being set to 45°.

(2.5) Total percent element composition of the metal element and O (oxygen)

[0033] From the viewpoint of enabling the film 3 to sufficiently function as an inorganic film, the total percent element composition of the metal element and O (oxygen) of the film 3 determined through measurement by the x-ray photoelectron spectroscopy (XPS method) is 70 atm% or greater, preferably 80 atm% or greater, more preferably 90 atm% or greater. Notably, the upper limit of the total percent element composition of the metal element and O (oxygen) is a value obtained by subtracting the percent element composition (atm%) of C (carbon) from 100 atm%. In the case where the composition of the film 3 is not uniform, the film 3 satisfies the requirement regarding the total percent element composition of the metal element and O (oxygen) when the composition of at least a portion of the film 3 falls within the above-described range.

(2.6) Relative density of film 3

[0034] From the viewpoint of enabling the film 3 to sufficiently exhibit the function of the film 3, the relative density of the film 3 is 90% or greater, preferably 95% or greater, more preferably 98% or greater. The relative density of the film 3 may be 100%.

[0035] The relative density of the film 3 is obtained by the following method. A TEM image of a cross section of the film 3 obtained by cutting the film 3 in the film-thickness direction is obtained. The area of pores in a field of view of 300 nm (vertical dimension) × 1000 nm (horizontal dimension) is measured. The relative density (%) is obtained in accordance with the following expression (1). The average of the relative densities of 10 fields of view is the relative density of the film 3. Notably, in the case where the thickness of the film 3 is smaller than the vertical size of 300 nm, measurement is performed in fields of view determined in accordance with the thickness of the film 3.

$$\text{Relative density (\%)} = \{(S1 - S2)/S1\} \times 100 \qquad (1)$$

(In the expression, S1 is the area (nm^2) of the field of view of 300 nm (vertical dimension) × 1000 nm (horizontal dimension), and S2 is the total area (nm^2) of pores in the field of view of 300 nm (vertical dimension) × 1000 nm (horizontal dimension))

(2.7) Amorphous

[0036] It is preferred that the film 3 is amorphous. The fact that the film 3 is amorphous can be confirmed by using a TEM image. When the film 3 is amorphous, it is expected that crystal grains do not come off and peculiar functions (such as smoothing the outermost surface by uniform film growth) are exhibited.

(2.8) Compound having at least one type of structure selected from C-H bond, C=O bond, and C-O bond

[0037] The film 3 preferably contains a compound having at least one type of structure selected from C-H bond, C=O bond, and C-O bond. Since the compound having at least one type of structure selected from C-H bond, C=O bond, and C-O bond vaporizes at a lower temperature as compared with elemental C (carbon) and induces contraction of the film 3, it is supposed that the denseness of the film 3 increases.

[0038] Also, since the compound having at least one type of structure selected from C-H bond, C=O bond, and C-O bond remains, it is supposed that the flexibility of the film 3 is maintained, and the adhesion of the film 3 to the substrate 5 is enhanced.

(2.9) Halogen element

[0039] The percent element composition of the halogen element as determined through measurement of the film 3 by x-ray photoelectron spectroscopy is preferably 0.1 atm% or greater, more preferably 0.3 atm% or greater, further preferably 0.5 atm% or greater. The upper limit value of the percent element composition of the halogen element is 3 atm% or less.

[0040] Since a small amount of halogen element is contained in the film 3, conceivably, the oxide film present on the surface of the substrate 5 is removed by the action of the halogen element, and the film 3 comes into direct contact with the substrate 5. As a result, the adhesion between the substrate 5 and the film 3 is secured.

(2.10) Metal element

[0041] No particular limitation is imposed on the metal element. From the viewpoint of causing the film 3 to function as a high quality protection film for the substrate 5, the metal element is preferably at least one or more metal elements selected from the group consisting of Al (aluminum), Ti (titanium), Mo (molybdenum), Cr (chromium), Mn (manganese), Fe (iron), Co (cobalt), Ni (nickel), Zr (zirconium), V (vanadium), W (tungsten), Ta (tantalum), Nb (niobium), and Sn (tin).

2. Method for manufacturing coated substrate 1

[0042] No particular limitation is imposed on a method for manufacturing the coated substrate 1 of the present disclosure.

[0043] A preferred manufacturing method will now be described below (see FIG. 3). The preferred manufacturing method is a method for manufacturing the coated substrate 1 by using a bath liquid 2 containing an organic solvent. The water content of the bath liquid 2 is less than 1 mass% and the bath liquid 2 contains at least one or more types of metal elements and at least one or more types of halogen elements. When a voltage is applied in a state in which the substrate 5 is immersed in the bath liquid 2, the film 3 is formed on the substrate 5, which serves as a negative electrode 7 (cathode). In the manufacturing method of the present disclosure, since electrodeposition is taken place on the negative electrode 7 side, oxidation of the substrate 5 can be suppressed as compared with the case where electrodeposition is taken place on the positive electrode 6 side (anode side).

(1) Bath liquid 2

[0044] The bath liquid 2 contains an organic solvent.

(1.1) Water content

[0045] From the viewpoint of guaranteeing the homogeneity of the film 3 and suppressing oxidation of the substrate 5, the water content of the bath liquid 2 is rendered less than 1 mass%. The water content is preferably less than 0.5 mass%, more preferably less than 0.1 mass%. The water content may be 0 mass%. The water content of the bath liquid 2 can be obtained by GC-MS analysis.

(1.2) Metal element

[0046] The bath liquid 2 contains at least one or more types of metal elements. No particular limitation is imposed on the metal elements. From the viewpoint of causing the film 3 to function as a high quality protection film for the substrate 5, the metal element is preferably at least one or more metal elements selected from the group consisting of Al (aluminum), Ti (titanium), Mo (molybdenum), Cr (chromium), Mn (manganese), Fe (iron), Co (cobalt), Ni (nickel), Zr (zirconium), V (vanadium), W (tungsten), Ta (tantalum), Nb (niobium), and Sn (tin). In the manufacturing method of the present disclosure, an oxide film depending on the metal element(s) in the bath liquid 2 is formed as the film 3.

[0047] The metal element(s) contained in the bath liquid 2 may be supplied as a result of elution of the positive electrode 6 (anode). In the case where the metal element(s) elutes from the positive electrode 6 into the bath liquid 2, control of film formation speed becomes easy, and continuous and stable formation of films on a plurality of substrates 5 becomes possible. In the case where the metal element(s) is supplied to the bath liquid 2 as a result of elution of the positive electrode 6, at least one or more types of electrodes selected from an electrode of Al, an electrode of Ti, and an electrode of Mo are preferably used as the positive electrode 6.

[0048] The metal element(s) in the bath liquid 2 may be supplied from a metal alkoxide and/or an inorganic metal compound. In the case where the metal element(s) is supplied as a result of dissolution of a metal alkoxide and/or an inorganic metal compound, it is possible to cope with an element which is difficult to supply by eluting the positive electrode 6 (anode). Also, in this case, it becomes possible to perform film formation in which composition ratios are controlled by combining a plurality of metal elements.

[0049] Examples of the metal alkoxide include an aluminum alkoxide, a titanium alkoxide, and a molybdenum alkoxide.

[0050] Examples of the aluminum alkoxide include an aluminum trialkoxide. Examples of the aluminum trialkoxide include aluminum tripropoxides (e.g., aluminum triisopropoxide and aluminum tri-n-propoxide), aluminum triethoxide, aluminum tributoxides (e.g., aluminum tri-sec-butoxide and aluminum tri-n-butoxide).

[0051] Examples of the titanium alkoxide include a titanium trialkoxide, a titanium tetraalkoxide, and a titanium tetraalkoxide is preferred. Examples of the titanium tetraalkoxide include titanium tetrapropoxides (e.g., titanium tetraisopropoxide and titanium tetra-n-propoxide), titanium tetramethoxide, titanium tetraethoxide, titanium tetrabutoxides (e.g., titanium tetraisobutoxide and titanium tetra-n-butoxide), titanium tetrapentoxides, titanium tetrahexoxides, and titanium tetra (2-ethylhexoxide).

[0052] Examples of the inorganic metal compound include aluminum chloride, aluminum bromide, aluminum iodide, and titanium iodide.

[0053] In the case where the metal element(s) in the bath liquid 2 is supplied from a metal alkoxide and/or an inorganic metal compound, no particular limitation is imposed on the metal element concentration of the bath liquid 2. In this case, from the viewpoint of forming a satisfactory film 3, the metal element concentration of the bath liquid 2 is preferably 1 ppm or greater and 100 ppm or less, more preferably 3 ppm or greater and 10 ppm or less, further preferably 4 ppm or greater and 6 ppm or less. Notably, "ppm" means "parts per million" and "mg/L." Notably, in the case where the bath liquid 2 contains a plurality of metal elements, the above-described metal element concentration means the total concentration with respect to the plurality of metal elements. The metal element concentration of the bath liquid 2 can be measured by ICP-MS analysis.

(1.3) Halogen element

[0054] The bath liquid 2 contains at least one or more types of halogen elements. Since the bath liquid 2 contains a halogen element(s), film formation is performed at a practical speed, and the film 3 is likely to become homogeneous. No particular limitation is imposed on the halogen element. From the viewpoint of enabling prompt progress of organic electrochemical reactions and causing the film 3 to function as a high quality protection film for the substrate 5, the halogen element(s) is preferably at least one or more halogen elements selected from the group consisting of Cl (chlorine), Br (bromine), and I (iodine).

[0055] No particular limitation is imposed on the halogen element concentration of the bath liquid 2. From the viewpoint of moderately reducing reaction speed, being advantageous for control of the homogeneity and thickness of the film 3, and preventing separation of the film 3, the halogen element concentration of the bath liquid 2 is preferably 1 ppm or greater and 20000 ppm or less, more preferably 5 ppm or greater and 2000 ppm or less, further preferably 10 ppm or greater and 100 ppm or less. Notably, "ppm" means "parts per million" and "mg/L." The halogen element concentration of the bath liquid 2 can be obtained from the amount of a halogen element(s) added at the time of making-up of the electrolytic bath or by ICP-MS analysis.

(1.4) Organic solvent

[0056] Since an organic solvent is used as the solvent of the bath liquid 2, generation of gas and oxidation of the substrate 5 itself during film formation are suppressed. From the viewpoint of satisfactory formation of the film 3, the solvent preferably contains at least one or more types of solvents selected from the group consisting of ketones and nitriles. In the case where the solvent contains a ketone and/or a nitrile, it is supposed that a condensation reaction occurs on the electrode surface (cathode surface) and electrodeposition becomes possible. Also, in the case where the solvent contains a ketone, conceivably, ketoenol tautomerism occurs in the presence of halogen, and the reactivity of the bath liquid 2 is enhanced.

(1.4.1) Ketone

[0057] No particular limitation is imposed on the ketone so long as the ketone is an organic solvent having a carbonyl group (-C(=O)-) other than ester bond.

[0058] Examples of the ketone include acetone, methyl ethyl ketone (MEK), 1-hexanone, 2-hexanone, 4-heptanone, 2-heptanone (methyl amyl ketone), 1-octanone, 2-octanone, 1-nonanone, 2-nonanone, diisobutyl ketone, methyl isobutyl ketone, acetylacetone, acetonylacetone, phenylacetone, acetophenone, methyl naphthyl ketone, cyclohexanone (CHN), and methylcyclohexanone. Among these, acetone and methyl ethyl ketone are preferred, because the film 3 is formed particularly satisfactorily.

(1.4.2) Nitrile

[0059] Nitrile is an organic solvent which contains a nitrile group (-CN) in its structure. Examples of the nitrile include acetonitrile, propionitrile, valeronitrile, and butyronitrile. Among these, acetonitrile is preferred, because the film 3 is formed particularly satisfactorily.

(2) Substrate 5

[0060] As to the "substrate 5," the description in the column entitled "(1) Substrate 5" in the above-described section entitled "1. Coated substrate 1" is applied as it is.

(3) Voltage application

[0061] By applying a voltage to the substrate 5 immersed in the bath liquid 2, a film 3 is formed on the substrate 5, which serves as the negative electrode 7. Specifically, the positive electrode 6 and the negative electrode 7 (the substrate 5) are immersed into the bath liquid 2, and a potential gradient is generated between the two electrodes.

[0062] Any of known electrically conductive substrates may be used as the positive electrode 6. In the case where the metal element(s) in the bath liquid 2 is supplied as a result of elution of the positive electrode 6, at least one or more types of electrodes selected from an electrode of Al, an electrode of Ti, and an electrode of Mo are preferably used as the positive electrode 6. No particular limitation is imposed on the shape, thickness, size, etc. of the positive electrode 6. The positive electrode 6 may be foil like, plate like, foam like, nonwoven fabric like, mesh like, felt like, or expanded metal like.

[0063] The positive electrode 6 and the negative electrode 7 are preferably disposed to face each other.

[0064] The positive electrode 6 and the negative electrode 7 are connected to a DC power supply, which can generate a potential gradient between the positive electrode 6 and the negative electrode 7.

[0065] For generation of a potential gradient between the positive electrode 6 and the negative electrode 7, in a state in which the positive electrode 6 and the negative electrode 7 are immersed in the bath liquid 2, a voltage (for example, constant voltage) is applied to the positive electrode 6 and the negative electrode 7 by the power supply connected to the positive electrode 6 and the negative electrode 7.

[0066] From the viewpoint of performing film formation at a practical speed, in the case where a constant voltage is applied, the potential gradient generated between the two electrodes is preferably 10 V or higher and 300 V or lower, more preferably 20 V or higher and 100 V or lower, further preferably 60 V or higher and 80 V or lower.

[0067] No particular limitation is imposed on an application time during which the volage is applied. The application time is, for example, preferably 10 seconds or longer and 300 seconds or shorter, more preferably 30 seconds or longer and 240 seconds or shorter, further preferably 60 seconds or longer and 180 seconds or shorter.

[0068] Notably, the voltage is not required to be a constant voltage and the magnitude of the voltage may be changed.

(4) Treatment process after film formation

[0069] After formation of the film 3, the amount of carbon in the film 3 may be reduced by means of heat treatment and/or light irradiation. By reducing the amount of carbon in the film 3 by means of heat treatment and/or light irradiation, it is possible to control the purity of the film 3 as an inorganic oxide film.

[0070] No particular limitation is imposed on the treatment temperature of the heat treatment. From the viewpoint of efficiently reducing the amount of carbon, the treatment temperature is preferably 100°C or higher and 1000°C or lower, more preferably 300°C or higher and 800°C or lower, further preferably 500°C or higher and 600°C or lower.

[0071] No particular limitation is imposed on the treatment time of the heat treatment. From the viewpoint of efficiently reducing the amount of carbon, the treatment time is preferably 1 minute or longer and 60 minutes or shorter, more preferably 5 minutes or longer and 45 minutes or shorter, further preferably 10 minutes or longer and 30 minutes or shorter.

[0072] No particular limitation is imposed on the wavelength of light used for light irradiation. From the viewpoint of efficiently reducing the amount of carbon, the wavelength of light is preferably 250 nm or longer and 1100 nm or shorter, more preferably 300 nm or longer and 800 nm or shorter, further preferably 400 nm or longer and 500 nm or shorter.

[0073] No particular limitation is imposed on the light irradiation time. From the viewpoint of efficiently reducing the amount of carbon, the light irradiation time is preferably 3 seconds or longer and 120 seconds or shorter, more preferably 5 seconds or longer and 60 seconds or shorter, further preferably 10 seconds or longer and 30 seconds or shorter.

[0074] Notably, reduction of the amount of carbon in the film 3 can be confirmed by XPS analysis.

3. Action and effects of coated substrate 1 of present embodiment

[0075] The coated substrate 1 of the present embodiment is excellent in functionality and/or durability, because the films 3 on the edge region S1 and the convex portion present region S3, which are likely to come into contact, in particular, with a surrounding environment when the coated substrate 1 is used, are selectively formed to be thicker.

[0076] According to the present embodiment, there is provided the novel coated substrate 1 which can be applied to various fields and can be mass produced.

[0077] The coated substrate 1 of the present embodiment can be formed without use of an expensive material or by using only a small amount of an expensive material. Therefore, the coated substrate 1 is advantageous in terms of cost.

[0078] Also, in the coated substrate 1 of the present embodiment, since post treatments, such as heat treatment and light irradiation, are not necessarily needed for formation of the film 3, it is possible to expand the choices of the material and shape of the substrate 5.

EXAMPLES

[0079] The present disclosure will be described further specifically by means of example.

[0080] Notably, in the following description, measurement conditions of XPS (x-ray photoelectron spectroscopy) are as follows.

[Measurement conditions]

[0081]

X-ray beam diameter: 100 μmΦ
Signal reception angle: 45.0°
Path energy: 140 eV
Ar etching for 30 seconds (etching rate: 10 nm/min corresponding to SiO_2)

1. Examples in which a metal element(s) is supplied into the bath liquid 2 as a result of elution of the positive electrode 6

(1) Example 1 (solvent: MEK, positive electrode 6: aluminum)

[0082] The film formation apparatus 11 shown in FIG. 3 was used. An aluminum wire was used as the positive electrode 6. A stainless plate was used as the negative electrode 7. The negative electrode 7 is a substrate 5 on which a film 3 is to be formed. Methyl ethyl ketone (MEK) was used as the solvent of the bath liquid 2. Iodine (halogen) was dissolved in the bath liquid 2 at a concentration of 600 ppm.

[0083] In a state in which the positive electrode 6 and the negative electrode 7 were immersed in the bath liquid 2, a voltage of 80 V was applied between the positive electrode 6 and the negative electrode 7 for three minutes.

[0084] Observation of a cross section of the negative electrode 7 under an FIB-SEM (focused ion beam scanning electron microscope) revealed that, as shown in FIG. 2, a film 3 of 700 nm was formed on the surface of the substrate 5. Analysis performed after Ar etching by XPS for 30 seconds revealed that the film 3 is aluminum oxide.

[0085] The percent element composition of carbon in the film 3 was 5.8 atm%, and the total percent element composition of aluminum and oxygen was 93.9 atm%.

[0086] The percent element composition of iodine in this film 3 was less than 0.1 atm% (lower measurement limit).

[0087] Since no crystal grain was observed in a TEM image of a cross section of the film 3 obtained by cutting the film 3 in the film-thickness direction, it was confirmed that the film 3 is amorphous.

[0088] The relative density of the film 3 determined by the following method was 100%.

[0089] Specifically, the relative density of the film 3 was determined as follows. A TEM image was obtained from a cross section of the film 3 obtained by cutting the film 3 in the film-thickness direction. The area of pores was measured in a field of view of 300 nm (vertical dimension) × 1000 nm (horizontal dimension). The relative density (%) was obtained in accordance with the following expression (1). The average of the relative densities of 10 fields of view is the relative density of the film 3. Notably, in the case where the thickness of the film 3 is smaller than the vertical size of 300 nm, measurement is performed in fields of view determined in accordance with the thickness of the film 3.

$$\text{Relative density (\%)} = \{(S1 - S2)/S1\} \times 100 \qquad (1)$$

(In the expression, S1 is the area (nm^2) of the field of view of 300 nm (vertical dimension) × 1000 nm (horizontal dimension), and S2 is the total area (nm^2) of pores in the field of view of 300 nm (vertical dimension) × 1000 nm (horizontal dimension))

(2) Example 2 (solvent: acetone, positive electrode 6: aluminum)

[0090] Acetone was used as the solvent of the bath liquid 2. Iodine (halogen) was dissolved in the bath liquid 2 at a concentration of 14 ppm. An experiment was carried out under the same conditions as Example 1, except for the above described points. Observation of a cross section of the negative electrode 7 under the FIB-SEM revealed that a film 3 of 130 nm was formed on the surface of the substrate 5. Analysis by means of XPS revealed that the film 3 is aluminum oxide.

[0091] The percent element composition of carbon in the film 3 was 6.5 atm%, and the total percent element composition of aluminum and oxygen was 93.3 atm%.

[0092] The percent element composition of iodine in this film 3 was 0.1 atm%.

[0093] Since no crystal grain was observed in a TEM image of a cross section of the film 3 obtained by cutting the film 3 in the film-thickness direction, it was confirmed that the film 3 is amorphous.

[0094] The relative density of the film 3 determined by the above-described method was 100%.

(3) Example 3 (solvent: MEK, positive electrode 6: titanium)

[0095] A titanium wire was used as the positive electrode 6. An experiment was carried out under the same conditions as Example 1, except for the above described point. Observation of a cross section of the negative electrode 7 under the FIB-SEM revealed that a film 3 of 90 nm was formed on the surface of the substrate 5. Analysis by means of XPS revealed that the film 3 is titanium oxide.

[0096] The percent element composition of carbon in the film 3 was 24.6 atm%, and the total percent element composition of titanium and oxygen was 78.7 atm%.

[0097] The percent element composition of iodine in this film 3 was 0.3 atm%.

[0098] Since no crystal grain was observed in a TEM image of a cross section of the film 3 obtained by cutting the film 3 in the film-thickness direction, it was confirmed that the film 3 is amorphous.

[0099] The relative density of the film 3 determined by the above-described method was 100%.

(4) Example 4 (solvent: acetone, positive electrode 6: titanium)

[0100] Acetone was used as the solvent of the bath liquid 2. Iodine (halogen) was dissolved in the bath liquid 2 at a concentration of 2400 ppm. An experiment was carried out under the same conditions as Example 3, except for the above described points. Observation of a cross section of the negative electrode 7 under the FIB-SEM revealed that a film 3 of 500 nm was formed on the surface of the substrate 5. Analysis by means of XPS revealed that the film 3 is titanium oxide.

[0101] The percent element composition of carbon in the film 3 was 9.2 atm%, and the total percent element composition of titanium and oxygen was 83.7 atm%.

[0102] The percent element composition of iodine in this film 3 was 0.4 atm%.

[0103] Since no crystal grain was observed in a TEM image of a cross section of the film 3 obtained by cutting the film 3 in the film-thickness direction, it was confirmed that the film 3 is amorphous.

[0104] The relative density of the film 3 determined by the above-described method was 100%.

(5) Example 5 (solvent: MEK, positive electrode 6: molybdenum)

[0105] A molybdenum wire was used as the positive electrode 6. An experiment was carried out under the same conditions as Example 1, except for the above described point. Observation of a cross section of the negative electrode 7 under the FIB-SEM revealed that a film 3 of 160 nm was formed on the surface of the substrate 5. Analysis by means of XPS revealed that the film 3 is molybdenum oxide.

[0106] The percent element composition of carbon in the film 3 was 14.8 atm%, and the total percent element composition of molybdenum and oxygen was 78.7 atm%.

[0107] The percent element composition of iodine in this film 3 was less than 0.1 atm% (detection limit or lower).

[0108] Since no crystal grain was observed in a TEM image of a cross section of the film 3 obtained by cutting the film 3 in the film-thickness direction, it was confirmed that the film 3 is amorphous.

[0109] The relative density of the film 3 determined by the above-described method was 100%.

(6) Example 6 (solvent: acetone, positive electrode 6: molybdenum)

[0110] Acetone was used as the solvent of the bath liquid 2. Iodine (halogen) was dissolved in the bath liquid 2 at a concentration of 2400 ppm. An experiment was carried out under the same conditions as Example 5, except for the above described points. Observation of a cross section of the negative electrode 7 under the FIB-SEM revealed that a film 3 of 480 nm was formed on the surface of the substrate 5. Analysis by means of XPS revealed that the film 3 is molybdenum oxide.

[0111] The percent element composition of carbon in the film 3 was 12.7 atm%, and the total percent element composition of molybdenum and oxygen was 78.0 atm%.

[0112] The percent element composition of iodine in this film 3 was less than 0.1 atm% (detection limit or lower).

[0113] Since no crystal grain was observed in a TEM image of a cross section of the film 3 obtained by cutting the film 3 in the film-thickness direction, it was confirmed that the film 3 is amorphous.

[0114] The relative density of the film 3 determined by the above-described method was 100%.

(7) Example 7 (solvent: acetonitrile, positive electrode 6: aluminum)

[0115] Acetonitrile was used as the solvent of the bath liquid 2. Iodine (halogen) was dissolved in the bath liquid 2 at a concentration of 2400 ppm. An experiment was carried out under the same conditions as Example 1, except for the above described points. Observation of a cross section of the negative electrode 7 under the FIB-SEM revealed that a film 3 of 140 nm was formed on the surface of the substrate 5. Analysis by means of XPS revealed that the film 3 is aluminum oxide. Oxygen which was not present in the bath liquid 2 was present in the film 3. It is supposed that oxygen was originated from water contained in the bath liquid 2 or moisture absorbed from the atmosphere.

[0116] The percent element composition of carbon in the film 3 was 9.8 atm%, and the total percent element composition of aluminum and oxygen was 90.1 atm%.

[0117] The percent element composition of iodine in this film 3 was 0.1 atm%.

[0118] Since no crystal grain was observed in a TEM image of a cross section of the film 3 obtained by cutting the film 3 in the film-thickness direction, it was confirmed that the film 3 is amorphous.

[0119] The relative density of the film 3 determined by the above-described method was 100%.

(8) Observation of films 3 in Examples 1 to 7 under FIB-SEM

[0120] Cross sections of the films 3 formed in Examples 1 to 7 were observed under the FIB-SEM. In each of Examples 1 to 7, the maximum thickness T1max of the film 3 formed on the edge region S1 of a surface S of the substrate 5 was greater than the thickness T2 of the film 3 formed on the inner region S2 of the surface S located inward of the edge region S1.

[0121] In each of Examples 1 to 7, the maximum thickness T1max of the film 3 formed on the edge region 1 was greater than the thickness T2 of the film 3 formed on the inner region S2 by 10% or more of the thickness T2.

[0122] In each of Examples 1 to 7, the thickness T of the film 3 decreased toward the inner region S2 from a position where the film 3 formed on the edge region S1 had the maximum thickness T1max.

2. Examples in which a metal element(s) is supplied into the bath liquid from metal alkoxide

(1) Example 8 (solvent: acetone, metal alkoxide: aluminum triisopropoxide)

[0123] The film formation apparatus 11 shown in FIG. 3 was used. A carbon electrode was used as the positive electrode 6. A stainless plate was used as the negative electrode 7. The negative electrode 7 is a substrate 5 forming a film 3 on the surface S. Acetone was used as the solvent of the bath liquid 2.

[0124] Aluminum triisopropoxide was dissolved in the bath liquid 2 at a concentration of 16 mg/L (16 ppm), and iodine (halogen) was dissolved in the bath liquid 2 at a concentration of 2400 mg/L (2400 ppm).

[0125] In a state in which the positive electrode 6 and the negative electrode 7 were immersed in the bath liquid 2, a voltage of 80 V was applied between the positive electrode 6 and the negative electrode 7 for three minutes.

[0126] Observation of a cross section of the negative electrode 7 under an FIB-SEM (focused ion beam scanning electron microscope) revealed that a film 3 of 140 nm was formed on the surface of the substrate 5. Analysis by means of XPS (x-ray photoelectron spectroscopy) revealed that the film 3 is aluminum oxide.

[0127] The percent element composition of carbon in the film 3 was 8.4 atm%, and the total percent element composition of aluminum and oxygen was 84.3 atm%.

[0128] The percent element composition of iodine in this film 3 was less than 0.1 atm% (detection limit or lower).

[0129] Since no crystal grain was observed in a TEM image of a cross section of the film 3 obtained by cutting the film 3 in the film-thickness direction, it was confirmed that the film 3 is amorphous.

[0130] The relative density of the film 3 determined by the above-described method was 100%.

(2) Example 9 (solvent: MEK, metal alkoxide: aluminum triisopropoxide)

[0131] Methyl ethyl ketone (MEK) was used as the solvent of the bath liquid 2. An experiment was carried out under the same conditions as Example 8, except for the above described point. Observation of a cross section of the negative electrode 7 under the FIB-SEM revealed that a film 3 was formed on the surface S of the substrate 5. Analysis by means of XPS revealed that the film 3 is aluminum oxide.

[0132] The percent element composition of carbon in the film 3 was 8.6 atm%, and the total percent element composition of aluminum and oxygen was 83.6 atm%.

[0133] The percent element composition of iodine in this film 3 was less than 0.1 atm% (detection limit or lower).

[0134] Since no crystal grain was observed in a TEM image of a cross section of the film 3 obtained by cutting the film 3 in the film-thickness direction, it was confirmed that the film 3 is amorphous.

[0135] The relative density of the film 3 determined by the above-described method was 100%.

(3) Example 10 (solvent : acetone, metal alkoxide: titanium tetraisopropoxide)

[0136] In place of aluminum triisopropoxide, titanium tetraisopropoxide was used. An experiment was carried out under the same conditions as Example 8, except for the above described point. Observation of a cross section of the negative electrode 7 under the FIB-SEM revealed that a film 3 was formed on the surface S of the substrate 5. Analysis by means of XPS revealed that the film 3 is titanium oxide.

[0137] The percent element composition of carbon in the film 3 was 8.8 atm%, and the total percent element composition of titanium and oxygen was 86.1 atm%.

[0138] The percent element composition of iodine in this film 3 was 1.3 atm%.

[0139] Since no crystal grain was observed in a TEM image of a cross section of the film 3 obtained by cutting the film 3 in the film-thickness direction, it was confirmed that the film 3 is amorphous.

[0140] The relative density of the film 3 determined by the above-described method was 100%.

(4) Example 11 (solvent : acetone, metal alkoxide: titanium tetra-n-propoxide)

[0141] In place of aluminum triisopropoxide, titanium tetra-n-propoxide was used. An experiment was carried out under the same conditions as Example 8, except for the above described point. Observation of a cross section of the negative electrode 7 under the FIB-SEM revealed that a film 3 was formed on the surface S of the substrate 5. Analysis by means of XPS revealed that the film 3 is titanium oxide.

[0142] The percent element composition of carbon in the film 3 was 9.5 atm%, and the total percent element composition of titanium and oxygen was 85.9 atm%.

[0143] The percent element composition of iodine in this film 3 was 0.9 atm%.

[0144] Since no crystal grain was observed in a TEM image of a cross section of the film 3 obtained by cutting the film 3 in the film-thickness direction, it was confirmed that the film 3 is amorphous.

[0145] The relative density of the film 3 determined by the above-described method was 100%.

(5) Observation of films 3 in Examples 8 to 11 under FIB-SEM

[0146] Cross sections of the films 3 formed in Examples 8 to 11 were observed under the FIB-SEM. In each of Examples 8 to 11, the maximum thickness T1max of the film 3 formed on the edge region S1 of a surface S of the substrate 5 was greater than the thickness T2 of the film 3 formed on the inner region S2 of the surface S located inward of the edge region S1.

[0147] In each of Examples 8 to 11, the maximum thickness T1max of the film 3 formed on the edge region S1 was greater than the thickness T2 of the film 3 formed on the inner region S2 by 10% or more of the thickness T2.

[0148] In each of Examples 8 to 11, the thickness T of the film 3 decreased toward the inner region S2 from a position where the film 3 formed on the edge region S1 had the maximum thickness T1max.

3. Analysis of film 3 by FT-IR

[0149] The films 3 formed in Examples 1, 2, 3, and 7 were analyzed by FT-IR. The measurement conditions are as follows.

Measurement method: One-time reflection ATR method
Scanning times: 64 times
Resolution: 4 cm^{-1}
Aperture: 150 μm

[0150] In each of the films 3, a peak which is conceivably attributed to C-H stretching was detected in the range of 3000 cm^{-1} to 2800 cm^{-1}.

4. Analysis of films 3 by XPS

[0151] The films 3 formed in Examples 1, 2, and 3 were analyzed by XPS. In each of the films 3, C=O bond and C-O bond were detected.

5. Difference in film formation speed among different types of solvents

[0152] The relation between electrodeposition time and deposition weight was investigated for different types of solvents.

[0153] The film formation apparatus 11 shown in FIG. 1 was used. An aluminum wire was used as the positive electrode 6. A stainless plate was used as the negative electrode 7. The negative electrode 7 serves as a substrate 5 forming a film 3 on the surface S. Various types of solvents such as acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone, and diisobutyl ketone were used as solvents of bath liquids 2. Iodine (halogen) was dissolved in each bath liquid 2 at a concentration of 2100 mg/L (2100 ppm).

[0154] In a state in which the positive electrode 6 and the negative electrode 7 were immersed in the bath liquid 2, a voltage of 80 V was applied between the positive electrode 6 and the negative electrode 7 for one to three minutes.

[0155] The graph of FIG. 4 shows the relation between application time (electrodeposition time) and deposition weight (deposition mass) for cases where the respective solvents were used. The deposition weight is the weight of the formed film.

[0156] It was confirmed from the graph of FIG. 4 that, as the electrodeposition time increases, the deposition weight increases. Also, it was confirmed from the graph of FIG. 4 that the smaller the number of carbon atoms of a hydrocarbon group of the solvent, the higher the deposition speed.

6. Relation between metal element concentration of bath liquid 2 and adhesiveness of film

[0157] A first sample (coated substrate 1) was produced in the same manner as in Example 1. After having pulled out the first sample from the bath liquid 2, a new stainless plate was immersed into the bath liquid 2, and a voltage was applied in the same manner as in Example 1, thereby producing a second sample. In the same manner, third and fourth samples were produced. When each sample was pulled out from the bath liquid 2, a portion of the bath liquid 2 was sampled, and the aluminum element concentration was measured by ICP-MS.

[0158] The graph of FIG. 5 shows the relation between the number of samples experimentally produced and the aluminum element concentration of the bath liquid 2. It was found from the graph of FIG. 5 that the aluminum element concentration tends to increase with the number of samples experimentally produced. In the fourth sample, the film 3 tended to separate from the substrate 5. Therefore, it was found that, for continuous production of samples, the aluminum element concentration is preferably 1 ppm or greater and 6 ppm or less.

7. Relation between halogen element concentration of the bath liquid 2 and adhesiveness of film

[0159] The film formation apparatus 11 shown in FIG. 3 was used. An aluminum wire was used as the positive electrode 6. A stainless plate was used as the negative electrode 7. The negative electrode 7 serves as a substrate 5 forming a film 3 on the surface S. Various types of solvents (i.e., acetone and methyl ethyl ketone (MEK)) were used as solvents of bath liquids 2. Iodine (halogen) was dissolved in the bath liquids 2 in amounts shown Table 1.

[0160] In a state in which the positive electrode 6 and the negative electrode 7 were immersed in the bath liquid 2, a voltage of 80 V was applied between the positive electrode 6 and the negative electrode 7 for three minutes, thereby producing a first sample (coated substrate 1). After having pulled out the first sample from the bath liquid 2, a new stainless plate was immersed into the bath liquid 2, and a voltage was applied in the same manner as in the case of the first sample, thereby producing a second sample. In the same manner, a third sample and subsequent samples were continuously produced.

[0161] The results are shown in Table 1. The evaluations in Table 1 are as follows.

A: The film 3 was formed. Adhesion between the film 3 and the substrate 5 was satisfactory.
B: The film 3 was formed. Adhesion between the film 3 and the substrate 5 was somewhat poor, and the film 3 tended to separate.

[0162] The results of Table 1 demonstrate that formation of the film 3 was possible irrespective of the iodine concentration. It was confirmed that, from the viewpoint of preventing separation of the film 3, the iodine concentration is preferably 0.001 g/L or greater and 0.10 g/L or less (1 mg/L or greater and 100 mg/L or less = 1 ppm or greater and 100 ppm or less).

Table 1

Solvent	Amount of iodine (g/L)	Film formation state				
		First sample	Second sample	Third sample	Fourth sample	Fiftieth sample
Acetone	0.014	A	A	A	A	A
	0.14	A	A	B	B	-
	0.6	A	B	B	B	-
	1.2	A	A	B	B	-
	2.4	A	A	A	B	-
MEK	0.014	A	A	A	A	A
	0.6	A	A	A	B	-
	1.2	A	A	A	B	-
	2.4	A	B	B	B	-

8. Study on type of substrate 5

[0163] Formation of the film 3 was attempted for cases where various types of substrates 5 were use. Instead of the stainless plate used as the negative electrode 7 in Example 1, a permalloy plate, a titanium plate, a copper plate, and a carbon plate were used, respectively. Experiments were carried out under the same conditions as in Example 1 except for the above-described point.

[0164] The film 3 was stably formed on each of the substrates 5. Therefore, it was confirmed that stable formation of the film 3 is possible irrespective of the type of the substrate 5.

9. Effects of Examples

[0165] According to the present examples, novel coated substrates 1 which can be applied to various fields and can be mass-produced are provided.

[0166] The present invention is not limited to the embodiment described in detail above and various modifications and changes are possible within the range shown in the claims of the present invention.

(Additional note)

[0167] The following inventions are contained in the present specification.

[1] A coated substrate in which a substrate is coated with a film, wherein

the thickness of the film is 1 nm or greater and less than 800 nm,
x-ray photoelectron spectroscopic measurement of the film shows that the total percent element composition of a metal element and O (oxygen) is 70 atm% or greater,
the relative density of the film is 90% or greater, and
at least one of the following conditions (1) and (2) is satisfied;
condition (1): the maximum thickness of the film formed on an edge region of a surface of the substrate is greater than the thickness of the film formed on an inner region of the surface located inward of the edge region, and
condition (2): the maximum thickness of the film formed on a convex portion present region of the surface of the substrate is greater than the thickness of the film formed on a convex portion absent region of the surface.

[2] The coated substrate recited in [1], wherein a portion of the substrate where the film is formed is electrically conductive.
[3] The coated substrate recited in [1] or [2], wherein the x-ray photoelectron spectroscopic measurement of the film shows that the percent element composition of C (carbon) is 0.1 atm% or greater and less than 20 atm%.
[4] The coated substrate recited in any one of [1] to [3], wherein the film is amorphous.
[5] The coated substrate recited in any one of [1] to [4], wherein the condition (1) is such that the maximum thickness of the film formed on the edge region is greater than the thickness of the film formed on the inner region by 10% or more of

the thickness of the film formed on the inner region.

[6] The coated substrate recited in any one of [1] to [5], wherein the condition (2) is such that the maximum thickness of the film formed on the convex portion present region is greater than the thickness of the film formed on the convex portion absent region by 10% or more of the thickness of the film formed on the convex portion absent region.

[7] The coated substrate recited in any one of [1] to [6], wherein the condition (1) is such that the thickness of the film decreases toward the inner region from a position where the film formed on the edge region has the maximum thickness.

[8] The coated substrate recited in any one of [1] to [7], wherein the condition (2) is such that the thickness of the film decreases toward the convex portion absent region from a position where the film formed on the convex portion present region has the maximum thickness.

[9] The coated substrate recited in any one of [1] to [8], wherein the metal element is at least one or more metal elements selected from the group consisting of Al (aluminum), Ti (titanium), Mo (molybdenum), Cr (chromium), Mn (manganese), Fe (iron), Co (cobalt), Ni (nickel), Zr (zirconium), V (vanadium), W (tungsten), Ta (tantalum), Nb (niobium), and Sn (tin).

REFERENCE SIGNS LIST

[0168]

1: coated substrate
2: bath liquid
3: film
5: sub strate
6: positive electrode
7: negative electrode
11: film formation apparatus
12: convex portion
S: surface
S1: edge region
S2: inner region
S3: convex portion present region
S4: convex portion absent region
SE: end portion
T: thickness
T1: thickness
T1max: maximum thickness
T2: thickness
T3: thickness
T3max: maximum thickness
T4: thickness
h: maximum height

Claims

1. A coated substrate in which a substrate is coated with a film, wherein

the thickness of the film is 1 nm or greater and less than 800 nm,
x-ray photoelectron spectroscopic measurement of the film shows that the total percent element composition of a metal element and O (oxygen) is 70 atm% or greater,
the relative density of the film is 90% or greater, and
at least one of the following conditions (1) and (2) is satisfied;
condition (1): the maximum thickness of the film formed on an edge region of a surface of the substrate is greater than the thickness of the film formed on an inner region of the surface located inward of the edge region, and
condition (2): the maximum thickness of the film formed on a convex portion present region of the surface of the substrate is greater than the thickness of the film formed on a convex portion absent region of the surface.

2. A coated substrate according to claim 1, wherein a portion of the substrate where the film is formed is electrically conductive.

3. A coated substrate according to claim 1 or 2, wherein the x-ray photoelectron spectroscopic measurement of the film shows that the percent element composition of C (carbon) is 0.1 atm% or greater and less than 20 atm%.

4. A coated substrate according to claim 1 or 2, wherein the film is amorphous.

5. A coated substrate according to claim 1 or 2, wherein the condition (1) is such that the maximum thickness of the film formed on the edge region is greater than the thickness of the film formed on the inner region by 10% or more of the thickness of the film formed on the inner region.

6. A coated substrate according to claim 1 or 2, wherein the condition (2) is such that the maximum thickness of the film formed on the convex portion present region is greater than the thickness of the film formed on the convex portion absent region by 10% or more of the thickness of the film formed on the convex portion absent region.

7. A coated substrate according to claim 1 or 2, wherein the condition (1) is such that the thickness of the film decreases toward the inner region from a position where the film formed on the edge region has the maximum thickness.

8. A coated substrate according to claim 1 or 2, wherein the condition (2) is such that the thickness of the film decreases toward the convex portion absent region from a position where the film formed on the convex portion present region has the maximum thickness.

9. A coated substrate according to claim 1 or 2, wherein the metal element is at least one or more metal elements selected from the group consisting of Al (aluminum), Ti (titanium), Mo (molybdenum), Cr (chromium), Mn (manganese), Fe (iron), Co (cobalt), Ni (nickel), Zr (zirconium), V (vanadium), W (tungsten), Ta (tantalum), Nb (niobium), and Sn (tin).

FIG. 1

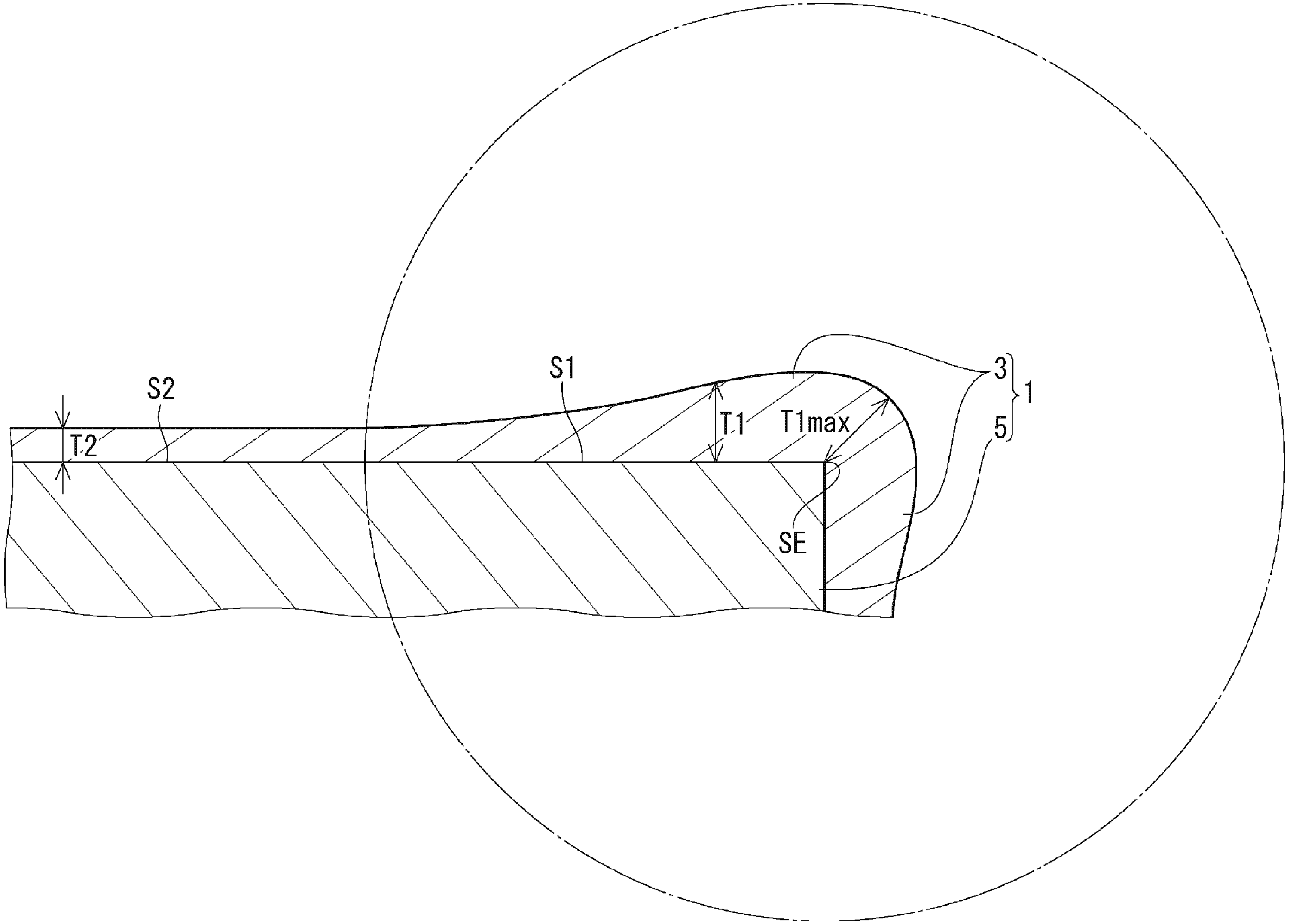


FIG. 2

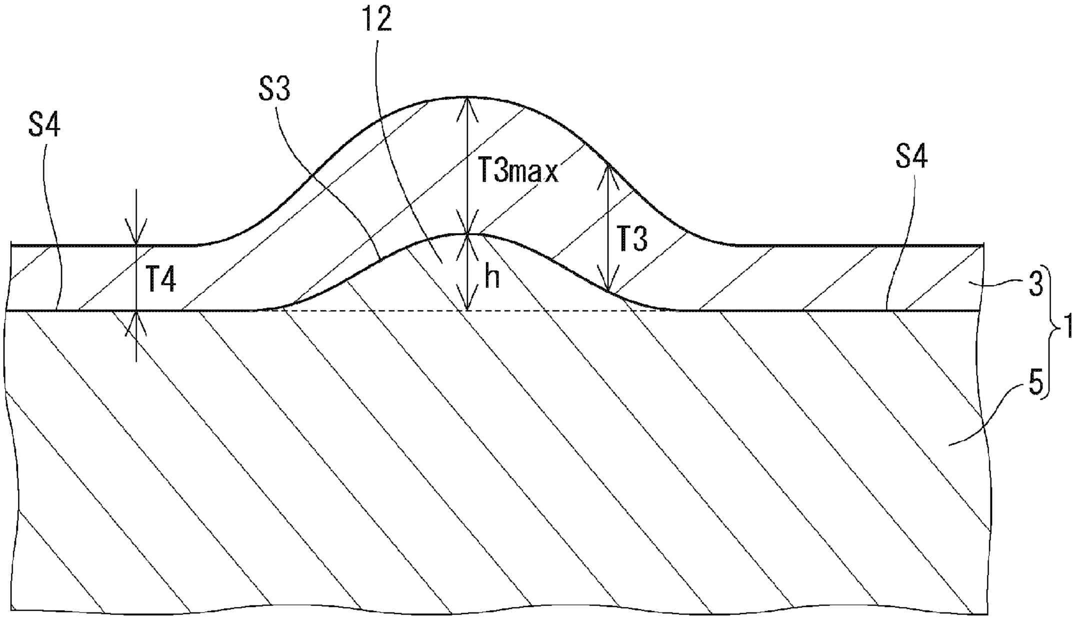


FIG. 3

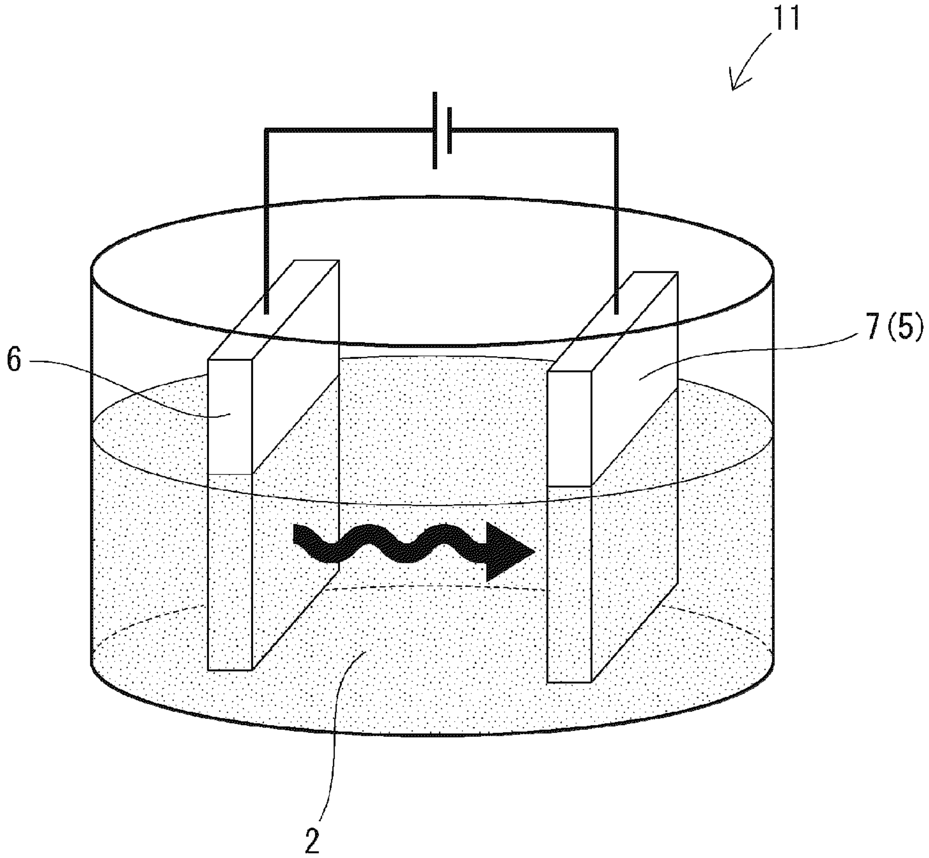
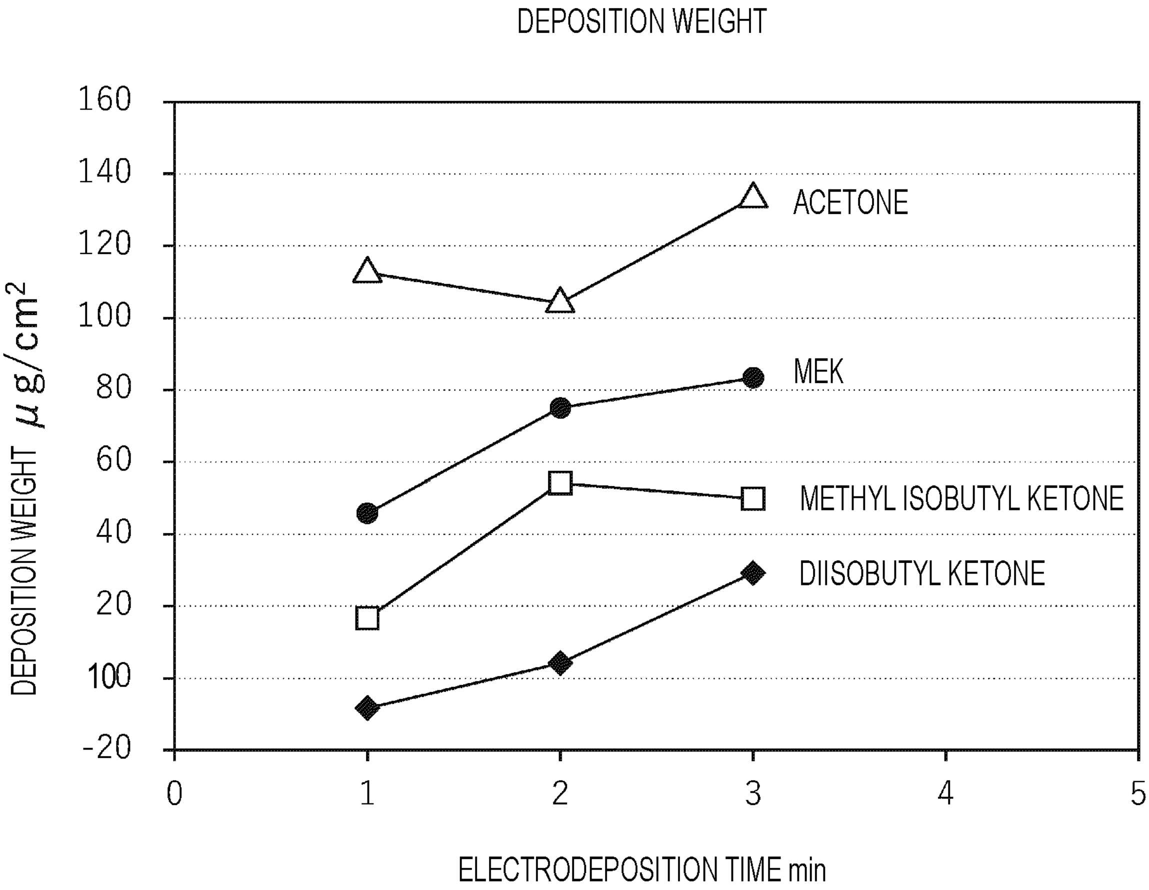


FIG. 4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DEPOSITION WEIGHT μg/cm²
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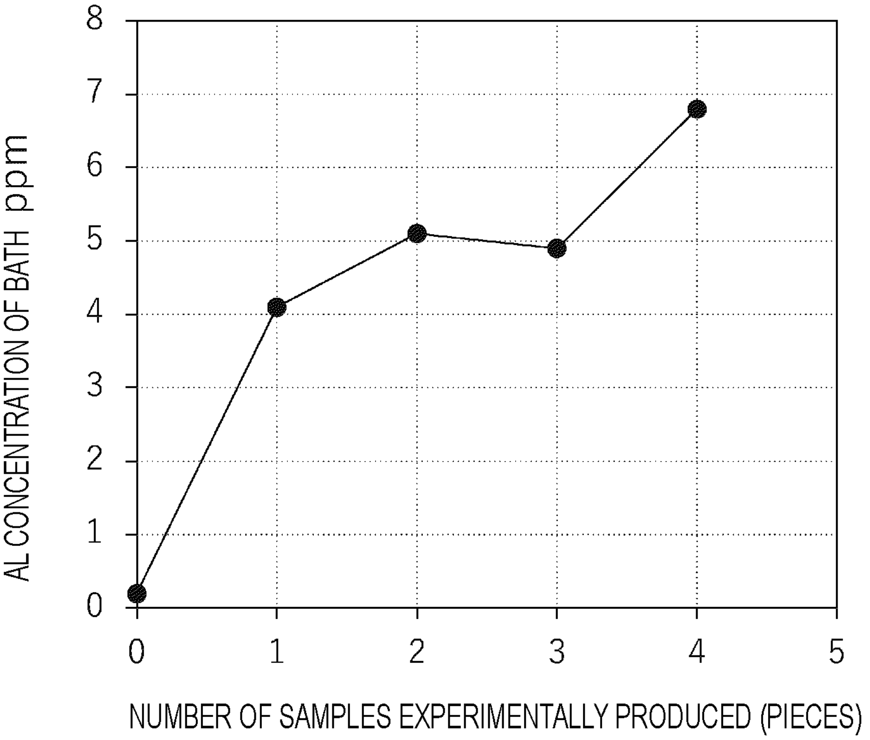
140
120
100
80
60
40
20
100
-20
0
1
2
3
4
5
ELECTRODEPOSITION TIME min
ACETONE
MEK
METHYL ISOBUTYL KETONE
DIISOBUTYL KETONE

FIG. 5


AL CONCENTRATION OF BATH ppm
8
7
6
5
4
3
2
1
0
0
1
2
3
4
5
NUMBER OF SAMPLES EXPERIMENTALLY PRODUCED (PIECES)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2023/026615

A. CLASSIFICATION OF SUBJECT MATTER

C25D 9/08(2006.01)i; ***C23C 26/00***(2006.01)i
FI: C25D9/08; C23C26/00 C

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C25D9/08; C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2023
Registered utility model specifications of Japan 1996-2023
Published registered utility model applications of Japan 1994-2023

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2020-006487 A (MITSUBISHI MATERIALS CORP.) 16 January 2020 (2020-01-16) claims, paragraphs [0033]-[0048], fig. 1	1-9
Y	JP 11-264066 A (HITACHI TOOL ENGINEERING, LTD.) 28 September 1999 (1999-09-28) paragraphs [0006]-[0008], [0013]-[0018], fig. 1	1-9
Y	JP 02-048103 A (SUMITOMO ELECTRIC INDUSTRIES, LTD.) 16 February 1990 (1990-02-16) p. 2, upper left column, line 14 to upper right column, line 19, fig. 1-3	1-9
Y	US 2014/0178659 A1 (WU SHANGHUA) 26 June 2014 (2014-06-26) paragraphs [0050]-[0054], [0075]-[0083], fig. 2	2-9
A	JP 2000-117509 A (MITSUBISHI MATERIALS CORP.) 25 April 2000 (2000-04-25) paragraphs [0004]-[0007]	1-9
A	JP 2012-233223 A (UNIVERISTY OF WASEDA) 29 November 2012 (2012-11-29) paragraphs [0014]-[0039], fig. 3	1-9

☑ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

* Special categories of cited documents:

"A"	document defining the general state of the art which is not considered to be of particular relevance
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"P"	document published prior to the international filing date but later than the priority date claimed
"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&"	document member of the same patent family

Date of the actual completion of the international search
14 September 2023

Date of mailing of the international search report
26 September 2023

Name and mailing address of the ISA/JP

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Authorized officer

Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2023/026615

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2010-105979 A (GENERAL ELECTRIC CO.) 13 May 2010 (2010-05-13) paragraphs [0053]-[0056]	1-9

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2023/026615

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 2020-006487 A	16 January 2020	(Family: none)	
JP 11-264066 A	28 September 1999	(Family: none)	
JP 02-048103 A	16 February 1990	(Family: none)	
US 2014/0178659 A1	26 June 2014	WO 2014/101517 A1 EP 2940178 A1 CN 104302804 A	
JP 2000-117509 A	25 April 2000	(Family: none)	
JP 2012-233223 A	29 November 2012	(Family: none)	
JP 2010-105979 A	13 May 2010	(Family: none)	

Form PCT/ISA/210 (patent family annex) (January 2015)

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- JP 2009147192 A **[0004]**
- JP 2015093821 A **[0004]**
- JP H9202606 A **[0004]**