

## SPECIFICATION

### Title of the Invention

5 SURFACE-TREATED ALUMINUM MATERIAL, METHOD OF  
MANUFACTURING THE SAME, AND MEMBER FOR SEMICONDUCTOR-  
PROCESSING APPARATUS

### TECHNICAL FIELD

10 [0001] The present invention relates to a surface-treated aluminum material, a method  
of manufacturing the same, and a member for a semiconductor-manufacturing apparatus.

### BACKGROUND ART

15 [0002] Aluminum materials composed of aluminum or aluminum alloy are utilized in  
various applications. Anodized coatings are sometimes provided on the surfaces of these  
aluminum materials for purposes such as surface protection.

20 [0003] For example, a component for a substrate-processing apparatus that performs  
plasma processing on a substrate is disclosed in Patent Document 1, wherein: a coating is  
formed on the surface of the component by an anodizing process, in which the component is  
connected to an anode of a DC power supply and is immersed in a solution that contains an  
organic acid as a main component, and a semi-sealing process using boiling water is  
performed on the coating.

### PRIOR ART LITERATURE

25 Patent Documents

[0004] Patent Document 1

Japanese Laid-open Patent Publication 2008-81815

### SUMMARY OF THE INVENTION

30 PROBLEMS TO BE SOLVED BY THE INVENTION

[0005] However, the component of Patent Document 1 has the problem that, because  
pores in the anodized coating are not completely closed up, durability against corrosive gases  
and plasma is low.

[0006] Meanwhile, a method is conceivable wherein the pores in the anodized coating of the component of Patent Document 1 are completely closed up in order to increase durability against corrosive gases and plasma. However, in this situation, cracks form more readily in the anodized coating when the temperature rises, and there is a risk that debris  
5 composed of small pieces of the anodized coating will be formed. To curtail the formation of such debris, there is a demand to further increase the heat resistance of aluminum materials that comprise anodized coatings on their surfaces.

[0007] The present invention was made in view of this background, and an object of  
10 the present invention is to provide: a surface-treated aluminum material that excels in corrosion resistance with regard to corrosive gases and plasma and is capable of curtailing the formation of cracks; a method of manufacturing the same; and a member for a semiconductor-manufacturing apparatus.

## 15 MEANS FOR SOLVING THE PROBLEMS

[0008] One aspect of the present invention is a surface-treated aluminum material comprising: a base material composed of aluminum or an aluminum alloy; and  
a protective coating formed on at least a portion of a surface of the base material and containing oxides of aluminum and hydrated oxides of aluminum;  
20 wherein:  
the thickness of the protective coating is 2  $\mu\text{m}$  or more; and  
when mass percentages of elements in the protective coating are analyzed in a depth direction by glow-discharge optical-emission spectrometry, ratio  $C_H/C_{Al}$  of an integrated hydrogen atom mass percentage  $C_H$  to an integrated aluminum atom mass percentage  $C_{Al}$ , in  
25 a range extending from a surface of the protective coating to a location at a depth of 1  $\mu\text{m}$ , is 0.2 or more and 0.7 or less.

[0009] Another aspect of the present invention is a method of manufacturing the surface-treated aluminum material according to the aforementioned aspect comprising:  
30 an anodizing-process step that forms an anodized coating having fine pores on the base material by subjecting the base material to an anodizing process; and  
thereafter, a sealing step that forms the protective coating on the base material by immersing the base material in hot water to seal the pores in the anodized coating;

wherein the product of hot-water temperature  $T$  [ $^{\circ}\text{C}$ ] and immersion time  $t$  [hours] in the sealing step is greater than  $20^{\circ}\text{C}\cdot\text{hours}$  and less than  $75^{\circ}\text{C}\cdot\text{hours}$ .

## EFFECTS OF THE INVENTION

5    **[0010]**       In the aforementioned surface-treated aluminum material (hereinafter referred to as "the aluminum material"), a protective coating, which has a thickness of  $2\text{ }\mu\text{m}$  or more and contains oxides of aluminum and hydrated oxides of aluminum, is provided on a surface of the base material. In addition, when analyzed in the depth direction by glow-discharge optical-emission spectrometry, the oxides and the hydrated oxides are distributed in the  
10   protective coating such that ratio  $C_{\text{H}}/C_{\text{Al}}$  of the integrated hydrogen atom mass percentage  $C_{\text{H}}$  to the integrated aluminum atom mass percentage  $C_{\text{Al}}$  is in the above-specified range. By providing such a protective coating on the base material, the aluminum material has high corrosion resistance and can curtail the formation of cracks.

15   **[0011]**       In addition, in the method for manufacturing the aluminum material according to the aforementioned aspect, after the anodizing process has been performed on the base material to form the anodized coating, the protective coating can be formed on the base material by sealing the pores in the anodized coating under the specific conditions described above. The aluminum material can thereby easily be obtained.

20   **[0012]**       In accordance with the aforementioned aspects, as described above, a surface-treated aluminum material that excels in corrosion resistance with regard to corrosive gases and plasma and is capable of curtailing the formation of cracks, a method of manufacturing the same, and a member for a semiconductor-manufacturing apparatus can be provided.

25

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0013]**       FIG. 1 is a cross-sectional view showing the principal parts of an aluminum material according to a working example.

FIG. 2 is a cross-sectional view showing the principal parts of a base material in a state in which an anodizing-process step has been completed in a process of manufacturing the aluminum material according to the working example.

30

FIG. 3 is an explanatory diagram showing a profile, in the depth direction, of the mass percentage of hydrogen atoms in the protective coating of Test Material S1.

## MODES FOR CARRYING OUT THE INVENTION

### **[0014]** (Aluminum Material)

The material constituting the base material in the aluminum material can be selected in accordance with the application of the aluminum material, as appropriate, from the group consisting of aluminum and aluminum alloys. For example, if attempting to reduce outgassing from the aluminum material, the base material is preferably constituted from a 1000-series aluminum or a 3000-series aluminum alloy. For example, an aluminum alloy having a chemical composition that contains 1.0 mass% or more and 1.5 mass% or less of Mn (manganese) and contains one or two or more elements selected from the group consisting of Si (silicon), Fe (iron), Cu (copper), Mg, Cr (chromium), Zn (zinc), and Ti (titanium) as (an) optional component(s), with the remainder being composed of Al and unavoidable impurities, can be used as the 3000-series aluminum alloy.

**[0015]** More specifically, aluminum having a chemical composition indicated by, for example, alloy numbers AA1100, AA1100A, AA1200, AA1200A, AA1300, AA1110, AA1120, AA1230, AA1230A, AA1235, AA1435, AA1145, AA1345, AA1445, AA1150, AA1350, AA1350A, AA1450, AA1370, AA1275, AA1185, AA1285, AA1188, AA1190, AA1290, AA1193, AA1385, AA1198, or AA1199 can be used as the 1000-series aluminum constituting the base material of the aluminum material.

**[0016]** In addition, an aluminum alloy having a chemical composition indicated by, for example, the alloy numbers AA3002, AA3102, AA3003, AA3103, AA3103A, AA3103B, AA3203, AA3403, AA3004, AA3004A, AA3104, AA3204, AA3304, AA3005, AA3005A, AA3105, AA3105A, AA3105B, AA3007, AA3107, AA3207, AA3207A, AA3307, AA3009, AA3010, AA3110, AA3011, AA3012, AA3012A, AA3013, AA3014, AA3015, AA3016, AA3017, AA3019, AA3020, AA3021, AA3025, AA3026, AA3030, AA3130, or AA3065 can be used as the 3000-series aluminum alloy constituting the base material of the aluminum material.

**[0017]** In addition, if attempting to increase the strength of the aluminum material, then the base material is preferably constituted from a 5000-series aluminum alloy or a 6000-series aluminum alloy. For example, an aluminum alloy having a chemical composition that contains 0.5 mass% or more and 5.0 mass% or less of Mg (magnesium) and contains one or two or more elements selected from the group consisting of Si, Fe, Cu, Mn, Cr, Zn, and Ti as

(an) optional component(s), with the remainder being composed of Al and unavoidable impurities, can be used as the 5000-series aluminum alloy. In addition, an aluminum alloy having a chemical composition that contains, for example, 0.3 mass% or more and 1.5 mass% or less of Mg and 0.2 mass% or more and 1.2 mass% or less of Si, and contains one or two or  
5 more elements selected from the group consisting of Fe, Cu, Mn, Cr, Zn, and Ti as (an) optional component(s), with the remainder being composed of Al and unavoidable impurities, can be used as the 6000-series aluminum alloy.

**[0018]** More specifically, an aluminum alloy having a chemical composition indicated by, for example, the alloy numbers AA5182, AA5183, AA5005, AA5005A, AA5205, AA5305, AA5505, AA5605, AA5006, AA5106, AA5010, AA5110, AA5110A, AA5210, AA5310, AA5016, AA5017, AA5018, AA5018A, AA5019, AA5019A, AA5119, AA5119A, AA5021, AA5022, AA5023, AA5024, AA5026, AA5027, AA5028, AA5040, AA5140, AA5041, AA5042, AA5043, AA5049, AA5149, AA5249, AA5349, AA5449,  
15 AA5449A, AA5050, AA5050A, AA5050C, AA5150, AA5051, AA5051A, AA5151, AA5251, AA5251A, AA5351, AA5451, AA5052, AA5252, AA5352, AA5154, AA5154A, AA5154B, AA5154C, AA5254, AA5354, AA5454, AA5554, AA5654, AA5654A, AA5754, AA5854, AA5954, AA5056, AA5356, AA5356A, AA5456, AA5456A, AA5456B, AA5556, AA5556A, AA5556B, AA5556C, AA5257, AA5457, AA5557, AA5657, AA5058, AA5059,  
20 AA5070, AA5180, AA5180A, AA5082, AA5182, AA5083, AA5183, AA5183A, AA5283, AA5283A, AA5283B, AA5383, AA5483, AA5086, AA5186, AA5087, AA5187, or AA5088 can be used as the 5000-series aluminum alloy constituting the base material of the aluminum material.

**[0019]** In addition, an aluminum alloy having a chemical composition indicated by, for example, the alloy numbers AA6101, AA6101A, AA6101B, AA6201, AA6201A, AA6401, AA6501, AA6002, AA6003, AA6103, AA6005, AA6005A, AA6005B, AA6005C, AA6105, AA6205, AA6305, AA6006, AA6106, AA6206, AA6306, AA6008, AA6009, AA6010, AA6110, AA6110A, AA6011, AA6111, AA6012, AA6012A, AA6013, AA6113,  
30 AA6014, AA6015, AA6016, AA6016A, AA6116, AA6018, AA6019, AA6020, AA6021, AA6022, AA6023, AA6024, AA6025, AA6026, AA6027, AA6028, AA6031, AA6032, AA6033, AA6040, AA6041, AA6042, AA6043, AA6151, AA6351, AA6351A, AA6451, AA6951, AA6053, AA6055, AA6056, AA6156, AA6060, AA6160, AA6260, AA6360, AA6460, AA6460B, AA6560, AA6660, AA6061, AA6061A, AA6261, AA6361, AA6162,

AA6262, AA6262A, AA6063, AA6063A, AA6463, AA6463A, AA6763, A6963, AA6064, AA6064A, AA6065, AA6066, AA6068, AA6069, AA6070, AA6081, AA6181, AA6181A, AA6082, AA6082A, AA6182, AA6091, or AA6092 can be used as the 6000-series aluminum alloy constituting the base material of the aluminum material.

5

**[0020]** A protective coating that contains oxides of aluminum and hydrated oxides of aluminum is provided on the base material. The protective coating is obtained by, for example, performing an anodizing process on the base material to form, on a surface of the base material, a porous anodized coating that is composed of the oxides of aluminum and has a plurality of pores, followed by performing a sealing process to close up the pores of the anodized coating with the hydrated oxides of aluminum.

**[0021]** The thickness of the protective coating is 2  $\mu\text{m}$  or more. Thereby, the base material can be protected from corrosive gases and plasma and the corrosion resistance of the aluminum material can be increased. From the viewpoint of corrosion resistance, there is no particular limitation on the upper limit of the thickness of the protective coating; the thicker the protective coating is made, the more the corrosion resistance of the aluminum material can be increased. From this viewpoint, the thickness of the protective coating is preferably 5  $\mu\text{m}$  or more, and more preferably 10  $\mu\text{m}$  or more. It is noted that, from the viewpoint of manufacturing, the upper limit of the thickness of the protective coating is, for example, 200  $\mu\text{m}$ . From the viewpoint of curtailing the formation of cracks in the protective coating, the thickness of the protective coating is preferably 100  $\mu\text{m}$  or less.

**[0022]** The oxides of aluminum and the hydrated oxides of aluminum in the protective coating are distributed such that, when the mass percentages of elements in the protective coating are analyzed in the depth direction by glow-discharge optical-emission spectrometry, ratio  $C_{\text{H}}/C_{\text{Al}}$  of the integrated hydrogen atom mass percentage  $C_{\text{H}}$  to the integrated aluminum atom mass percentage  $C_{\text{Al}}$ , in a range extending from the surface of the protective coating to a location at a depth of 1  $\mu\text{m}$ , becomes 0.20 or more and 0.70 or less. The integrated value ratio  $C_{\text{H}}/C_{\text{Al}}$  indicates the quantity of hydrated oxides present in the vicinity of the surface of the protective coating, meaning that the higher the value of ratio  $C_{\text{H}}/C_{\text{Al}}$ , the greater the quantity of hydrated oxides present in the vicinity of the surface of the protective coating.

[0023] Accordingly, in a protective coating having an integrated value ratio  $C_H/C_{Al}$  of 0.20 or more, it is conceivable that the pores formed by the anodizing process will be sufficiently closed up by the hydrated oxides. Therefore, by setting the ratio  $C_H/C_{Al}$  in the protective coating to 0.20 or more, ingress of corrosive gases and plasma into the pores can  
5 be curtailed and the corrosion resistance of the aluminum material can be increased. From the viewpoint of further increasing the corrosion resistance of the aluminum material, the value of the integrated value ratio  $C_H/C_{Al}$  is preferably 0.22 or more, more preferably 0.24 or more, yet more preferably 0.26 or more, particularly preferably 0.28 or more, and most preferably 0.30 or more.

10

[0024] On the other hand, if the integrated value ratio  $C_H/C_{Al}$  is less than 0.20, then the closing up of the pores will tend to be insufficient, and there is a risk that it will lead to a decrease in the corrosion resistance of the aluminum material.

15 [0025] In addition, if the value of the integrated value ratio  $C_H/C_{Al}$  becomes too high, then there is a risk that cracks will tend to form in the protective coating when the temperature of the aluminum material rises. Although the cause of this is not entirely clear, the following reasons, for example, are conceivable. It is conceivable that, if the value of the integrated value ratio  $C_H/C_{Al}$  is too high, then the protective coating enters a state in which  
20 the quantity of the hydrated oxides is too great or a state in which the crystallinity of the hydrated oxides is too high. Therefore, it is conceivable that, if the value of the ratio  $C_H/C_{Al}$  is too high, then the difference between the thermal expansion coefficients of the base material, the oxides of aluminum, and the hydrated oxides of aluminum will cause non-uniform thermal expansion in the protective coating, and cracks will tend to form when the  
25 temperature rises.

[0026] From the viewpoint of curtailing the formation of cracks in the protective coating, the value of the integrated value ratio  $C_H/C_{Al}$  is set to 0.70 or less. From the same viewpoint, the value of the ratio  $C_H/C_{Al}$  is preferably 0.68 or less, more preferably 0.66 or  
30 less, and yet more preferably 0.64 or less.

[0027] When configuring the preferred range of the integrated value ratio  $C_H/C_{Al}$  in the protective coating, the upper and lower limits of the integrated value ratio  $C_H/C_{Al}$  described above can be arbitrarily combined. For example, the preferred range of the

integrated value ratio  $C_H/C_{Al}$  may be 0.22 or more and 0.68 or less, 0.24 or more and 0.68 or less, 0.26 or more and 0.66 or less, 0.28 or more and 0.66 or less, or 0.30 or more and 0.64 or less.

5     **[0028]**           Specifically, a method of calculating the integrated value ratio  $C_H/C_{Al}$  in the protective coating is as follows. First, after cleaning the surface of the aluminum material, a glow-discharge optical-emission analyzer (for example, a "GD750" manufactured by SPECTRUMA Analytik GmbH) is used to obtain optical emission intensity profiles for aluminum atoms and hydrogen atoms in the depth direction of the protective coating. At this  
10    time, the measurement conditions of the glow-discharge optical-emission analyzer are: anode diameter: 2.5 mm, output: 25 W, and gas pressure: 3.5 hPa, and the optical emission intensity capture interval is 0.2–0.24 seconds. It is noted that, when measured under such conditions, the sputtering speed of the protective coating is approximately 50–90 nm/s.

15    **[0029]**           The optical emission intensity profiles for aluminum atoms and hydrogen atoms in the depth direction thus obtained are converted into mass percentage profiles based on a calibration curve prepared in advance. The mass percentages of the various atoms are then integrated over a range extending from the surface of the protective coating to a location at a depth of 1  $\mu\text{m}$  to calculate the integrated hydrogen atom mass percentage  $C_H$  and the  
20    integrated aluminum atom mass percentage  $C_{Al}$ . The integrated value ratio  $C_H/C_{Al}$  can be calculated by dividing the integrated hydrogen atom mass percentage  $C_H$  by the integrated aluminum atom mass percentage  $C_{Al}$  obtained as described above.

**[0030]**           The mass reduction amount per unit of area of the aluminum material in a  
25    sealing degree test performed using the method stipulated in JIS H8683-2:2013 is preferably 0.2  $\text{g}/\text{dm}^2$  or less. In this situation, the corrosion resistance of the aluminum material can be further increased.

**[0031]**           It is noted that a specific method of the sealing degree test is as follows. First,  
30    35 mL of phosphoric acid and 20 g of chromic anhydride are dissolved in water to prepare 1 L of a test solution. Next, a test piece, which includes the protective coating, is extracted from the aluminum material, and the surface area of the protective coating on the test piece is measured. After removing contamination from the surface of this test piece, the mass of the

test piece is measured. The test piece is then immersed in the test solution, which is held at a temperature of  $38^{\circ}\text{C} \pm 1^{\circ}\text{C}$ , for  $15 \text{ min} \pm 5 \text{ s}$ .

**[0032]** After immersion of the test piece in the test solution has been completed, the test piece is cleaned with running water, then further cleaned with deionized water or distilled water. After sufficiently drying the cleaned test piece, the mass of the test piece is measured.

**[0033]** Surface area  $A$  (unit:  $\text{dm}^2$ ) of the protective coating of the test piece, mass  $m_1$  (unit: g) of the test piece before immersion in the test solution, and mass  $m_2$  (unit: g) of the test piece after immersion in the test solution obtained as described above can be used to calculate mass reduction amount  $\delta_A$  (unit:  $\text{g}/\text{dm}^2$ ) per unit of area based on Equation (1) below.

$$\delta_A = (m_1 - m_2)/A \quad (1)$$

**[0034]** As described above, the aluminum material excels in corrosion resistance with regard to corrosive gases, plasma, and the like, and the formation of cracks in the protective coating can be curtailed even if the temperature rises. For this reason, the aluminum material is suitable for applications such as covers provided around fans of heating and cooking equipment, members for semiconductor-manufacturing apparatuses, and the like. More specifically, the aluminum material is suitable for use in, for example: chambers in semiconductor-manufacturing apparatuses, such as film-forming apparatuses and etching apparatuses; components disposed within such chambers; and the like. Examples of film-forming apparatuses include physical vapor deposition (PVD) apparatuses and chemical vapor deposition (CVD) apparatuses. In addition, examples of etching apparatuses include dry-etching apparatuses and the like.

**[0035]** (Method of Manufacturing an Aluminum Material)

A method of manufacturing an aluminum material comprises:

an anodizing-process step that forms an anodized coating having fine pores on the base material by subjecting the base material to an anodizing process; and thereafter, a sealing step that forms a protective coating on the base material by immersing the base material in hot water to seal the pores in the anodized coating.

In addition, the product of hot-water temperature  $T$  (unit:  $^{\circ}\text{C}$ ) and immersion time  $t$  (unit: hours) in the sealing step is greater than  $20^{\circ}\text{C}\cdot\text{hours}$  and less than  $75^{\circ}\text{C}\cdot\text{hours}$ .

**[0036]** In the anodizing-process step, the anodized coating can be formed on the surface of the base material by passing a DC current between the base material and a counter electrode in a state in which the base material and the counter electrode are immersed in an electrolyte solution. The anodized coating thus formed comprises a barrier layer, which is densely formed on the base material, and a porous layer, which is formed on the barrier layer and has numerous pores. The barrier layer and the porous layer are constituted from oxides of aluminum, such as alumina.

**[0037]** The electrolyte solution used in the anodizing-process step may be, for example, an acidic electrolyte solution that contains an electrolyte such as sulfuric acid or phosphoric acid, or may be an alkaline electrolyte solution that contains an electrolyte such as sodium metaborate. From the viewpoint of more easily forming the anodized coating having the desired structure in the anodizing-process step, and, in turn, more easily forming the protective coating, the electrolyte solution used in the anodizing-process step preferably is an acidic electrolyte solution, more preferably is an acidic electrolyte solution that contains an inorganic acid as the electrolyte, and yet more preferably is an acidic electrolyte solution that contains sulfuric acid as the electrolyte. It is noted that anions originating from the electrolyte are sometimes incorporated into the interior of the anodized coating formed on the surface of the aluminum material by the anodizing-process step; for example, in an anodizing process using sulfuric acid, an anodized coating that contains sulfur originating from sulfuric acid ions is formed.

**[0038]** The current density of the DC current in the anodizing process can be set, for example, in a range of 1 mA/cm<sup>2</sup> or more and 20 mA/cm<sup>2</sup> or less, as appropriate. In addition, the temperature of the electrolyte solution in the anodizing-process step can be set, for example, in a range of 0°C or higher and 40°C or lower, as appropriate.

**[0039]** The thickness of the anodized coating formed in the anodizing-process step is preferably 2 μm or more. By making the thickness of the anodized coating 2 μm or more, the thickness of the protective coating after the sealing step can be more easily made to be 2 μm or more.

**[0040]** In the sealing step, the base material, on the surface of which the anodized coating was formed in the anodizing-process step, is immersed in hot water. When the anodized coating is immersed in hot water, the oxides of aluminum constituting the anodized coating reacts with the water to form hydrated oxides. Owing to these hydrated oxides closing up the pores of the anodized coating, the anodized coating becomes a protective coating.

**[0041]** In the sealing step, the base material is immersed in hot water such that the product of temperature  $T$  (unit:  $^{\circ}\text{C}$ ) of the hot water in which the base material is immersed and immersion time  $t$  (unit: hours) is greater than  $20^{\circ}\text{C}\cdot\text{hours}$  and less than  $75^{\circ}\text{C}\cdot\text{hours}$ , preferably is  $21^{\circ}\text{C}\cdot\text{hours}$  or more and  $73^{\circ}\text{C}\cdot\text{hours}$  or less, and more preferably is  $23^{\circ}\text{C}\cdot\text{hours}$  or more and  $71^{\circ}\text{C}\cdot\text{hours}$  or less. By immersing the base material in hot water such that the product of the hot-water temperature and the immersion time is greater than  $20^{\circ}\text{C}\cdot\text{hours}$ , the oxides of aluminum constituting the anodized coating can sufficiently react with the hot water, and thereby the pores of the anodized coating can be sufficiently closed up. A protective coating that excels in corrosion resistance can thereby be formed. If the product of the hot-water temperature and the immersion time is  $20^{\circ}\text{C}\cdot\text{hours}$  or less, then the reaction between the oxides of aluminum and the hot water will be insufficient, and the closing up of the pores will tend to be insufficient. Therefore, in this situation, there is a risk that it will lead to a decrease in the corrosion resistance of the aluminum material. From the viewpoint of more reliably obtaining a protective coating having excellent corrosion resistance, the product of the hot-water temperature and the immersion time is preferably  $21^{\circ}\text{C}\cdot\text{hours}$  or more, and more preferably is  $23^{\circ}\text{C}\cdot\text{hours}$  or more.

**[0042]** On the other hand, if the product of the hot-water temperature and the immersion time is too high, then there is a risk that cracks will tend to form in the protective coating when the temperature of the aluminum material rises. One conceivable cause of this is an excessive reaction between the oxides of aluminum and the hot water. From the viewpoint of curtailing the formation of cracks in the protective coating and improving the heat resistance of the aluminum material, the product of the hot-water temperature and the immersion time is set to be less than  $75^{\circ}\text{C}\cdot\text{hours}$ . From the same viewpoint, the product of the hot-water temperature and the immersion time is preferably  $73^{\circ}\text{C}\cdot\text{hours}$  or less, and more preferably is  $71^{\circ}\text{C}\cdot\text{hours}$  or less.

**[0043]** Hot-water temperature T in the sealing step is preferably 50°C or higher, more preferably is 60°C or higher, and yet more preferably is 70°C or higher. By using high-temperature hot water in the sealing step, the immersion time necessary to achieve the desired sealing degree can easily be shortened. As a result, the productivity of the aluminum material  
5 can be further improved. It is noted that the upper limit of hot-water temperature T in the sealing step is 150°C. That is, in the sealing step, the base material may be immersed in boiling water, or a superheated water vapor may be brought into contact with the base material.

10 **[0044]** The base material used in the anodizing-process step may be prepared by any method.

For example, the method of manufacturing the aluminum material may further comprise:

a casting step that fabricates an ingot composed of aluminum or aluminum alloy;  
15 a homogenizing-process step that performs a homogenizing process by holding the ingot at a temperature of 500°C or higher and 560°C or lower for 5 hours or more and 10 hours or less; and

a hot-rolling step that fabricates the base material by subjecting the ingot, which had been subjected to the homogenizing process, to hot rolling at a temperature of 500°C or  
20 higher and 560°C or lower.

**[0045]** For example, DC casting can be employed as the casting method in the casting step. Although there is no particular limitation on the thickness of the ingot obtained in the casting step, the ingot may have a thickness of, for example, 600 mm or more.  
25

**[0046]** In the homogenizing-process step, the homogenizing process is performed by holding the ingot obtained in the casting step at a temperature of 500°C or higher and 560°C or lower for 5 hours or more and 10 hours or less. By setting the hold temperature and hold time in the homogenizing process to within the above-specified ranges, the structure of the  
30 ingot can be sufficiently homogenized.

**[0047]** In the hot-rolling step, the ingot, which had been subjected to the homogenizing process, is subjected to hot rolling at a temperature of 500°C or higher and 560°C or lower. The base material can be obtained thereby. If the start temperature in the hot

rolling is too low, then the deformation resistance of the ingot will become high, and there is a risk that this will lead to the formation of cracks in the ingot during rolling and thus to a reduction of productivity. On the other hand, if the start temperature in the hot rolling is too high, then there is a risk of the ingot melting locally owing to work-induced heat generation  
5 during the hot rolling.

**[0048]** In the aforementioned manufacturing method, the base material obtained as described above may be provided to the anodizing-process step as is. In addition, the manufacturing method may comprise, after the hot-rolling step has been performed and  
10 before the anodizing-process step will be performed, a heat-treatment step that performs a heat treatment, such as annealing, as necessary, on the base material.

**[0049]** Furthermore, the manufacturing method may comprise, after the hot-rolling step has been performed and before the anodizing-process step will be performed, a  
15 preprocessing step that subjects the base material to a pre-process. Examples of base material preprocesses include: degreasing processes, such as alkali-degreasing processes; and polishing processes, such as mechanical polishing, chemical polishing, and electrolytic polishing. In the preprocessing step, one of the aforementioned preprocesses may be performed alone or two or more preprocesses may be performed in combination as  
20 appropriate according to the desired characteristics of the aluminum material.

**[0050]** In the situation in which an alkali-degreasing process is performed in the preprocessing step, the luster of the anodized coating obtained after the anodizing process can be reduced and an aluminum material having a non-glossy external appearance can be  
25 obtained. In addition, in the situation in which a polishing process is performed in the preprocessing step, then the luster of the anodized coating obtained after the anodizing process can be increased and an aluminum material having a glossy external appearance can be obtained. From the viewpoint of further increasing the luster of the aluminum material, it is preferable to perform an electrolytic polishing process on the base material in the  
30 preprocessing step.

[Working Examples]

**[0051]** Working examples of the surface-treated aluminum material and a method of manufacturing the same will be described with reference to FIG. 1 to FIG. 3. As shown in

FIG. 1, a surface-treated aluminum material 1 according to the present example comprises: a base material 2 composed of aluminum or an aluminum alloy; and a protective coating 3 comprising oxides of aluminum and hydrated oxides of aluminum and formed on at least a portion of the surface of the base material 2. The thickness of the protective coating 3 is 2  $\mu\text{m}$  or more. In addition, when the mass percentages of elements in the protective coating 3 are analyzed in the depth direction by glow-discharge optical-emission spectrometry, ratio  $C_{\text{H}}/C_{\text{Al}}$  of the integrated hydrogen atom mass percentage  $C_{\text{H}}$  to the integrated aluminum atom mass percentage  $C_{\text{Al}}$ , in a range extending from the surface of the protective coating 3 to a location at a depth of 1  $\mu\text{m}$ , is 0.2 or more and 0.7 or less.

**[0052]** Specific examples of the aluminum material 1 (Test Materials S1–S5) are shown in Table 1. The method of manufacturing Test Materials S1–S5 was, for example, as follows. First, an aluminum sheet having a chemical composition indicated by the alloy number A6016 and a thickness of 1.1 mm was prepared as the base material 2. A preprocess of an anodizing process was performed on this base material 2. Specifically, an alkaline etching process was performed as a preprocess by immersing the base material 2 in an aqueous solution of sodium hydroxide having a concentration of 5 mass% and a temperature of 55°C. Subsequently, a desmutting treatment was performed by immersing the base material 2 in nitric acid having a concentration of 30 mass%. Subsequently, a chemical polishing process was performed by immersing the base material 2 in a mixed solution in which phosphoric acid and sulfuric acid were mixed at a temperature of 85°C and the volumetric ratio of phosphoric acid:sulfuric acid = 7:3. After the chemical polishing process, a desmutting treatment was performed again under conditions the same as the conditions described above.

**[0053]** After preprocessing of the base material 2 was performed as described above, an anodizing process was performed on the base material 2 to form an anodized coating 30 on the surface of the base material 2. The electrolyte solution used in the anodizing process was an aqueous solution of sulfuric acid having a concentration of 15 mass%, and the temperature of the electrolyte solution was 5°C. In addition, the current density in the anodizing process was 10 mA/cm<sup>2</sup>, and the treatment time was 60 min. The anodized coating 30 thus formed is a so-called porous-type anodized coating, and, as shown in FIG. 2, comprises a barrier layer 31, which is formed on the base material 2, and a porous layer 32, which is formed on the barrier layer 31 and has numerous pores 321. It is noted that the thickness of the anodized

coating 30 formed by performing the anodizing process under the conditions described above is approximately 15  $\mu\text{m}$ .

5 [0054] After having performed the anodizing process, a sealing process is performed by immersing the base material in hot water under the conditions shown in Table 1. Test Materials S1–S5 shown in Table 1 can be obtained thereby. It is noted that Test Materials R1–R3 shown in Table 1 are test materials for comparison with Test Materials S1–S5. The method of manufacturing Test Materials R1–R3 is the same as the method of manufacturing Test Materials S1–S5, except that the hot-water temperature and the immersion time in the  
10 sealing process were modified as shown in Table 1.

[0055] Next, a method of evaluating the various characteristics of Test Materials S1–S5 and Test Materials R1–R3 shown in Table 1 will be described.

15 [0056] [Distribution of Hydrogen Atoms and Aluminum Atoms]

After having cleaned the surfaces of the test materials, a glow-discharge optical-emission analyzer (a "GD750" manufactured by SPECTRUMA Analytik GmbH) was used to obtain optical emission intensity profiles for aluminum atoms and hydrogen atoms in the depth direction of the protective coating. The measurement conditions of the glow-discharge  
20 optical-emission analyzer were: anode diameter: 2.5 mm, output: 25 W, and gas pressure: 3.5 hPa, and the optical emission intensity capture interval was 0.2–0.24 s. It is noted that, when measured under such conditions, the sputtering speed of the protective coating is approximately 50–90 nm/s.

25 [0057] The optical emission intensity profiles for aluminum atoms and hydrogen atoms in the depth direction thus obtained are converted to mass percentage profiles based on a calibration curve prepared in advance. A profile of the mass percentage of hydrogen atoms in Test Material S1 is shown in FIG. 3 as one example. In FIG. 3, the ordinate is the hydrogen atom mass percentage (unit: mass%) and the abscissa is the depth (unit:  $\mu\text{m}$ ) from  
30 the surface of the protective coating. In the profiles thus obtained, the mass percentages of the various atoms were then integrated over a range extending from the surface of the protective coating to a location at a depth of 1  $\mu\text{m}$  to calculate the integrated hydrogen atom mass percentage  $C_H$  and the integrated aluminum atom mass percentage  $C_{Al}$ . Ratio  $C_H/C_{Al}$  is

calculated by dividing the integrated hydrogen atom mass percentage  $C_H$  by the integrated aluminum atom mass percentage  $C_{Al}$  obtained as described above.

**[0058]** [Sealing Degree of Protective Coating]

5           A sealing degree test was performed using the method stipulated in JIS H8683-2:2013 and a mass reduction amount per unit of area for each test material was determined.

**[0059]** [Heat Resistance]

10           Heat resistance was evaluated based on the base material exposure ratio as measured using the following method. First, the test material was heated for 4 hours in an oven set to a temperature of 200°C. After removing the test material from the oven and cooling to room temperature, an evaluation region was established on the protective coating, and portions other than the evaluation region on the surface of the test material were covered with silicone resin.

15

**[0060]**           Next, an aqueous solution of NaCl having a concentration of 5 mass% and acetic acid having a concentration of 99.7% were prepared, and a measurement solution was prepared by adding the acetic acid to the NaCl aqueous solution such that the volumetric ratio of the NaCl aqueous solution to the acetic acid resulted in NaCl aqueous solution:acetic acid = 1000:1. A test piece, a counter electrode, and a reference electrode, which were electrically connected to a potentiostat, were immersed in this solution and left standing for 30 min to stabilize the electric potential of the measurement area. It is noted that, for example, an Ag/AgCl electrode can be used as the reference electrode.

25           **[0061]**           After the electric potential of the measurement area had stabilized, the potentiostat was used to apply a voltage between the test piece and the counter electrode, and the electric potentials of the measurement area were swept at a sweep rate of 20 mV/min until the electric potentials of the measurement area reached -2,000 mV relative to the reference electrode. A polarization curve for the post-heated test material was obtained by measuring the current density flowing to the measurement area at this time. In addition, a polarization curve for the base material was obtained by performing a similar measurement using the base material after the preprocessing of the anodizing process had been performed using the method described above.

30

[0062] Next, the center of an electric-potential region indicating the diffusion-limited current of hydrogen was determined in the polarization curve for the base material. The current density at the center of the electric-potential region was then calculated. In addition, in the polarization curve for the post-heated test material, the current density at the same electric potential as at the center of the electric-potential region in the polarization curve for the base material described above was calculated.

[0063] The current density calculated based on the polarization curve of the post-heating test material can be used as an indicator of the contact-surface area between the base material of the post-heating test material and the measurement solution; the higher the current density value is, the greater the contact-surface area between the base material and the measurement solution is. Accordingly, it was possible to use the ratio of the current density calculated using the post-heated test piece to the current density calculated using the base material as an indicator of the rate of increase in the surface area of the base material that was exposed by heating. More specifically, if, for example, defects, such as cracks, had formed in the protective coating of the post-heating test material, then the base material was sometimes exposed by such cracks. Accordingly, the current-density ratio of the post-heating test material to the base material became large in this situation. Table 1 shows the current-density ratio for each test material.

[0064] [Table 1]

|                  | Sealing-Process Step         |                        |               | $C_H/C_{Al}$ | Sealing Test                               | Heat Resistance       |
|------------------|------------------------------|------------------------|---------------|--------------|--------------------------------------------|-----------------------|
|                  | Hot-Water Temperature T (°C) | Immersion Time t (min) | Txt (°C · hr) |              | Mass Reduction Amount (g/dm <sup>2</sup> ) | Current-Density Ratio |
| Test Material S1 | 100                          | 15                     | 25            | 0.34         | 0.028                                      | $3 \times 10^{-4}$    |
| Test Material S2 | 100                          | 30                     | 50            | 0.59         | 0.015                                      | $12 \times 10^{-4}$   |
| Test Material S3 | 70                           | 30                     | 35            | 0.32         | 0.090                                      | $6 \times 10^{-4}$    |
| Test Material S4 | 70                           | 45                     | 53            | 0.47         | 0.076                                      | $16 \times 10^{-4}$   |
| Test Material S5 | 70                           | 60                     | 70            | 0.62         | 0.026                                      | $8 \times 10^{-4}$    |
| Test Material R1 | 100                          | 45                     | 75            | 0.75         | 0.015                                      | $23 \times 10^{-4}$   |
| Test Material R2 | 70                           | 15                     | 18            | 0.13         | 0.473                                      | $1 \times 10^{-4}$    |
| Test Material R3 | 100                          | 60                     | 100           | 1.21         | 0.010                                      | $21 \times 10^{-4}$   |

[0065] As shown in Table 1, Test Materials S1–S5 were subjected, in the sealing step, to a sealing process such that the products of the hot-water temperature and the immersion time were within the above-specified range. Therefore, the ratio  $C_H/C_{Al}$  of the integrated hydrogen atom mass percentage  $C_H$  to the integrated aluminum atom mass percentage  $C_{Al}$  in these test materials was within the above-specified range. In addition, these test materials had a low mass reduction amount in the sealing degree test and excelled in corrosion resistance with regard to corrosive gases, plasma, and the like. Furthermore, even in the situation in which the current-density ratio was low and the temperature had risen, these test materials could curtail the formation of cracks in the protective coating.

10

[0066] On the other hand, because the product of the hot-water temperature and the immersion time was higher than the above-specified range in the sealing processes for Test Material R1 and Test Material R3, the hydration reaction between the oxides of aluminum and the hot water proceeded excessively. For this reason, Test Material R1 and Test Material R3 had higher current-density ratios than Test Materials S1–S5, and cracks were more likely to form therein at increased temperatures.

15

[0067] Because the product of the hot-water temperature and the immersion time was lower than the above-specified range in the sealing process for Test Material R2, closing up of the pores in the anodized coating was insufficient. Therefore, Test Material R2 had a higher mass reduction amount in the sealing degree test and inferior corrosion resistance than Test Materials S1–S5.

20

[0068] Aspects of the surface-treated aluminum material and the method of manufacturing the same according to the present invention were described above on the basis of the working examples; however, the specific aspects of the surface-treated aluminum material and the method of manufacturing the same according to the present invention are not limited to the aspects in the working examples, and the configurations thereof can be modified, as appropriate, within a scope such that the gist of the present invention is not impaired.

25

30

## CLAIMS

1. A surface-treated aluminum material comprising:
  - a base material composed of aluminum or an aluminum alloy; and
  - 5 a protective coating formed on at least a portion of a surface of the base material and containing oxides of aluminum and hydrated oxides of aluminum;wherein:
  - the thickness of the protective coating is 2  $\mu\text{m}$  or more; and
  - when mass percentages of elements in the protective coating are analyzed in a depth
  - 10 direction by glow-discharge optical-emission spectrometry, the ratio  $C_{\text{H}}/C_{\text{Al}}$  of an integrated hydrogen atom mass percentage  $C_{\text{H}}$  to an integrated aluminum atom mass percentage  $C_{\text{Al}}$ , in a range extending from a surface of the protective coating to a location at a depth of 1  $\mu\text{m}$ , is 0.2 or more and 0.7 or less.
- 15 2. The surface-treated aluminum material according to claim 1, wherein when a sealing degree test is performed using the method stipulated in JIS H8683-2:2013, a mass reduction amount per unit of area is 0.2  $\text{g}/\text{dm}^2$  or less.
3. A member for a semiconductor-manufacturing apparatus composed of the surface-treated
- 20 aluminum material according to claim 1 or 2.
4. A method of manufacturing the surface-treated aluminum material according to claim 1 or 2, comprising:
  - an anodizing-process step that forms an anodized coating having fine pores on the
  - 25 base material by subjecting the base material to an anodizing process; and
  - thereafter, a sealing step that forms the protective coating on the base material by immersing the base material in hot water to seal the pores in the anodized coating;
  - wherein the product of hot-water temperature  $T$  [ $^{\circ}\text{C}$ ] and immersion time  $t$  [hr] in the sealing step is greater than  $20^{\circ}\text{C}\cdot\text{hours}$  and less than  $75^{\circ}\text{C}\cdot\text{hours}$ .

30