

DESCRIPTION

METHOD FOR MANUFACTURING ANODIZED ALUMINUM OR ALUMINUM ALLOY MEMBER HAVING EXCELLENT CORROSION RESISTANCE AND INSULATION 5 CHARACTERISTICS, AND SURFACE-TREATED SEMICONDUCTOR DEVICE

Technical Field

[0001] The present invention relates to a method of forming an anodic oxidation coat having excellent corrosion
10 resistance and insulation properties on the surface of an aluminum or aluminum alloy member, and to an aluminum or aluminum alloy member having an anodic oxidation coat manufactured using the method. More particularly, the present invention relates to a method of forming an anodic
15 oxidation coat having high hardness and excellent corrosion resistance and insulation properties without internal defects in an anodic oxidation coating layer, and to an internal member of a device for manufacturing a semiconductor or a display, the internal member being coated with an anodic
20 oxidation coat manufactured using the method.

[0002]

Background Art

[0003] Vacuum plasma apparatuses are widely used in a process field for realizing semiconductor elements or other
25 ultra-fine shapes. As examples of use of the vacuum plasma

apparatuses, there are a PECVD (plasma enhanced chemical vapor deposition) apparatus for forming a deposition film on a substrate according to a chemical vapor deposition method using plasma, a sputtering apparatus for forming a deposition film according to a physical method, and a dry-etching apparatus for etching a substrate or a coating material on a substrate in a desired pattern. In the vacuum plasma apparatuses, a semiconductor element is etched or an ultra-fine shape is obtained using a high-temperature plasma.

[0004] Therefore, since a high-temperature plasma is generated in the vacuum plasma apparatus, a chamber and internal parts thereof are damaged, and certain elements and contaminant particles are formed on the surfaces of the chamber and the parts thereof. Thus, there is a high likelihood of contamination of the interior of the chamber.

[0005] Meanwhile, a corrosive gas containing halogen elements such as Cl, F, and Br or elements such as O, N, H, S, and C is introduced as a reaction gas used in a device for manufacturing a semiconductor. Accordingly, the chamber or the inner members of the chamber require resistance to corrosion by the above gases, and also require plasma resistance because a halogen-based plasma is generated during the process in a device for manufacturing a semiconductor or liquid crystal.

[0006] Moreover, in a semiconductor-etching process, since some of the members in the chambers are connected to a high-voltage power supply unit, arcing occurs when insulation properties are poor. Accordingly, excellent non-
5 conductivity is also required.

[0007] Meanwhile, aluminum is mainly used as a material used in a semiconductor apparatus because it is conductive, easy to manufacture, and available at a reasonable price.

[0008] However, aluminum easily reacts with halogens
10 such as chlorine, fluorine, and bromine to thus generate AlCl_3 , Al_2Cl_6 , AlF_3 , or AlBr_3 . An aluminum-fluorine compound may be stripped from a portion of the surface of the treating device and thus cause corrosion of the portion, and may serve as a source of particulate contamination in the
15 treatment chamber (and parts manufactured in the chamber).

[0009] Further, many compounds containing aluminum and chlorine and many compounds containing aluminum and bromine have volatility and also generate gases under semiconductor-processing conditions, and these gases leave the aluminum
20 substrate. Due to this, spaces are formed in the structure. The spaces destabilize the structure and cause problems of low integrity of the surface thereof.

[0010] Accordingly, examples of a preferable means for protecting the aluminum surface in a semiconductor device
25 include an anodizing-alumina coating method. The anodizing

treatment method is an electrolytic oxidation process of forming an integral coating including the aluminum oxide, which is relatively porous, on the aluminum surface.

[0011] As a method of forming an anodic oxidation coat,
5 a method of controlling an electrolytic solution at a low temperature or a method of performing electrolysis at a high current density when the anodic oxidation coat is formed is employed. However, when the anodic oxidation coat is formed using the method, there are problems in that the occurrence
10 of cracks in the anodic oxidation coat is increased and in that a large amount of energy is required.

[0012] As a conventional technology of a method of forming an anodic oxidation coat, Japanese Patent No. 4660760 (2011.01.14.) has proposed a method of forming a
15 high-hardness anodic oxidation coat using a sulfuric-acid-based electrolytic solution added with alcohol. However, the above-mentioned prior document has a problem in that it is difficult to control the change in the concentration of alcohol in the electrolytic solution due to anodizing
20 treatment.

[0013] Further, Korean Patent No. 10-0664900 (2007.01.04.) proposed a method of performing anodizing-surface treatment using an electrolytic solution in which a small amount of oxalic acid is added to sulfuric acid.
25 However, although the above-mentioned prior document

discloses anodizing treatment conditions for obtaining an oxidation coat thickness of 50 to 60 μm in a device for manufacturing a semiconductor, the above document has problems in that, since a high applied current must be used
5 in order to form a coat having a desired thickness, a number of defects are formed in the coating layer and corrosion resistance is reduced.

[0014] Therefore, despite the development of the technologies described above, there remains the need to
10 develop a method of treating the surface of a semiconductor device using an aluminum or aluminum alloy material that is capable of improving corrosion resistance and insulation properties of the semiconductor device.

[0015]

15 **Disclosure**

Technical Problem

[0016] Accordingly, the main object of the present invention is to provide a method of manufacturing an anodized aluminum or aluminum alloy member having excellent
20 insulation properties and corrosion resistance to the gases used during a semiconductor-manufacturing process, and a surface-treated semiconductor device.

[0017]

Technical Solution

[0018] In order to accomplish the above object, the present invention provides a method of forming an oxidation coat of an aluminum-containing member of a device for manufacturing a semiconductor or a display. The aluminum-
5 containing member is coated with an anodic oxidation coat on the surface thereof. The method includes a) mixing a sulfuric acid, an oxalic acid, and a tartaric acid to manufacture an electrolytic solution, and b) forming an anodic oxidation coat on the surface of an aluminum or
10 aluminum alloy member using the electrolytic solution manufactured in step a).

[0019] According to an embodiment, the content weight ratio of the sulfuric acid, oxalic acid, and tartaric acid in step a) may be 9 to 11 : 2.5 to 3.5 : 0.3 to 0.7.

15 **[0020]** Further, according to an embodiment, the concentration of the electrolytic solution may be 1 to 10 wt%.

[0021] Further, according to an embodiment, in the forming the anodic oxidation coat in step b), an applied
20 current may be 0.8 to 1.7 A/dm² and a temperature of the electrolytic solution may be 8 to 22°C.

[0022] Further, according to an embodiment, the anodic oxidation coat may have a thickness of 50 to 60 μm.

[0023] Meanwhile, the present invention provides an
25 aluminum or aluminum alloy member of a device for

manufacturing a semiconductor or a display. The member is manufactured using the above-described method of forming the oxidation coat of the aluminum-containing member of the device for manufacturing the semiconductor or the display.

5 **[0024]** The present invention provides an aluminum-containing member of a device for manufacturing a semiconductor or a display. The aluminum-containing member is coated with an anodic oxidation coat having a hardness of 370 to 425 Hv and a withstanding voltage of 1500 to 2000 V,
10 and a corrosion resistance may be 120 minutes or more.

[0025] Further, the present invention may provide an aluminum-containing member of a device for manufacturing a semiconductor or a display, the aluminum-containing member being coated with an anodic oxidation coat having hardness
15 of 370 to 425 Hv and a corrosion resistance of 120 minutes or more. The present invention may also provide an aluminum-containing member of a device for manufacturing a semiconductor or a display, the aluminum-containing member being coated with an anodic oxidation coat having a
20 withstanding voltage of 1500 to 2000 V and a corrosion resistance of 120 minutes or more.

[0026]

Advantageous Effects

[0027] In a method of forming an anodic oxidation coat
25 having excellent corrosion resistance and insulation

properties on the surface of an aluminum or aluminum alloy member according to the present invention, it is possible to obtain a coating thickness of 50 μm or more without internal defects in an anodic oxidation coating layer.

5 [0028] Further, excellent corrosion resistance is ensured against gases used in a device for manufacturing a semiconductor, and excellent insulation properties are ensured against high voltage in a chamber of the device for manufacturing a semiconductor.

10 [0029]

Description of Drawings

[0030] FIG. 1 is a cross-sectional view showing a schematic structure in which an anodic oxidation coat is formed on the surface of an aluminum or aluminum alloy

15 member; and

[0031] FIG. 2 shows SEM images of Example 3 and Comparative Example 7, FIG. 2(a) is a measurement image of a cross-section in which an oxidation coat is formed in Comparative Example 7, and FIG. 2(b) is a measurement image

20 of a cross-section in which an oxidation coat is formed in Example 3.

[0032]

[0033] [Description of the Reference Numerals]

[0034] 1: Electrolytic solution 4: Base substrate 7:

25 Cell

[0035] 2: Porous layer interface 5: Porous layer
[0036] 3: Pore 6: Barrier layer
[0037]

Mode for Invention

5 [0038] Unless defined otherwise, all technical and
scientific terms used herein have the same meanings as
commonly understood by a person skilled in the art to which
the present invention pertains. In general, the
nomenclature used herein is well known and commonly used in
10 the art.

[0039] Throughout the present specification, when a part
is said to "include" a certain component, it means that the
component may further include other components, and does not
necessarily exclude other components unless otherwise
15 specified.

[0040] The present invention relates to a method of
manufacturing an aluminum or aluminum alloy member of a
device for manufacturing a semiconductor or a display. The
aluminum or aluminum alloy member has an anodic oxidation
20 coat formed on the surface thereof. The method includes a)
mixing sulfuric acid, oxalic acid, and tartaric acid to
manufacture an electrolytic solution, and b) forming an
anodic oxidation coat on the surface of the aluminum or
aluminum alloy member using the electrolytic solution
25 manufactured in step a).

[0041] In order to manufacture the aluminum or aluminum alloy member on which the anodic oxidation coat is formed according to the present invention, the electrolytic solution including the sulfuric acid, the oxalic acid, and the tartaric acid mixed therein is used. Accordingly, an anodic oxidation coat of 50 μm or more may be formed even when using a low applied current compared to a conventional sulfuric acid bath using a mixed bath to which sulfuric acid, oxalic acid, and organic materials are added. Since the low applied current is used compared to sulfuric acid bath, defects may be prevented from forming in the anodic oxidation coat, thus increasing corrosion resistance.

[0042] Further, unlike the sulfuric acid bath, an oxalic acid bath using a mixed bath, to which oxalic acid, tartaric acid, and organic materials are added, has high corrosion resistance because an anodic oxidation coat having no defects therein is formed using a low applied current. However, the hardness and insulation properties are poor due to the small thickness thereof. In contrast, in the present invention, a coating layer having a thickness of 50 μm or more may be formed even using a low applied current. Accordingly, superior corrosion resistance, hardness, and insulation properties are ensured compared to a conventional method of forming an anodic oxidation coat.

[0043] Therefore, in the case of the aluminum or aluminum alloy member on which the anodic oxidation coat is formed according to the present invention, the sulfuric acid, the oxalic acid, and the tartaric acid are mixed with
5 each other at a predetermined ratio to thus form the anodic oxidation coat. Accordingly, a coating layer having a thickness of 50 μm or more may be formed using a low applied current, and the corrosion resistance of the coating layer may be improved, thus extending a product life. Further,
10 since the insulation properties are excellent, the occurrence of arcing of a semiconductor device or a device for manufacturing a display, which is connected to a high-voltage power supply unit, may be reduced.

[0044] Further, according to an embodiment, the content
15 weight ratio of the sulfuric acid, the oxalic acid, and the tartaric acid in step a) may be 9 to 11 : 2.5 to 3.5 : 0.3 to 0.7, and the concentration of the electrolytic solution may be 1 to 10 wt%.

[0045] When the ratio of the sulfuric acid, the oxalic
20 acid, and the tartaric acid is different from the above-described ratio, it is difficult to form an anodic oxidation coat of 50 μm or more, which is excellent in terms of corrosion resistance and withstanding voltage properties, using low current.

[0046] When the content of the sulfuric acid is greater than the above-described ratio, a high current and a low temperature of the electrolytic solution are required in order to form a coat of 50 μm or more, but corrosion
5 resistance may be reduced. When the content of the oxalic acid and the tartaric acid is greater than the above-described ratio, it is difficult to form an anodic oxidation coat of 50 μm or more at low current, and the withstanding voltage and hardness may be reduced even though a coating
10 having excellent corrosion resistance is capable of being obtained.

[0047] Meanwhile, when the anodic oxidation coat is formed in step b), the applied current is preferably 0.8 to 1.7 A/dm^2 , and the temperature of the electrolytic solution
15 may be 8 to 22°C.

[0048] When the applied current is less than 0.8 A/dm^2 , it is difficult to obtain a coating thickness of 50 μm or more, and the hardness, withstanding voltage, and corrosion resistance of the coating layer are reduced. When the
20 applied current is more than 1.7 A/dm^2 , the withstanding voltage and corrosion resistance of the coating layer may be reduced.

[0049] Further, when the temperature of the electrolytic solution is out of the range of 8 to 22°C, there may be a

problem in that the withstanding voltage and corrosion resistance of the coating layer are reduced.

[0050] Further, according to an embodiment of the present invention, the thickness of the anodic oxidation coat may be 50 μm or more, and more preferably 50 to 60 μm .

[0051] The structure in which the anodic oxidation coat is formed on the surface of the aluminum or aluminum alloy member according to the present invention may be examined in more detail in connection with FIG. 1.

10 **[0052]** FIG. 1 is a cross-sectional view showing the schematic structure in which the anodic oxidation coat is formed on the surface of the aluminum or aluminum alloy member.

[0053] When an aluminum or aluminum alloy member 4 is immersed in an electrolytic solution 1 and current is then applied thereto, a barrier layer 6 having no pores 3 is formed first. When current is continuously applied to a member 4 in which the barrier layer 6 is formed, a porous layer 5 having the pores 3 therein grows. The pore 3 and the cells 7 of the porous layer 5 grow due to growth and erosion depending on the composition, temperature, and applied current of the electrolytic solution in a porous layer interface 2, which is situated at the uppermost part and which is in contact with the electrolytic solution 1, and the barrier layer 6.

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[0054] Therefore, in the present invention, the pore 3 and the cells 7 of the oxidation coat may grow in the electrolytic solution including the sulfuric acid, the oxalic acid, and the tartaric acid mixed therein at a
5 predetermined ratio without defects, which are considered a problem in the conventional technology, thereby providing an anodic oxidation coat having excellent corrosion resistance and insulation properties for a device for manufacturing a semiconductor or a display.

10 **[0055]** Further, the present invention provides an aluminum or aluminum alloy member of a device for manufacturing a semiconductor or a display, which is manufactured using the method of manufacturing the aluminum or aluminum alloy member of the device for manufacturing the
15 semiconductor or display. An anodic oxidation coat is formed on the surface of the aluminum or aluminum alloy member.

[0056] Moreover, according to the present invention, an aluminum-containing member of a device for manufacturing a
20 semiconductor or a display, which is coated with an anodic oxidation coat having a hardness of 370 to 425 Hv and a withstanding voltage of 1500 to 2000 V, may be manufactured. The corrosion resistance of the aluminum-containing member may be 120 minutes or more.

[0057] Further, the anodic oxidation coat having hardness of 370 to 425 Hv and corrosion resistance of 120 minutes or more may be applied on a member of a device for manufacturing a semiconductor or a display. Also, the
5 anodic oxidation coat having withstanding voltage of 1500 to 2000 V and corrosion resistance of 120 minutes or more may be applied on a member of a device for manufacturing a semiconductor or a display.

[0058]

10 **[0059]** Hereinafter, the present invention will be described in more detail with reference to Examples. However, the following Examples are only to illustrate the invention, and the content of the present invention is not limited by the following Examples.

15 **[0060]** [Example]

[0061] In the Examples, an anodic oxidation coat is formed on the surface of an aluminum alloy according to the present invention.

[0062] <Example 1>

20 **[0063]** First, an aluminum alloy (Al6061) specimen having a length of 50 mm, a width of 50 mm, and a height of 5 mm was prepared by performing cutting. Thereafter, the surface of the specimen was polished to obtain a predetermined surface roughness. The polishing was performed using
25 Scotch-Brite (#400), but other known techniques may be used.

During the Scotch-Brite treatment, the surface roughness of the specimen was adjusted to Ra of 0.28 to 0.64 μm .

[0064] Thereafter, anodizing treatment was performed in an electrolytic solution including sulfuric acid (95% sulfuric acid), oxalic acid (100% oxalic acid), and tartaric acid (99% tartaric acid) mixed at a weight ratio of 10 : 3 : 0.5 and having a concentration of 5 wt% (solvent: DI water) at a temperature of 20°C with an applied current of 1 A/dm², thus obtaining an anodic oxidation coat. Aluminum was used as an anode (+) and lead was used as a cathode (-).

[0065]

[0066] <Examples 2 to 8>

[0067] The anodic oxidation coats of Examples 2 to 8 were obtained using the same method as in Example 1 under the same condition as in Example 1, except for the weight ratio of the electrolytic solution and the anodizing treatment process time. The conditions for generating the anodic oxidation coat are described in Table 1 below.

[0068]

[0069] <Comparative Examples 1 to 8>

[0070] The anodic oxidation coats of Comparative Examples 1 to 8 were obtained using the same method as in Example 1 under the same conditions as in Example 1, except for the weight ratio of the electrolytic solution and the anodizing treatment process time. The conditions for

generating the anodic oxidation coat are described in Table 1 below.

[0071]

[0072] [Experimental Example 1]

5 **[0073]** In order to check the physical properties of the anodic oxidation coats of Examples 1 to 8 and Comparative Examples 1 to 8, the physical properties were analyzed under the following conditions. As apparatuses for analyzing the physical properties, an external-current-type thickness
10 gauge (Positector 6000, DeFelsko), a Vickers hardness tester (HM 810-124K, Mitutoyo), and a withstanding voltage tester (HIPOT TESTER 19052, Chroma) were used.

[0074] Further, as a corrosion resistance test, a hydrochloric acid bubble test was performed. In the
15 hydrochloric acid bubble test, a PVC pipe having a diameter of 2 mm was attached to the specimen using a sealant. 2 ml of hydrochloric acid diluted to 5 wt% was added thereto, and the time at which the first bubbles were generated was noted.

20 **[0075]** The anodizing conditions and physical property analysis results of Examples 1 to 8 and Comparative Examples 1 to 8 are shown in Table 1 and FIG. 2 below.

[0076]

[0077] [Table 1]

	Electrolytic solution	Coating	Measured value	Proces
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	ratio			thickness (μm)				storage time (min)
	Sulfuric acid	Oxalic acid	Tartaric acid		Hardness (Hv)	Withstanding voltage (V)	Corrosion resistance (min)	
Example 1	10	3	0.5	30	421	828	120 or more	80
Example 2	10	3	0.5	45	396	1915	120 or more	120
Example 3	10	3	0.5	55	393	2398	120 or more	150
Example 4	10	3	0.5	60	387	2510	120 or more	180
Example 5	11	2.7	0.5	55	412	2122	120 or more	150
Example 6	11	3.2	0.5	55	386	1874	120 or more	150
Example 7	9	2.7	0.5	55	388	2236	120 or more	150
Example 8	9	3.2	0.5	55	379	1755	120 or more	150
Comparative Example 1	5	3	0.5	30	364	750	120 or more	80
Comparative Example 2	15	3	0.5	55	401	1423	20	150
Comparative Example 3	10	1.5	0.5	55	417	1389	50	150
Comparative Example 4	10	4.5	0.5	40	361	1945	120 or more	120

Comparative Example 5	10	3	1	35	394	1603	120 or more	80
Comparative Example 6	10	3	0.1	55	377	1432	75	150
Comparative Example 7	10	1	–	55	428	1029	16	80
Comparative Example 8	–	9	1	30	357	735	120 or more	80

[0078] With respect to the results of the physical property analysis experiments of Examples 1 to 8 and Comparative Examples 1 to 8, in the case of Examples 1 to 4, in which the weight ratio of the sulfuric acid, the oxalic acid, and the tartaric acid was fixed to 10 : 3 : 0.5 and the process time was changed, a coating thickness of 50 μm or more was obtained and the hardness, withstanding voltage, and corrosion resistance were excellent when the process time was 150 minutes.

[0079] On the other hand, when the process time was less than 150 minutes, it could be seen that the desired coating thickness was not obtained and the withstanding voltage was reduced even though the hardness was high and the corrosion resistance was favorable. When the process time was more than 150 minutes, it could be seen that a large coating

thickness was obtained and that the hardness, withstanding voltage, and corrosion resistance were similar to those of the specimen in the case of a process time of 150 minutes.

[0080] Further, from the comparison of Comparative Examples 1 to 8, it could be seen that the hardness was favorable but the withstanding voltage and corrosion resistance were reduced when the content of sulfuric acid was increased. When the content of sulfuric acid was low compared to the weight ratio of the present invention, it was confirmed that the hardness was similar but the withstanding voltage and corrosion resistance were slightly reduced.

[0081] Further, when the content of oxalic acid was reduced, it was confirmed that the corrosion resistance was reduced. In contrast, when the content of each of oxalic acid and tartaric acid was high compared to the weight ratio of the present invention, it was confirmed that the corrosion resistance was improved, but the hardness was reduced because the relative content of sulfuric acid was reduced.

[0082] Accordingly, it was confirmed that the weight ratio of the sulfuric acid, oxalic acid, and tartaric acid in the electrolytic solution for forming the anodic oxidation coat was preferably 9 to 11 : 2.5 to 3.5 : 0.3 to 0.7, and that an anodic oxidation coat having a coating

layer thickness of 50 μm or more and appropriate hardness, withstanding voltage, and corrosion resistance was obtained.

[0083] Further, FIG. 2 shows SEM images of Example 3 and

Comparative Example 7, FIG. 2(a) is a measurement image of a

5 cross-section in which an oxidation coat is formed in

Comparative Example 7, and FIG. 2(b) is a measurement image

of a cross-section in which an oxidation coat is formed in

Example 3. In FIG. 2(a), the anodic oxidation coat was

formed under the same conditions as in a conventional

10 sulfuric acid method, and it was confirmed that multiple

defects were present. In 2(b), it was confirmed that there

were few defects.

[0084]

[0085] Although the specific parts of the present

15 invention have been described in detail above, the present

invention is not limited to what is illustrated in the

drawings, and it will be apparent to those skilled in the

art that the specific descriptions are only preferred

embodiments, and that the scope of the present invention is

20 not limited thereby. Therefore, the substantial scope of

the present invention will be defined by the appended claims

and their equivalents.

CLAIMS

1. A method of forming an oxidation coat of an aluminum-containing member of a device for manufacturing a semiconductor or a display, the method comprising:

a) mixing a sulfuric acid, an oxalic acid, and a tartaric acid to manufacture an electrolytic solution; and

b) forming an anodic oxidation coat on a surface of an aluminum or aluminum alloy member using the electrolytic solution manufactured in step a).

2. The method of claim 1, wherein a content weight ratio of the sulfuric acid, the oxalic acid, and the tartaric acid in the step a) is 9 to 11 : 2.5 to 3.5 : 0.3 to 0.7.

3. The method of claim 1, wherein a concentration of the electrolytic solution is 1 to 10 wt%.

4. The method of claim 1, wherein in the forming the anodic oxidation coat of step b), an applied current is 0.8 to 1.7 A/dm² and a temperature of the electrolytic solution is 8 to 22°C.

5. The method of claim 1, wherein the anodic oxidation coat has a thickness of 50 to 60 μm.

6. An aluminum-containing member having an anodic oxidation coat of a device for manufacturing a semiconductor or a display, the anodic oxidation coat being formed on a surface thereof using the method of any one of claims 1 to 5.

7. An aluminum-containing member of a device for manufacturing a semiconductor or a display, the aluminum-containing member being coated with an anodic oxidation coat having a hardness of 370 to 425 Hv and a withstanding voltage of 1500 to 2000 V.

8. The aluminum-containing member of claim 7, wherein the aluminum-containing member is coated with the anodic oxidation coat having a corrosion resistance of 120 minutes or more.

9. An aluminum-containing member of a device for manufacturing a semiconductor or a display, the aluminum-containing member being coated with an anodic oxidation coat having a hardness of 370 to 425 Hv and a corrosion resistance of 120 minutes or more.

10. An aluminum-containing member of a device for manufacturing a semiconductor or a display, the aluminum-

containing member being coated with an anodic oxidation coat having a withstanding voltage of 1500 to 2000 V and a corrosion resistance of 120 minutes or more.