

ELECTROLYTE FOR FORMING ANODIC OXIDE FILM, METHOD OF FORMING
ANODIC OXIDE FILM, AND ANODIC OXIDE FILM AND MEMBER FOR
SEMICONDUCTOR DEVICE MANUFACTURED THEREBY

CROSS REFERENCE TO RELATED APPLICATION

The present application claims priority to Korean Patent Application No. 10-2024-0081462, filed June 21, 2024, the entire contents of which is incorporated herein for all purposes by this reference.

BACKGROUND

1. Technical Field

The present disclosure relates to an electrolyte for forming an anodic oxide film, a method of forming an anodic oxide film, and an anodic oxide film and a member for a semiconductor device manufactured thereby. More specifically, the present disclosure relates to an electrolyte capable of improving the corrosion resistance of an anodic oxide film, a method of forming an anodic oxide film, and an anodic oxide film and a member for a semiconductor device manufactured thereby.

2. Description of the Related Art

Vacuum plasma devices are widely used to manufacture semiconductor devices. However, vacuum plasma devices involve the use of high-temperature plasma and highly corrosive reactive gases, so problems with damage to parts or members within semiconductor manufacturing devices may occur.

Among such semiconductor manufacturing devices, showerhead

members made of aluminum are being used, for example, in chemical vapor deposition (CVD) devices. A showerhead member, a part constituting CVD devices, dry etching devices, and the like, is mounted on the upper or lower portion of a semiconductor wafer in a process chamber to manufacture semiconductors and serves to spray reactive gases for deposition and etching and control process temperature.

FIG. 1 is a diagram illustrating a typical showerhead.

A showerhead 10 is a structure installed in a process chamber to spray a reactive gas onto a semiconductor wafer so that the reactive gas can make even contact with the wafer. To spray the reactive gas, a plurality of spray nozzles 12 in fine hole form is formed in the showerhead 10.

In CVD processes, a corrosive gas containing a fluorine (F)-based halogen element serves as a reactive gas. Accordingly, such formed showerheads made of aluminum react with reactive gases, leading to corrosion. In other words, the reaction between aluminum and fluorine may result in the formation of an AlF_x layer, which may cause changes in the concentration of the reactive gas in a process chamber, leading to deterioration in initial process stabilization and a decrease in process efficiency. The long-term use of such corroded members causes the AlF_x layer to peel off from the member, generating particulate impurities in the process chamber. The cost of replacing expensive showerheads also results in increased process costs.

To prevent the members of semiconductor manufacturing devices from being corroded by reactive gases, the surface of such members is coated with an oxide film using methods such as anodic oxidation treatment, electroplating, vapor phase growth,

and the like. The showerhead 10 has a complex structure in which a plurality of fine holes is formed, so a coating is typically formed by chemical methods. Among all chemical coating methods, CVD or atomic layer deposition (ALD) are high-cost processes, so anodic oxidation (anodizing), a relatively low-cost chemical immersion method, is preferred.

Examples of anodic oxidation include methods using sulfuric acid, oxalic acid, a mixture of sulfuric acid and chromic acid, and the like. In the case of forming an anodic oxide film using such anodic oxidation, deviations in the hole size of each spray nozzle 12 of the showerhead may occur when the thickness of the anodic oxide film is increased to protect aluminum members. In addition, due to the high-temperature process, cracks may occur in the anodic oxide film.

When the thickness of an anodic oxide film is reduced to 1 μm or smaller to address these problems, corrosion resistance may deteriorate due to the structural characteristics of the anodic oxide film containing a porous layer. This is because, when forming an existing anodic oxide film to have a thickness of 500 nm or greater, a porous layer containing pores is formed in the anodic oxide film.

Ammonium borate, an alkaline component, and tartaric acid or malic acid, which are organic acids, can be used to form an anodic oxide film without a porous layer. However, defects occur inside a coating layer when forming the oxide film to have a thickness of 200 nm or greater with the use of ammonium borate. In addition, when the thickness of the oxide film becomes 300 nm or greater with the use of tartaric acid or malic acid, not only a porous layer is formed, but also an oxide film having a thickness of 500 nm or greater fails to be formed, which is

problematic.

In the case of using ammonium borate in the related art, an anodic oxide film has been formed using 4 to 15 wt% of ammonium borate under the following conditions: a supplied current in the range of 0.1 to 0.5 A/dm² and an electrolyte temperature in the range of 20°C to 60°C. In this case, a barrier layer having a thickness of 200 nm can be formed. However, when the thickness of the anodic oxide film becomes 200 nm or greater, there have been problems with multiple defects occurring within the film. In the case of using an electrolyte by mixing tartaric acid and malic acid, an anodic oxide film has been formed using 4 to 15 wt% of tartaric acid and malic acid under the following conditions: a supplied current in the range of 0.1 to 0.5 A/dm² and an electrolyte temperature in the range of 20°C to 60°C. In this case, when the thickness of the barrier layer becomes 300 nm or greater, a porous layer is formed, and a barrier layer having a thickness of 500 nm or greater fails to be formed, which has been problematic.

SUMMARY

One aspect of the present disclosure aims to improve the corrosion resistance of an anodic oxide film.

Another aspect of the present disclosure aims to provide an anodic oxide film without forming a porous layer.

One embodiment of the present disclosure provides an electrolyte for forming an anodic oxide film, the electrolyte including citric acid and an additive, wherein the citric acid accounts for 3.0 wt% or more and 6.0 wt% or less based on 100 wt% of the electrolyte, the additive includes one or more

selected from among tartaric acid, sulfuric acid, and sodium acetate, and the additive accounts for 0.5 wt% or more and 4.0 wt% or less based on 100 wt% of the electrolyte.

One embodiment of the present disclosure provides the electrolyte for forming the anodic oxide film, wherein the electrolyte includes 1.5 wt% or more and 2.5 wt% or less of one or more selected from among the tartaric acid, the sulfuric acid, and the sodium acetate.

One embodiment of the present disclosure provides the electrolyte for forming the anodic oxide film, wherein the electrolyte includes: about 6.0 wt % of the citric acid, about 1.0 wt% of the tartaric acid, 0 wt% or more and about 0.5 wt% or less of the sulfuric acid, and 0 wt% or more and about 0.5 wt% or less of the sodium acetate.

One embodiment of the present disclosure provides the electrolyte for forming the anodic oxide film, wherein the electrolyte includes: about 6.0 wt% of the citric acid, about 0.5 wt% of the sulfuric acid, and 0 wt% or more and about 0.5 wt% or less of the sodium acetate.

One embodiment of the present disclosure provides a method of forming an anodic oxide film, the method including the following steps: preparing an electrolyte including 3.0 wt% or more and 6.0 wt% or less of citric acid and 0.5 wt% or more and 4.0 wt% or less of an additive, based on 100 wt% of the electrolyte; and forming an anodic oxide film on a metal member by immersing the metal member in the electrolyte, wherein the additive includes one or more selected from among tartaric acid, sulfuric acid, and sodium acetate.

One embodiment of the present disclosure provides the method of forming the anodic oxide film, wherein the electrolyte

includes 1.5 wt% or more and 2.5 wt% or less of one or more selected from among the tartaric acid, the sulfuric acid, and the sodium acetate.

One embodiment of the present disclosure provides the method of forming the anodic oxide film, wherein the electrolyte includes: about 6.0 wt % of the citric acid, about 1.0 wt% of the tartaric acid, 0 wt% or more and about 0.5 wt% or less of the sulfuric acid, and 0 wt% or more and about 0.5 wt% or less of the sodium acetate.

One embodiment of the present disclosure provides the method of forming the anodic oxide film, wherein when forming the anodic oxide film, a current to be supplied to the electrolyte is 0.1 A/dm² or more and 1.0 A/dm² or less.

One embodiment of the present disclosure provides the method of forming the anodic oxide film, wherein when forming the anodic oxide film, the electrolyte has a temperature of 20°C or higher and 30°C or lower.

One embodiment of the present disclosure provides the method of forming the anodic oxide film, wherein the time required for forming the anodic oxide film is 100 minutes or more and 150 minutes or less.

One embodiment of the present disclosure provides the method of forming the anodic oxide film, wherein the anodic oxide film is formed to have a thickness of 500 nm or greater and 900 nm or smaller.

One embodiment of the present disclosure provides the method of forming the anodic oxide film, wherein the metal member is formed of aluminum or an aluminum alloy.

One embodiment of the present disclosure provides the method of forming the anodic oxide film, wherein the metal member

is a showerhead.

One embodiment of the present disclosure provides an anodic oxide film manufactured by the method described above.

One embodiment of the present disclosure provides the anodic oxide film, wherein the anodic oxide film includes a barrier layer without a porous layer, and the anodic oxide film has a thickness of 500 nm or greater and 900 nm or smaller.

One embodiment of the present disclosure provides a member for a semiconductor device, the member being manufactured by the method described above.

According to embodiments of the present disclosure, an anodic oxide film without forming a porous layer can be provided, thereby improving the corrosion resistance of a member for a semiconductor manufacturing device.

In addition, according to embodiments of the present disclosure, an anodic oxide film with improved corrosion resistance can be formed without increasing the thickness.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a diagram illustrating a typical showerhead;

FIG. 2 is a diagram schematically illustrating a typical anodic oxide film being formed on the surface of an aluminum member;

FIG. 3 is a flowchart illustrating a method of forming an anodic oxide film according to one embodiment of the present disclosure;

FIG. 4 is an image for one example of the present disclosure, the image taken using a focused ion beam scanning electron microscope (FIB-SEM); and

FIG. 5 is an FIB-SEM image for one comparative example.

DETAILED DESCRIPTION

Hereinafter, although embodiments disclosed herein will be described in detail with reference to the attached drawings, the same reference numerals will be assigned to refer to the same components regardless of numerals in the drawings, and redundant descriptions thereof will be omitted. Hereinafter, in the following description of the embodiments according to the present disclosure, when each layer (film), region, pattern, or structure is described as being formed "on" or "under" another substrate, layer (film), area, pad, or pattern, it can be "directly" formed "on" or "under" another substrate, layer (film), region, pad, or pattern or can be "indirectly" formed with other intervening layers being present. In addition, the criteria for determining whether each layer is on or under another are based on the drawings. In the drawings, the thickness and size of each layer are exaggerated, omitted, or schematically illustrated for convenience and clarity of explanation. In addition, the size of each component does not utterly reflect the actual size.

In this description, terms such as "including," "having," or "comprising" are used to specify the presence of certain features, integers, steps, operations, elements, or some or combinations thereof but should not be construed as precluding the presence or possibilities of one or more other features, integers, steps, operations, elements, or some or combinations thereof in addition to the foregoing.

Although terms such as first or second may be used to

describe various components, such components are not limited by these terms, and these terms are used only to distinguish one component from another.

In addition, in the following description of the embodiments disclosed herein, when a detailed description of related known technology is deemed to obscure the gist of the embodiments disclosed herein, such a detailed description will be omitted.

The attached drawings are provided only to help the understanding of the embodiments disclosed herein. Furthermore, the technical idea disclosed herein is not limited by the attached drawings and should be construed as covering all changes, modifications, equivalents, or alternatives that fall within the spirit and technical scope of the present disclosure.

Hereinafter, the embodiments of the present disclosure will be described in detail with reference to the drawings.

FIG. 2 is a diagram schematically illustrating a typical anodic oxide film being formed on the surface of an aluminum member.

Anodic oxidation, a method of forming a metal film, forms a film by primarily anodizing aluminum or an aluminum alloy and can be applied to magnesium, zinc, titanium, and the like. The description of the anodic oxidation will be based on a member formed of aluminum or an aluminum alloy (hereinafter referred to as "aluminum member") as one example.

Water molecules in electrolyte solutions made of sulfuric acid, oxalic acid, chromic acid, and the like are electrolyzed into hydrogen ions (H^+) and hydroxyl group (OH^-) by electrolysis. The resulting hydrogen ions move to a cathode, combine with electrons between the electrolyte solution and the surface of

the cathode, and are released as hydrogen gas. When an aluminum member 4 on which an anodic oxide film is to be formed is used as an anode and subjected to electrolysis, an anodic oxide film (Al_2O_3) is formed on the surface of the aluminum member 4.

Referring to FIG. 2, when immersing the aluminum member 4 in an electrolyte 1 and supplying current, a barrier layer 6 without pores 3 is formed. The electrolyte 1 may be made of sulfuric acid, oxalic acid, chromic acid, or a mixture thereof. When continuously supplying current to the aluminum member 4 on which the barrier layer 6 is formed, a porous layer 5 containing pores 3 grows. In this case, depending on the composition, temperature, and supplied current of the electrolyte 1, a structure made of pores 3 and cells 7 is formed between the uppermost interface 2 of the porous layer, being in contact with the electrolyte 1, and the barrier layer 6.

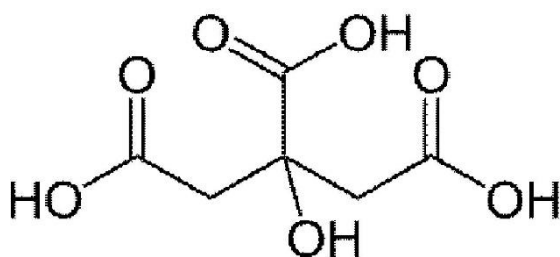
As described above, when the anodic oxide film contains pores 3, the corrosion resistance of the anodic oxide film deteriorates when the thickness of the anodic oxide film is reduced. Thus, to address problems of pore formation in the case of existing methods using sulfuric acid, oxalic acid, and a mixture of sulfuric acid and chromic acid, one embodiment of the present disclosure provides a method of forming an anodic oxide film for forming the barrier layer 6 having a thickness of 500 nm or greater without forming a porous layer in the anodic oxide film. In one embodiment of the present disclosure, an electrolyte in which a predetermined additive is mixed in citric acid is used.

FIG. 3 is a flowchart illustrating a method of forming an anodic oxide film according to one embodiment of the present disclosure.

According to one embodiment of the present disclosure, a member for a semiconductor device, on which the anodic oxide film is to be formed, is a member formed of a metal and may be an aluminum member, that is, a member formed of aluminum or an aluminum alloy. For example, the member for the semiconductor device may be a showerhead formed of aluminum or an aluminum alloy.

To form the anodic oxide film, according to one embodiment of the present disclosure, an electrolyte in which citric acid and an additive are mixed in deionized water is prepared (S100). Based on 100 wt% of the electrolyte, 3 wt% or more and 6 wt% or less of citric acid is mixed. When citric acid accounts for less than 3 wt%, an anodic oxide film having a great thickness may be challenging to form under low current conditions. When citric acid accounts for more than 6 wt%, surface defects and cross-sectional defects are highly likely to occur, making control over the thickness of the anodic oxide film challenging.

Citric acid has the chemical formula $C_6H_8O_7$, and the structural formula thereof is shown below.



As the additive, tartaric acid, sulfuric acid, or sodium acetate may be used. Alternatively, a mixture of two or more of the foregoing may be used. Based on 100 wt% of the electrolyte, 0.5 wt% or more and 4.0 wt% or less, preferably 1.5 wt% or more and 2.5 wt% or less, and more preferably 1.5 wt% or more and 2.0 wt% or less of the additive including one

or more selected from among tartaric acid, sulfuric acid, or sodium acetate is mixed. When the additive accounts for less than 0.5 wt%, a barrier layer having a thickness of 500 nm or greater may be challenging to form. When the additive accounts for more than 4.0 wt%, the characteristics of the barrier layer of the anodic oxide layer may deteriorate, leading to deterioration in the corrosion resistance of the film.

The prepared electrolyte is supplied to an electrolysis tank, and a metal member, such as a showerhead formed of aluminum or an aluminum alloy, is immersed in the electrolyte, followed by forming an anodic oxide film (S102). In one embodiment of the present disclosure, a current of 0.1 A/dm² or more and 1.0 A/dm² or less may be supplied to form the anodic oxide film. When the supplied current is less than 0.1 A/dm², an anodic oxide film having a thickness of 500 nm or greater may be challenging to form. When the supplied current exceeds 1.0 A/dm², the reaction between aluminum and acid increases, so the growth rate of the anodic oxide film may increase, leading to defects.

The electrolyte may have a temperature of 20°C or higher and 30°C or lower. When the temperature of the electrolyte is lower than 20°C, the growth rate of the anodic oxide film may be reduced. When the temperature of the electrolyte exceeds 30°C, the growth rate of the anodic oxide film may be excessively increased, leading to defects. In addition, an increase in the surface roughness of the anodic oxide film makes the formation of a uniform film challenging. Furthermore, the treatment process time required for forming the anodic oxide film may be 1 minute or more and 150 minutes or less, which is preferably 100 minutes or more and 150 minutes or less and more preferably 120 minutes or more and 140 minutes or less, or may be about

130 minutes. In this case, "about" may refer to a deviation of $\pm 5\%$.

In one embodiment of the present disclosure, tartaric acid and sodium acetate, serving as the additive, improve the electrical conductivity of the electrolyte. Thus, by efficiently delivering current, an anodic oxide film without a porous layer may be formed. In addition, sodium acetate is a weak base, so control over the acidity of the electrolyte allows the anodic oxide film to be formed uniformly and evenly. When the content of sulfuric acid is high, oxidizing properties may be improved, enabling a uniform film to be formed while having a great thickness. However, a porous layer may be formed, leading to deterioration in corrosion resistance. Therefore, in one embodiment of the present disclosure, a small amount of sulfuric acid is added to promote oxidation and ensure uniform film growth, thereby increasing the thickness of the barrier layer.

According to one embodiment of the present disclosure, when forming the anodic oxide film, control over a point in time that the porous layer is formed in the barrier layer prevents the growth of the porous layer and enables the barrier layer to grow uniformly. In addition, the anodic oxide film is formed to have a thickness of 500 nm or greater through control over the growth of the barrier layer and the porous layer, thus keeping an AlF_x layer from being formed by the reaction between the aluminum member and a reactive gas, such as fluorine, to prevent the aluminum member from corrosion. According to one embodiment of the present disclosure, the anodic oxide film having a thickness of 500 nm or greater and 900 nm or smaller, which is preferably 500 nm or greater and 800 nm or smaller, may be formed without

forming the porous layer. In addition, the barrier layer having a thickness greater than those of existing barrier layers by about 1.5 times or more may be formed without forming the porous layer.

Table 1 shows the conditions of examples and comparative examples of the present disclosure.

[Table 1]

Classification	Electrolyte (wt%)				Process conditions		
	Citric acid	Tartaric acid	Sulfuric acid	Sodium acetate	Current	Temperature	Time
Example 1	6.0	1.0	0	0	0.2	30	150
Example 2	6.0	0	0.5	0	0.2	30	150
Example 3	6.0	1.0	0.5	0	0.2	30	150
Example 4	6.0	0	0.5	0.5	0.2	30	150
Example 5	6.0	0	0	0.5	0.2	30	150
Example 6	6.0	1.0	0.5	0.5	0.2	30	150
Example 7	3.0	3.0	0.5	0.5	0.2	30	100
Comparative Example 1	6.0	0	0	0	0.2	30	150
Comparative Example 2	0	6.0	0	0	0.2	30	70
Comparative Example 3	0	0	12.0	0	1.0	0	2
Comparative Example 4	0	1.0	6.0	0.5	0.2	30	10

In Table 1, the units of the current, temperature, and time are A/dm², °C, and minutes, respectively. The thickness of each barrier layer was measured using an FIB-SEM.

The detailed descriptions of the examples of the present disclosure are as follows.

[Example 1]

An aluminum alloy Al6061 was cut to 10 mm in length, 100 mm in width, and 10 mm in height and prepared as a specimen on which an anodic oxide film was to be formed. The specimen was

not subjected to separate polishing treatment. Anodic oxidation was conducted using such a prepared specimen as an anode (+) and lead (Pb) as a cathode (-).

In Example 1, 6.0 wt% of citric acid and 1.0 wt% of tartaric acid were mixed in deionized water to prepare an electrolyte. The specimen was immersed in the electrolyte to conduct the anodic oxidation for 150 minutes under the following conditions: a supplied current of 0.2 A/dm² and an electrolyte temperature of 30°C.

[Example 2]

The same specimen as that in Example 1 was used. In Example 2, 6.0 wt% of citric acid and 0.5 wt% of sulfuric acid were mixed in deionized water to prepare an electrolyte. The specimen was immersed in the electrolyte to conduct anodic oxidation for 150 minutes under the following conditions: a supplied current of 0.2 A/dm² and an electrolyte temperature of 30°C.

[Example 3]

The same specimen as that in Example 1 was used. In Example 3, 6.0 wt% of citric acid, 1.0 wt% of tartaric acid, and 0.5 wt% of sulfuric acid were mixed in deionized water to prepare an electrolyte. The specimen was immersed in the electrolyte to conduct anodic oxidation for 150 minutes under the following conditions: a supplied current of 0.2 A/dm² and an electrolyte temperature of 30°C.

[Example 4]

The same specimen as that in Example 1 was used. In Example 4, 6.0 wt% of citric acid, 0.5 wt% of sulfuric acid, and 0.5

wt% of sodium acetate were mixed in deionized water to prepare an electrolyte. The specimen was immersed in the electrolyte to conduct anodic oxidation for 150 minutes under the following conditions: a supplied current of 0.2 A/dm² and an electrolyte temperature of 30°C.

[Example 5]

The same specimen as that in Example 1 was used. In Example 5, 6.0 wt% of citric acid and 0.5 wt% of sodium acetate were mixed in deionized water to prepare an electrolyte. The specimen was immersed in the electrolyte to conduct anodic oxidation for 150 minutes under the following conditions: a supplied current of 0.2 A/dm² and an electrolyte temperature of 30°C.

[Example 6]

The same specimen as that in Example 1 was used. In Example 6, 6.0 wt% of citric acid, 1.0 wt% of tartaric acid, 0.5 wt% of sulfuric acid, and 0.5 wt% of sodium acetate were mixed in deionized water to prepare an electrolyte. The specimen was immersed in the electrolyte to conduct anodic oxidation for 150 minutes under the following conditions: a supplied current of 0.2 A/dm² and an electrolyte temperature of 30°C.

[Example 7]

The same specimen as that in Example 1 was used. In Example 7, 3.0 wt% of citric acid, 3.0 wt% of tartaric acid, 0.5 wt% of sulfuric acid, and 0.5 wt% of sodium acetate were mixed in deionized water to prepare an electrolyte. The specimen was immersed in the electrolyte to conduct anodic oxidation for 100 minutes under the following conditions: a supplied current of

0.2 A/dm² and an electrolyte temperature of 30°C.

In the comparative examples for comparison with the examples of the present disclosure, the same specimen as that in Example 1 was used. When using sulfuric acid in the comparative examples, anodic oxidation treatment was conducted using an electrolyte to which 170 to 190 g/L of sulfuric acid was added, under the following conditions: a supplied current in the range of 0.5 to 2.5 A/dm² and an electrolyte temperature in the range of -4°C to 20°C. Such conditions are oxidation treatment conditions typically required for semiconductor manufacturing devices, that is, anodic oxidation treatment conditions to obtain an anodic oxide film having a thickness in the range of 10 to 100 μm. When forming an anodic oxide film under such conditions, a porous layer is formed even in the case of a thin anodic oxide film whose thickness is at a level of 1.0 μm, leading to deterioration in corrosion resistance.

The detailed descriptions of the comparative examples are as follows.

[Comparative Example 1]

In Comparative Example 1, 6.0 wt% of citric acid was mixed in deionized water to prepare an electrolyte. The specimen was immersed in the electrolyte to conduct anodic oxidation for 150 minutes under the following conditions: a supplied current of 0.2 A/dm² and an electrolyte temperature of 30°C.

[Comparative Example 2]

In Comparative Example 2, 6.0 wt% of tartaric acid was mixed in deionized water to prepare an electrolyte. The specimen was immersed in the electrolyte to conduct anodic oxidation for

70 minutes under the following conditions: a supplied current of 0.2 A/dm² and an electrolyte temperature of 30°C.

[Comparative Example 3]

In Comparative Example 3, 12.0 wt% of sulfuric acid was mixed in deionized water to prepare an electrolyte. The specimen was immersed in the electrolyte to conduct anodic oxidation for 2 minutes under the following conditions: a supplied current of 1.0 A/dm² and an electrolyte temperature of 0°C.

[Comparative Example 4]

In Comparative Example 4, 1 wt% of tartaric acid, 6.0 wt% of sulfuric acid, and 0.5 wt% of sodium acetate were mixed in deionized water to prepare an electrolyte. The specimen was immersed in the electrolyte to conduct anodic oxidation for 10 minutes under the following conditions: a supplied current of 0.2 A/dm² and an electrolyte temperature of 30°C.

Crack occurrence tests, corrosion resistance tests, and peel tests were conducted for the specimens of the examples and comparative examples described above.

The crack occurrence tests were conducted through heat treatment at a temperature of 300°C, and the peel tests involved diluting NaOH to 1.0 wt% and HCl to 10.0 wt% and then dipping each anodized specimen under a room-temperature condition to measure the time during which current flowed.

HCl bubble tests were conducted for the corrosion resistance tests. The HCl bubble tests involved attaching a PVC pipe with a diameter of 2.0 mm to each specimen using a sealant and then injecting 3.0 mL of HCl diluted to 1.0 wt% into the

pipe to measure the time at which bubbles were initially generated. The anodic oxide film was peeled off by HCl, and the time for HCl and aluminum to react and form bubbles was measured, thus enabling the evaluation of the adhesion between the anodic oxide film and the aluminum member. In the HCl bubble tests, the anodic oxide films formed on each specimen of the examples and the comparative examples were formed identically to have a total thickness of 1,000.0 nm. In this case, some anodic oxide film of the comparative examples includes a barrier layer and a porous layer.

Table 2 shows the test results.

[Table 2]

Classification	Crack occurrence test	Peel test (minutes)	HCl bubble test (minutes)	Barrier layer thickness (nm)
Example 1	X	5	18	600
Example 2	X	5	18	600
Example 3	X	6	22	700
Example 4	X	6	21	750
Example 5	X	4	15	550
Example 6	X	8	26	800
Example 7	X	5	17	600
Comparative Example 1	X	5	14	450
Comparative Example 2	X	5	13	350
Comparative Example 3	o	1	8	Not formed
Comparative Example 4	o	1	8	Not formed

In Table 2, "X" in the crack occurrence tests indicates that cracks do not occur, and "o" indicates that the cracks occur.

Referring to Table 2, the barrier layers in Examples 1 to

7 were formed to have a thickness of 500 nm or greater. In addition, the peel tests show the results of 4 minutes or more, and the HCl bubble tests show the results of 15 minutes or more, meaning that excellent characteristics are exhibited.

FIG. 4 is an FIB-SEM image for one example of the present disclosure, and FIG. 5 is an FIB-SEM image for one comparative example.

Specifically, FIG. 4 is a cross-sectional image for Example 6, and FIG. 5 is a cross-sectional image for Comparative Example 3.

Referring to FIG. 4, it is confirmed that, in the case of Example 6 of the present disclosure, a porous layer is not formed, and the barrier layer is formed to have a thickness of about 510 nm or greater. On the other hand, referring to FIG. 5, it is confirmed that, in Comparative Example 3, a plurality of pores is formed vertically within the anodic oxide film (arrow parts in FIG. 5).

Although the present disclosure has been described hereinabove with certain details, such as specific components, as well as limited embodiments and drawings, these are provided only to help a more comprehensive understanding of the present disclosure, and the present disclosure is not limited to the above embodiments. In addition, those skilled in the art to which the present disclosure pertains will be able to make various modifications and variations without departing from the essential characteristics of the present disclosure. Therefore, it should be noted that the spirit of the present disclosure is not limited to the embodiments described above. Rather, the scope of the present disclosure should be construed as covering not only the appended claims but also all modifications and

equivalents thereof. Furthermore, each of the embodiments may be applied in combination with each other as needed.

CLAIMS

1. An electrolyte for forming an anodic oxide film, the electrolyte comprising:

citric acid; and

an additive,

wherein the citric acid accounts for 3.0 wt% or more and 6.0 wt% or less based on 100 wt% of the electrolyte,

the additive comprises one or more selected from among tartaric acid, sulfuric acid, and sodium acetate, and

the additive accounts for 0.5 wt% or more and 4.0 wt% or less based on 100 wt% of the electrolyte.

2. The electrolyte of claim 1, wherein the electrolyte comprises 1.5 wt% or more and 2.5 wt% or less of one or more selected from among the tartaric acid, the sulfuric acid, and the sodium acetate.

3. The electrolyte of claim 1, wherein the electrolyte comprises:

6.0 wt % of the citric acid;

1.0 wt% of the tartaric acid;

0 wt% or more and 0.5 wt% or less of the sulfuric acid;

and

0 wt% or more and 0.5 wt% or less of the sodium acetate.

4. The electrolyte of claim 1, wherein the electrolyte comprises:

6.0 wt% of the citric acid;

0.5 wt% of the sulfuric acid; and

0 wt% or more and 0.5 wt% or less of the sodium acetate.

5. A method of forming an anodic oxide film, the method comprising:

preparing an electrolyte comprising 3.0 wt% or more and 6.0 wt% or less of citric acid and 0.5 wt% or more and 4.0 wt% or less of an additive, based on 100 wt% of the electrolyte; and

forming an anodic oxide film on a metal member by immersing the metal member in the electrolyte,

wherein the additive comprises one or more selected from among tartaric acid, sulfuric acid, and sodium acetate.

6. The method of claim 5, wherein the electrolyte comprises 1.5 wt% or more and 2.5 wt% or less of one or more selected from among the tartaric acid, the sulfuric acid, and the sodium acetate.

7. The method of claim 5, wherein the electrolyte comprises:

6.0 wt % of the citric acid;

1.0 wt% of the tartaric acid;

0 wt% or more and 0.5 wt% or less of the sulfuric acid;

and

0 wt% or more and 0.5 wt% or less of the sodium acetate.

8. The method of claim 5, wherein when forming the anodic oxide film, a current to be supplied to the electrolyte is 0.1 A/dm² or more and 1.0 A/dm² or less.

9. The method of claim 5, wherein when forming the anodic oxide film, the electrolyte has a temperature of 20°C or higher and 30°C or lower.

10. The method of claim 5, wherein a time required for forming the anodic oxide film is 100 minutes or more and 150 minutes or less.

11. The method of claim 5, wherein the anodic oxide film is formed to have a thickness of 500 nm or greater and 900 nm or smaller.

12. The method of claim 5, wherein the metal member is formed of aluminum or an aluminum alloy.

13. The method of claim 12, wherein the metal member is a showerhead.

14. An anodic oxide film manufactured by the method of any one of claims 5 to 13.

15. The anodic oxide film of claim 14, wherein the anodic oxide film comprises a barrier layer without a porous layer, and the anodic oxide film has a thickness of 500 nm or greater and 900 nm or smaller.

16. A member for a semiconductor device, the member being manufactured by the method of any one of claims 5 to 13.

17. The electrolyte of claim 1, wherein the anodic oxide film comprises no porous layer, and

the anodic oxide film has a thickness of 500 nm or greater and 900 nm or smaller.

18. The method of claim 5, wherein the anodic oxide film comprises no a porous layer, and

the anodic oxide film has a thickness of 500 nm or greater and 900 nm or smaller.