# SURFACE TREATMENT MATERIAL FOR SEMICONDUCTOR MANUFACTURING SYSTEM AND METHOD FOR PRODUCING SAME

## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

The invention relates to a semiconductor manufacturing system's surface treatment material for use in a system (hereinafter referred to as a semiconductor manufacturing system) wherein film deposition, etching, and so forth are carried out for manufacturing a semiconductor, and a liquid crystal display, and a method for producing the same.

### 2. Description of the Related Art

Since a corrosive gas serving as a reactive gas, an etching gas, and a cleaning gas, containing halogen such as Cl, F, Br, is introduced into a vacuum chamber used in the semiconductor manufacturing system (vacuum film-deposition system) such as a CVD system, a PVD system, a dry etching system, corrosion resistance against the corrosive gas (hereinafter referred to as gas corrosion resistance) is required of the vacuum chamber. Further, because halogen plasma is often generated inside the vacuum chamber, corrosion resistance against the plasma (hereinafter referred to as plasma resistance) is regarded important. And a vacuum chamber fabricated of aluminum or aluminum alloy, light in weight, and excellent in thermal conductivity, has lately been adopted in such applications as described.

However, since aluminum or aluminum alloy does not have sufficient corrosion resistance against gas, and corrosion resistance against plasma, various surface modification technologies for enhancement in

those characteristics have since been proposed. For example, there have been disclosed technologies whereby fluorination is applied to an aluminum substrate or an aluminum alloy substrate, as technologies for achieving enhancement in the corrosion resistance against gas, and the corrosion resistance against plasma (refer to Patent Documents 1 to 8, respectively).

More specifically, in Patent Document 1, there has been disclosed a method for forming a corrosion-resistant protective coating to form an aluminum protective layer containing 3 to 18 mass% of fluorine. In Patent Document 2, there has been disclosed a corrosion-resistant protective coating containing 3 to 18 mass% of fluorine, and a method for producing the same. In Patent Document 3, there has been disclosed a corrosion-resistant aluminum article having a magnesium halide composed of magnesium fluoride. In Patent Document 4, there have been disclosed a processing system wherein an aluminum based material in contact with an atmosphere inside a process chamber has its surface replaced with fluorine in advance to be then coated, and a method for coating the aluminum based material.

In Patent Document 5, a metallic material or a metallic coating, having a surface provided with a fluorinated layer not less than 1 μm thick, formed thereon, after forced oxidation of the surface, and a method for fluorination. In Patent Documents 6, 7, respectively, there have been disclosed aluminum alloy for use in coating-forming process, having a coating formed by fluorination, an aluminum alloy material excellent in corrosion resistance, and a method for producing the same.

Further, in Patent Document 8, there have been disclosed a vacuum

chamber material including a layer composed mainly of aluminum oxide, and aluminum fluoride, and a method for producing the same.

[Patent Document 1] JP - B No. 2831488

[Patent Document 2] JP - A No. 4 (1992) - 263093

[Patent Document 3] JP - A No. 8 (1996) - 181048

[Patent Document 4] JP - A No. 7 (1995) - 273053

[Patent Document 5] JP - A No. 11 (1999) - 92912

[Patent Document 6] JP - A No. 2003 - 119539

[Patent Document 7] JP - A No. 2003 - 119540

[Patent Document 8] JP - A No. 11 (1999) - 61410

However, a conventional material obtained by applying fluorination to an aluminum substrate or an aluminum alloy substrate, for use in the semiconductor manufacturing system, and so forth, has a problem described hereunder.

Surfaces of an anodic oxidation coating, and so forth, formed over a substrate, undergo fluorination upon application of a fluorination process, however, there are times when electrical properties of the material undergo a change with time during use of the semiconductor manufacturing system by the agency of fluorine at the time of the fluorination, thereby causing an optimum film deposition condition to be varied. In order to prevent occurrence of such a problem, it is effective to form a stable fluorinated layer containing fluorine in high concentration, however, conventional technologies have had a problem in that it has been difficult to form the fluorinated layer containing fluorine in high concentration.

## SUMMARY OF THE INVENTION

The present invention has been developed in view of the problems described in the foregoing, and it is an object of the invention to provide a surface treatment material for use in a semiconductor manufacturing system, capable of improving the time change, occurring to electrical properties of the material during use of the semiconductor manufacturing system, and a method for producing the same.

In order to solve those problems, the inventor, et al. of the present invention have carried out studies on the following matters.

With the surface-treatment material for use in the semiconductor manufacturing system, there are occasions when sealing is applied thereto in an attempt to enhance chemical stability in an anodic oxidation coating formed on a substrate, and it has been presumed in the past that the surface of the anodic oxidation coating becomes insusceptible to fluorination due to application of the sealing. However, the inventor, et al. have found out as a result of strenuous studies that the surface of the anodic oxidation coating with the sealing applied thereto is, in reality, prone to fluorination with greater ease, and that a stable fluorinated layer with fluorine in high concentration can be formed on the surface of the anodic oxidation coating, thereby having completed the present invention.

More specifically, a surface-treatment material of a semiconductor manufacturing system, according to the invention is a surface-treatment material of a semiconductor manufacturing system, for use in a semiconductor manufacturing system, and the surface-treatment material includes a substrate made of aluminum, or aluminum alloy, an

anodic oxidation coating formed over the surface of the substrate, with sealing applied thereto, and a fluorine-enriched layer formed over the surface of the anodic oxidation coating, wherein fluorine concentration in the fluorine-enriched layer is not less than 1 mass%.

With the surface-treatment material of the semiconductor manufacturing system, stability in electrical characteristics of the surface-treatment material is enhanced by the formation of a stable fluorine-enriched layer with fluorine in high concentration, over the surface of the anodic oxidation coating. Accordingly, time-dependent variation in the electrical characteristics during operation of the semiconductor manufacturing system can be inhibited.

A method for producing a surface-treatment material of a semiconductor manufacturing system, according to the invention, is a method for producing a surface-treatment material of a semiconductor manufacturing system, for use in a semiconductor manufacturing system, and the method includes an anodic oxidation coating forming step, a sealing step, and a fluorine-enriched layer forming step.

With the method for producing the surface-treatment material of the semiconductor manufacturing system, an anodic oxidation coating is formed over the surface of a substrate made of aluminum, or aluminum alloy in the an anodic oxidation coating forming step, sealing is applied to the anodic oxidation coating in the sealing step, and a fluorine-enriched layer with fluorine enriched to a fluorine concentration not less than 1 mass% is formed over the surface of the anodic oxidation coating with the sealing applied thereto in the fluorine-enriched layer forming step.

Further, in the fluorine-enriched layer forming step, the fluorine-enriched layer is preferably formed by immersing the substrate with the anodic oxidation coating formed thereon, subjected to the sealing, in an aqueous solution containing fluorine.

With the adoption of the method for producing the surface-treatment material of the semiconductor manufacturing system, the fluorine-enriched layer can be formed with ease, and fluorine concentration can be controlled to not less than 1 mass% with greater ease.

With the surface-treatment material of the semiconductor manufacturing system according to the invention, stability in the electrical characteristics of the surface-treatment material can be enhanced. Accordingly, time-dependent variation in the electrical characteristics during operation of the semiconductor manufacturing system can be inhibited, so that the film deposition condition, and so forth, in the semiconductor manufacturing system, are stabilized. Furthermore, the gas corrosion resistance, and the plasma resistance can be enhanced.

With the method for producing the surface-treatment material of the semiconductor manufacturing system, according to the invention, the stable fluorine-enriched layer with fluorine in high concentration can be formed over the surface of the anodic oxidation coating in the fluorine-enriched layer forming step by applying the sealing to the anodic oxidation coating in the sealing step. By so doing, it is possible to produce the surface-treatment material of the semiconductor manufacturing system, having enhanced stability in the electrical

characteristics thereof. Further, it is possible to produce the surface-treatment material of the semiconductor manufacturing system, excellent in the gas corrosion resistance, and the plasma resistance.

Furthermore, since the fluorine-enriched layer is formed by immersing the substrate with the anodic oxidation coating formed thereon, subjected to the sealing, in the aqueous solution containing fluorine, the fluorine-enriched layer can be formed with ease, and fluorine concentration can be controlled with greater ease.

**BRIEF DESCRIPTION OF THE DRAWINGS**

Embodiment(s) of the present invention will be described in detail based on the following figures, wherein:

Fig. 1 is a sectional view schematically showing a configuration of a surface-treatment material of a semiconductor manufacturing system; and

Fig. 2 is a sectional view schematically showing a structure of an anodic oxidation coating of the surface-treatment material of the semiconductor manufacturing system.

**DESCRIPTION OF THE PREFERRED EMBODIMENTS**

Now, a surface-treatment material for use in a semiconductor manufacturing system, and a method for producing the same, according to the present invention, are described in detail with reference to the accompanying drawings. Fig. 1 is a sectional view schematically showing a configuration of a surface-treatment material of a semiconductor manufacturing system, and Fig. 2 is a sectional view schematically

showing a structure of an anodic oxidation coating of the surface-treatment material of the semiconductor manufacturing system.

First, there is described hereinafter the surface-treatment material for use in the semiconductor manufacturing system.

**<<Surface-treatment material for use in a semiconductor manufacturing system>>**

As shown in Fig. 1, a surface- treatment material 1 for use in a semiconductor manufacturing system (hereinafter referred to merely as a surface-treatment material 1, where appropriate) includes a substrate 2 made of aluminum, or aluminum alloy (hereinafter referred to merely as aluminum alloy, where appropriate), an anodic oxidation coating 3 formed over the surface of the substrate 2, with sealing applied thereto, and a fluorine-enriched layer 4 formed over the surface of the anodic oxidation coating 3. And fluorine concentration in the fluorine-enriched layer 4 is not less than 1 mass%.

In this connection, the semiconductor manufacturing system according to the present invention refers to a system used in the step of manufacturing a semiconductor, a liquid crystal display, and so forth (film deposition, etching, and so forth), that is, a film-deposition system including, for example, a CVD system, PVD system, dry etching system, and so forth.

Now, respective constituents of the surface-treatment material 1 are described hereinafter.

**<Substrate>**

For the substrate 2 of the surface- treatment material 1, use is

made of an aluminum alloy (aluminum or aluminum alloy). For aluminum, use is made of, for example, pure aluminum of 1000 series while the aluminum alloy includes, for example, Al-Cu-Mg alloy of 2000 series, Al-Mn alloy of 3000 series, Al-Si alloy of 4000 series, Al-Mg alloy of 5000 series, Al-Mg-Si alloy of 6000 series, Al-Zn-Mg alloy of 7000 series, and so forth.

In this connection, in the case where an aluminum alloy containing Mg is used for the substrate 2, Mg content is preferably not less than 0.1 mass%, more preferably not less than 0.3 mass%. It is preferable to use 5000 series aluminum alloy, and 6000 series aluminum alloy, as, for example, wall material of a chamber, in particular, among the surface-treatment material 1, because those alloys are excellent in terms of mechanical strength, thermal conductivity, electrical conductivity, gas corrosion resistance, plasma resistance, and so forth. In the case of the 5000 series aluminum alloy, alloy composition at least includes preferably not more than 0.5 mass% of Si, and 0.5 to 6.0 mass% of Mg while in the case of the 6000 series aluminum alloy, alloy composition at least includes preferably 0.2 to 1.2 mass% of Si, and 0.4 to 1.5 mss % of Mg. However, there is no particular limitation to the aluminum alloy for use in the substrate 2, and use may be made of any aluminum alloy that can be generally used in the semiconductor manufacturing system.

The substrate 2 varies in form depending on an application location of the surface- treatment material 1, but is preferably formed of rolled material, extruded material, or forged material. Accordingly, the substrate 2 is fabricated by the conventional known method of rolling,

extrusion, or forging.

**<Anodic oxidation coating>**

As shown in Fig. 2, the anodic oxidation coating 3 is a cell assembly having a basic structure composed of cells 8, each in the shape of a hexagonal pillar, having a pore 5 at the center thereof, being a composite coating with a porous layer (a portion of the anodic oxidation coating 3, with the pores 5 provided therein) 6, stacked on a barrier layer (a layer without the pores 5, interjacent between the porous layer 6, and the substrate 2) 7. Further, at least a portion of the anodic oxidation coating 3 is preferably boehmite, or pseudo-boehmite. Further, if the anodic oxidation coating 3 described as above is formed over a surface of the substrate 2, this will provide the surface-treatment material 1 according to the invention with the gas corrosion resistance, and the plasma resistance. Herein, the surface of the substrate 2 includes not only the entire surface of the substrate 2 but also only a portion thereof, with the anodic oxidation coating 3 thereon. For example, if the anodic oxidation coating 3 is formed on at least a surface of the substrate 2, in contact with a wafer, this will suffice when the surface-treatment material 1 is used as a lower electrode of a CVD system. In Fig. 2, the fluorine-enriched layer 4 to be described later is not shown.

Further, there is no particular limitation to film-thickness of the anodic oxidation coating 3, however, in order to enable the anodic oxidation coating 3 to exhibit satisfactory gas corrosion resistance, and plasma resistance, it is recommendable that the film-thickness thereof, in combination with a thickness of the fluorine-enriched layer

4, is preferably not less than 1 μm, more preferably not less than 5 μm, and still more preferably not less than 10 μm. However, if the film-thickness of the anodic oxidation coating 3 is excessively large, cracking is prone to occur to the coating owing to effects of internal stress, and so forth, and further causing the coating to be susceptible to exfoliation, so that the film-thickness including the thickness of the fluorine-enriched layer 4 is preferably not more than 100 μm, more preferably not more than 80 μm, and still more preferably not more than 70 μm. Further, control of the film-thickness can be effected by controlling an anodizing condition to be described later in the present description.

The anodic oxidation coating 3 is subjected to sealing as described later in the present description. The sealing is effective in the formation of the fluorine-enriched layer 4, and the fluorine-enriched layer 4 with fluorine in high concentration not less than 1 mass% can be formed on the surface of the anodic oxidation coating 3 by fluorination of the anodic oxidation coating 3 as described later.

**<Fluorine-enriched Layer>**

The fluorine-enriched layer 4 is a layer with fluorine in high concentration, formed by applying fluorination as described later to the substrate 2 with the anodic oxidation coating 3 formed thereon (to the anodic oxidation coating 3). With the present invention, fluorine concentration in the fluorine-enriched layer 4 is set to not less than 1 mass%. Stability in electrical characteristics of the surface-treatment material 1 is enhanced by the formation of the

fluorine-enriched layer 4 containing fluorine in high concentration not less than 1 mass%.

Further, measurement of fluorine concentration can be executed by, for example, EPMA analysis of the surface of the anodic oxidation coating 3 including the fluorine-enriched layer 4. In this case, "fluorine concentration 1 mass%" indicates a value obtained by the EPMA analysis of the surface of the anodic oxidation coating 3 including the fluorine-enriched layer 4.

Herein, "stability in electrical characteristics" means whether or not a leak current is low in value and stable. If the electrical characteristics are stable, occurrence of abnormal discharge (arcing, nonuniformity of the deposited film) by a CVD process can be inhibited, so that deviation from specification, such as occurrence of arcing, and nonuniformity of the deposited film, can be preemptively prevented. The abnormal discharge can be inhibited by raising voltage resistance of the anodic oxidation coating 3 (that is, by lowering the leak current). $Al_2O_3$ as the main constituent of the anodic oxidation coating 3 is an insulator, however, crystalline water is present in the anodic oxidation coating 3, so that the crystalline water acts as a carrier, thereby enabling electron transfer. Current caused by the electron transfer is a leak current, and if the leak current is excessively large, this will cause occurrence of the abnormal discharge.

More specifically, if fluorine concentration in the fluorine-enriched layer 4 is not less than 1 mass%, it is possible to inhibit time-dependent variation in the electrical characteristics during operation of the semiconductor manufacturing system, so that the

film deposition condition, and so forth, in the semiconductor manufacturing system, are stabilized.

If the fluorine concentration of the fluorine-enriched layer 4 is less than 1 mass%, it is not possible to obtain an advantageous effect of enhancement in the stability in the electrical characteristics. Accordingly, the fluorine concentration is set to not less than 1 mass%. There is no particular limitation to the upper limit of the fluorine concentration, however, if the fluorine concentration is in excess of about 50 mass%, this will cause the advantageous effect of fluorine content to reach saturation. Accordingly, the upper limit of the fluorine concentration is preferably set to not more than about 50 mass%.

Now, a method for producing a surface-treatment material for a semiconductor manufacturing system is described hereinafter with reference to Fig. 1, as appropriate.

**<<Method for producing a surface-** treatment **material for a semiconductor manufacturing system>>**

The method for producing the surface-treatment material 1 for a semiconductor manufacturing system includes an anodic oxidation coating forming step, a sealing step, and a fluorine-enriched layer forming step.

The respective steps are described hereinafter.

**<Anodic oxidation coating forming step>**

The anodic oxidation coating forming step is a step for forming the anodic oxidation coating 3 by anodizing, over the surface of the substrate 2 made of aluminum, or aluminum alloy.

In anodizing, an aluminum alloy is immersed in an electrolyte,

and a voltage is applied thereto to thereby form an aluminum oxide film on the surface of the aluminum alloy by taking advantage of an oxidation phenomenon attributable to oxygen generated at an anode. Further, with the anodizing, a variety of methods including a direct current method, an alternating current method, and a AC- DC overlapping method are used as an energization method for anodizing.

There is no particular limitation to kinds of solution for use in electrolyzation at the anodizing, and use may be made of any inorganic acid selected from the group consisting of sulfuric acid, phosphoric acid, chromic acid, boric acid, phosphorous acid, sulfurous acid, and so forth, and any organic acid selected from the group consisting of formic acid, oxalic acid, sulfamic acid, malonic acid, maleic acid, tartaric acid, and so forth. However, from the viewpoint of optionally controlling an electrolytic voltage for anodizing in a wide range, it is preferable to use a solution containing not less than 1 g / L of oxalic acid or phosphoric acid. Furthermore, if at least one kind of element (hereinafter referred to as an addition element) selected from the group consisting of S, N, P, F, B, and C is contained in the solution, or a compound having those addition elements is added to the solution, this will cause the gas corrosion resistance, plasma resistance, and so forth to be enhanced, so that the respective elements, in amounts not less than 1 g / L, is more preferably added. When the addition elements are to be contained in the electrolyte, a method for adding the inorganic acid, or the organic acid may be adopted, and by use of, for example, a combined solution (containing C, and S) of oxalic acid, and sulfuric acid, a combined solution (containing S, P) of sulfuric acid, and

phosphoric acid, and a combined solution (containing S, B, C) of sulfuric acid, boric acid, and maleic acid, those elements can be contained in an electrolytic solution.

There is no particular limitation to a bath temperature (liquid temperature) of the electrolyte at the time of anodizing, and the bath temperature may be 0°C, however, in the case of using, for example, an oxalic acid solution in order to obtain a sufficient coating-growth speed to thereby enhance anodizing efficiency, the bath temperature is preferably set to not lower than 10°C. Furthermore, in order to render the coating insusceptible to dissolvent to thereby render the coating insusceptible to having a defect, and to form a desired anodic oxidation coating with greater ease, the bath temperature is preferably set to not higher than 40°C, and more preferably set to not higher than 35°C.

There is no particular limitation to the electrolytic voltage at the time anodizing, and it need only be sufficient to control the electrolytic voltage as appropriate according to a coating growth speed, concentration of the electrolyte, and so forth. In the case of using, for example, an oxalic acid solution, if the electrolytic voltage is low, there can be occasions when it becomes difficult to have a sufficient coating growth speed, thereby deteriorating anodizing efficiency. Further, if the electrolytic voltage is high, there can be occasions when the coating becomes prone to dissolvent with ease, and a defect occurs to the coating. Accordingly, the electrolytic voltage is preferably in a range of 10 to 120 V.

Further, there is no particular limitation to an anodizing time

length either, and it need only be sufficient to decide process time by calculating a time length of magnitude sufficient to obtain a desired coating thickness.

**<Sealing step>**

The sealing step is a step for applying sealing to the anodic oxidation coating 3.

With the present invention, in order to form a stable fluorine-enriched layer 4 with fluorine in high concentration, the sealing whereby the anodic oxidation coating 3 (the porous layer 6) is brought into contact with water at high temperature is applied thereto after the anodizing. A sealing method includes a method for immersing the anodic oxidation coating 3 (the substrate 2 with the anodic oxidation coating 3 formed thereon) in hot water (hydrothermal immersion), or a method for exposing the anodic oxidation coating 3 to steam. In the case of the sealing through exposure to steam, it need only be sufficient to adjust process conditions as appropriate such that the anodic oxidation coating 3 is in a sealing state such as, for example, steam being kept at a high temperature (for example, not lower than 100°C), and so forth. However, if excessive progress in coating expansion occurs to the vicinity of the surface of the coating, there is a possibility of occurrence of a crack propagating throughout the film thickness of the coating. As a result, that will lead to deterioration in the gas corrosion resistance, the plasma resistance, and so forth with respect to the surface-treatment material 1. Accordingly, there arise the needs for fine control of temperature at the time of the sealing, process time, and so forth. Particularly, in the case of the sealing through exposure

to steam, finer control is required, so that the sealing by hot water is recommendable. And temperature of hot water, and process time are decided upon as appropriate according to the kind of an electrolyte used in anodizing, the film-thickness of the anodic oxidation coating 3, and conditions under which a crack occurs to the anodic oxidation coating 3, however, conditions of (70 to 100°C) x (5 to 300 minutes) are preferable.

**<Fluorine-enriched layer forming step>**

The fluorine-enriched layer forming step is a step (hereinafter referred to also as a step for fluorination as appropriate) for forming the fluorine-enriched layer 4 with fluorine enriched to a fluorine concentration not less than 1 mass%, formed over the surface of the anodic oxidation coating 3 with the sealing applied thereto.

There is no particular limitation to a method for fluorination, however, the fluorine-enriched layer 4 with fluorine enriched to a concentration not less than 1 mass% is preferably formed by immersing the substrate 2 with the anodic oxidation coating 3 formed thereon, subjected to the sealing during the sealing step, in an aqueous solution containing fluorine. That is, the anodic oxidation coating 3 is immersed in the aqueous solution containing fluorine, thereby causing the fluorine-enriched layer 4 to be formed. With the adoption of such a method as described, the fluorine-enriched layer 4 can be formed with ease, and fluorine concentration can be controlled to not less than 1 mass% with greater ease.

The aqueous solution containing fluorine can include, for example, an aqueous solution of 0.5 to 1.0 mol / L of hydrofluoric acid, a buffer

solution of hydrofluoric acid (an aqueous solution of HF combined with $NH_4F$), and so forth. However, there is no particular limitation to the aqueous solution containing fluorine, and use may be made of any aqueous solution containing fluorine, capable of forming the fluorine-enriched layer 4.

In fluorination, control is exercised such that the fluorine concentration in the fluorine-enriched layer 4 is rendered to become not less than 1 mass%. As previously described, stability in the electrical characteristics of the surface-treatment material 1 is enhanced by causing the fluorine concentration to be not less than 1 mass%. The control of the fluorine concentration can be effected by adjusting as appropriate time that the substrate 2 is immersed in the aqueous solution containing fluorine (fluorination time), and temperature of the aqueous solution containing fluorine (fluorination temperature).

In this connection, fluorination is to be executed under standard fluorination conditions that the substrate 2 is immersed in the aqueous solution of 0.5 to 1.0 mol/L of hydrofluoric acid, at about 25°C, for 1 to 2 minutes. By applying fluorination under those conditions, the fluorine concentration in the fluorine-enriched layer 4 can be rendered not less than 1 mass% with ease.

Further, as the method for fluorination, it is also possible to execute fluorination by applying heat treatment to the substrate 2 with the anodic oxidation coating 3 formed thereon, subjected to the sealing, (to the anodic oxidation coating 3) in an atmosphere of a fluorine-containing gas.

For the fluorine-containing gas, use can be made of at least one kind of gas selected from the group consisting of $F_2$, HF, $CF_4$, $C_2F_6$, $CHF_3$, $NF_3$, and so forth. It need only be sufficient to bring those gases into contact with the anodic oxidation coating 3. Heat treatment time (fluorination time) is preferably not less than 1 minute, and more preferably not less than 20 minutes. Heat treatment temperature (fluorination temperature) may be in a temperature range of 0 to 500°C, and is preferably not lower than 60°C, more preferably not lower than 100°C. Use may be made of fluorine plasma, or a mixture of a fluorine-containing gas and fluorine plasma besides the fluorine-containing gas. Further, because a forming rate at which the fluorine-enriched layer 4 is formed, and a state of the fluorine-enriched layer 4 will vary according to an atmospheric state of a fluorine-containing atmosphere composed of gas and plasma, the fluorine concentration can be caused to be not less than 1 mass% by adjusting as appropriate the fluorination time, and the fluorination temperature.

Having described the present invention as above, it is to be pointed out that the method for producing the surface-treatment material, according to the invention, may comprise other steps between the respective steps, or before or after the respective steps if the respective steps are not adversely affected in carrying out the invention, the other steps including a substrate preparation step for preparing the substrate 2 for use in the anodic oxidation coating forming step by, for example, reducing the substrate 2 to be used to a predetermined size, and polishing the surface thereof, a removal step for removing

unwanted substance such as refuse, and so forth, and a drying process for causing the substrate 2 (the anodic oxidation coating 3, the fluorine-enriched layer 4) to be dried after the respective steps.

Further, the method for producing the surface-treatment material 1 for use in the semiconductor manufacturing system, according to the invention, is intended for application to an aluminum alloy, but the same may be applied to members made of material other than aluminum alloy, such as a magnesium alloy material, a stainless steel material as an iron alloy material, and so forth.

**Working Examples**

Next, with respect to the surface-treatment material 1 for use in the semiconductor manufacturing system, according to the invention, and the method for producing the same, respective working examples thereof, meeting requirements of the invention, are compared with respective comparative examples thereof, failing to meet the requirements of the invention, thereby specifically describing the invention.

First, an aluminum alloy substrate made of JIS specification 6061 alloy was immersed in an anodizing liquid under respective conditions shown in Table 1, and anodizing (the direct current method) was applied to the aluminum alloy substrate, thereby having formed an anodic oxidation coating. Subsequently, the aluminum alloy substrate with the anodic oxidation coating formed thereon was immersed in pure water at a predetermined temperature for predetermined time, as shown in Table 1, thereby having applied the sealing thereto. Then, the aluminum alloy substrate subjected to the sealing was immersed in an aqueous solution

of 0.5 mol / L of hydrofluoric acid (an aqueous solution of HF), having a liquid temperature at 25°C, for one minute, and fluorination was applied thereto, thereby having formed a fluorine-enriched layer. As shown in Table 1, with some of the aluminum alloy substrates, the sealing and / or fluorination were not applied (refer to the comparative examples). With respect to testpieces produced as above, fluorine concentration in the fluorine-enriched layer was measured, and stability in the electrical characteristics thereof was evaluated.

**[Measurement of fluorine concentration]**

The measurement of fluorine concentration was conducted by execution of EPMA (Electron-beam Probe Micro-Analyzer) analysis of the surface of each of the testpieces.

EPMA analysis was executed by use of an X-ray microanalyzer manufactured by Japan Electron Co., JXA - 8000 RL, under conditions of an acceleration voltage: 15 kV, an irradiation current: 0.2 μA, and an analysis region: ϕ 100 μm.

**[Stability in electrical characteristics]**

Stability in electrical characteristics was evaluated by measuring a leak current. For measurement of the leak current, use was made of a source meter manufactured by Keithley Instruments, Inc. In a method for measurement of the leak current, an Au anode of ϕ 2.5 mm, and 200 nm in thickness was produced on an anodic oxidation coating by sputtering. A probe of a tungsten needle was placed on the Au anode, and a voltage up to 1000 V was applied thereto at a rate of 2 V / sec, thereby having measured the leak current. Measurement environments of

room temperature at 25°C, and humidity at 40 % were adopted.

As for evaluation criteria, testpieces having a leak current not more than 0.1 nA / $cm^2$ per unit film-thickness upon application of 300 V is were determined as excellent (A) in stability of the electrical characteristics while testpieces having a leak current in excess of 0.1 nA / $cm^2$ were determined as poor (B) in stability of the electrical characteristics.

Results of those evaluations are shown in Table 1. In Table 1, sign [-] indicates testpieces wherein it was not possible to measure fluorine concentration since the fluorine-enriched layer was not formed. Furthermore, film-thickness indicates the film-thickness of films in whole including the fluorine-enriched layer.

Table 1

| Testpiece No. | Working example / Comparative example | Anodizing condition | | | Film-thickness (μm) | Sealing condition | Fluorination | Surface fluorine concentration (mass%) | Leak current per unit film-thickness upon application of 300 V(nA/cm²) | stability in electrical characteristics |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Anodizing liquid | voltage (V) | Liquid temperature (°C) | | | | | | |
| 1 | Working example | Sulfuric acid 100g/L | 20 | 10 | 19.2 | 100°C×10min | Yes | 2.05 | 0.07 | A |
| 2 | Working example | Sulfuric acid 150g/L | 25 | 0 | 19.1 | 100°C×30min | Yes | 2.51 | 0.09 | A |
| 3 | Working example | Sulfuric acid 200g/L | 15 | 10 | 19.9 | 90°C×45min | Yes | 2.32 | 0.01 | A |
| 4 | Working example | Oxalic acid 10g/L | 60 | 10 | 20.8 | 80°C×5min | Yes | 1.18 | 0.08 | A |
| 5 | Working example | Oxalic acid 30g/L | 40 | 20 | 19.9 | 85°C×10min | Yes | 1.82 | 0.02 | A |
| 6 | Working example | Oxalic acid 60g/L | 40 | 30 | 19.6 | 90°C×10min | Yes | 2.20 | 0.07 | A |
| 7 | Working example | Sulfuric acid 150g/L Oxalic acid 25g/L | 10 | 0 | 19.1 | 85°C×10min | Yes | 1.69 | 0.04 | A |
| 8 | Working example | Sulfuric acid 200g/L Oxalic acid 20g/L | 10 | 10 | 19.6 | 100°C×10min | Yes | 2.08 | 0.07 | A |
| 9 | Working example | Oxalic acid 30g/L Sulfuric acid 2g/L | 60 | 20 | 19.2 | 80°C×5min | Yes | 1.28 | 0.04 | A |
| 10 | Working example | Oxalic acid 40g/L Sulfuric acid 5g/L | 40 | 15 | 20.0 | 100°C×10min | Yes | 2.09 | 0.05 | A |
| 11 | Comparative example | Sulfuric acid 100g/L | 20 | 10 | 20.9 | 100°C×10min | None | — | 8.81 | B |
| 12 | Comparative example | Sulfuric acid 150g/L | 25 | 0 | 19.7 | 100°C×30min | None | — | 9.66 | B |
| 13 | Comparative example | Sulfuric acid 200g/L | 15 | 10 | 19.8 | None | Yes | 0.48 | 6.13 | B |
| 14 | Comparative example | Oxalic acid 10g/L | 60 | 10 | 19.1 | 80°C×5min | None | — | 8.65 | B |
| 15 | Comparative example | Oxalic acid 30g/L | 40 | 20 | 20.6 | None | Yes | 0.59 | 2.99 | B |
| 16 | Comparative example | Oxalic acid60g/L | 40 | 30 | 19.2 | None | Yes | 0.36 | 6.06 | B |
| 17 | Comparative example | Sulfuric acid 150g/L Oxalic acid 25g/L | 10 | 0 | 19.8 | None | Yes | 0.48 | 4.50 | B |
| 18 | Comparative example | Sulfuric acid 200g/L Oxalic acid 20g/L | 10 | 10 | 20.1 | None | Yes | 0.84 | 2.12 | B |
| 19 | Comparative example | Oxalic acid 30g/L Sulfuric acid 2g/L | 60 | 20 | 20.1 | None | Yes | 0.78 | 1.83 | B |
| 20 | Comparative example | Oxalic acid 40g/L Sulfuric acid 5g/L | 40 | 15 | 20.6 | None | None | — | 6.81 | B |

As shown in Table 1, with testpiece Nos. 1 to 10, each thereof was a working example meeting a range of the requirements of the invention, so that stability in the electrical characteristics thereof was found excellent.

On the other hand, with testpiece Nos. 11 to 20, each thereof was a comparative example failing to meet the range of the requirements of the invention, so that the following defects were found.

With the testpiece Nos. 11, 12, respectively, fluorination was not applied thereto, and a fluorine-enriched layer was not formed on the surface of the testpiece, so that stability in the electrical characteristics thereof was found poor. With the testpiece No. 13, sealing was not applied thereto, so that fluorine concentration was less than 1 mass%, and stability in the electrical characteristics thereof was found poor. With the testpiece No. 14, fluorination was not applied thereto, so that a fluorine-enriched layer was not formed on the surface of the testpiece, and stability in the electrical characteristics thereof was found poor. With the testpiece Nos. 15 to 19, respectively, sealing was not applied thereto, so that fluorine concentration on the surface of the testpiece was less than 1 mass%, and stability in the electrical characteristics thereof was found poor. With the testpiece No. 20, neither sealing nor fluorination was applied thereto, so that a fluorine-enriched layer was not formed on the surface of the testpiece, and stability in the electrical characteristics thereof was found poor.

Thus, with respect to the surface- treatment material 1 for use in the semiconductor manufacturing system, according to the invention, and the method for producing the same, the preferred embodiment, and

working examples are shown, and described in details, however, it is to be understood that the invention be not limited by any of the details of description. Obviously, many modifications, variations, and so forth may be made in the invention without departing from the spirit and scope of the invention

**What is claimed is:**

1. A surface-treatment material of a semiconductor manufacturing system, for use in a semiconductor manufacturing system, said surface-treatment material comprising:

a substrate made of aluminum, or aluminum alloy;

an anodic oxidation coating formed over the surface of the substrate, with sealing applied thereto; and

a fluorine-enriched layer formed over the surface of the anodic oxidation coating, wherein

fluorine concentration in the fluorine-enriched layer is not less than 1 mass%.

2. A method for producing a surface- treatment material of a semiconductor manufacturing system, for use in a semiconductor manufacturing system, said method comprising:

an anodic oxidation coating forming step for forming an anodic oxidation coating over the surface of a substrate made of aluminum, or aluminum alloy;

a sealing step for applying sealing to the anodic oxidation coating; and

a fluorine-enriched layer forming step for forming a fluorine-enriched layer with fluorine enriched to a fluorine concentration not less than 1 mass% over the surface of the anodic oxidation coating with the sealing applied thereto.

3. The method for producing a surface-treatment material of a semiconductor manufacturing system, according to claim 2, wherein in the fluorine-enriched layer forming step, the fluorine-enriched layer is formed by immersing the substrate with the anodic oxidation coating formed thereon, subjected to the sealing during the sealing step, in an aqueous solution containing fluorine.