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HAVING BOTH DURABILITY AND LOW
POLLUTING PROPERTY**(75) Inventors: **Koji Wada**, Kobe-shi (JP); **Jun
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C25D 11/02 (2006.01)(52) **U.S. Cl.** **205/50**(57) **ABSTRACT**

An anodized aluminum alloy material is formed of an aluminum alloy having a Mg content between 0.1 and 2.0% by mass, a Si content between 0.1 and 2.0% by mass, a Mn content between 0.1 and 2.0% by mass, and an Fe, a Cr and a Cu content of 0.03% by mass or below and containing Al and unavoidable impurities as other components, and is coated with an anodic oxide film. Parts of the anodic oxide film at different positions with respect to thickness of the anodic oxide film have different hardnesses, respectively, and the difference in Vickers hardness between a part having the highest hardness and a part having the lowest hardness is Hv 5 or above.

ANODIZED ALUMINUM ALLOY MATERIAL HAVING BOTH DURABILITY AND LOW POLLUTING PROPERTY

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates to an aluminum alloy material and, more particularly, to an anodized aluminum alloy material intended for forming members of the vacuum chambers of apparatuses for manufacturing semiconductor devices and liquid crystal devices, such as CVD systems, PVD systems, ion-implanting systems, sputtering systems and dry etching systems, and those placed in the vacuum chambers.

[0003] 2. Description of the Related Art

[0004] Reactive gases, etching gases, and corrosive gases containing halogen as a cleaning gas are supplied into the vacuum chambers of apparatuses for manufacturing semiconductor devices and liquid crystal devices, such as CVD systems, PVD systems, ion-implanting systems, sputtering systems and dry etching systems. Therefore, the vacuum chambers are required to have corrosion resistance to corrosive gases (hereinafter, referred to as "corrosive gas resistance"). Since a halogen plasma is often produced in the vacuum chamber, resistance to plasmas (hereinafter, referred to as "plasma resistance") is also important (refer to JP-A Nos. 2003-34894 and 2004-225113). Recently, aluminum and aluminum alloy materials have been used for forming the members of the vacuum chamber because aluminum and aluminum alloy materials are light and excellent in thermal conductivity.

[0005] Since aluminum and aluminum alloy materials are not satisfactory in corrosive gas resistance and plasma resistance, various surface quality improving techniques for improving those properties have been proposed. However, those properties are still unsatisfactory and further improvement of those properties is desired.

[0006] Coating an aluminum or an aluminum alloy material with a hard anodic oxide film having a high hardness is effective in improving plasma resistance. The hard anodic oxide film is resistant to the abrasion of a member by a plasma having high physical energy and hence is capable of improving plasma resistance (refer to JP-A 2004-225113).

[0007] Although the plasma resistance may be improved simply by coating an aluminum or an aluminum alloy material with a hard anodic oxide film, the hard anodic oxide film is liable to crack. Once cracks penetrate the anodic oxide film, the corrosive gas reaches the aluminum or the aluminum alloy body of the anodized aluminum or aluminum alloy member through the cracks penetrating the anodic oxide film (hereinafter, referred to as "through cracks") and the aluminum or the aluminum alloy material is corroded.

[0008] Therefore, an anodic oxide film having not only a high hardness, but also durability (crack resistance and corrosive gas resistance) is desired.

[0009] When the Fe content of an aluminum alloy is reduced with a view to suppress the contamination of a semiconductor wafer or a substrate for a liquid crystal display with Fe, an anodic oxide film having a low Fe content can be formed. However, such an anodic oxide film is harder, and the crack resistance and durability of such an anodic oxide film

are worse. Therefore, this field desires improving durability (crack resistance and corrosive gas resistance) without enhancing polluting property.

SUMMARY OF THE INVENTION

[0010] The present invention has been made in view of the foregoing problems and it is therefore an object of the present invention to provide an anodized aluminum alloy having a high hardness, durability and low polluting property.

[0011] An anodized aluminum alloy material in a first aspect of the present invention is formed of an aluminum alloy having a Mg content between 0.1 and 2.0% ("%" signifies "mass %" herein unless otherwise specified), a Si content between 0.1 and 2.0%, a Mn content between 0.1 and 2.0%, and an Fe, a Cr and a Cu content of 0.03% or below and containing Al and unavoidable impurities as other components, and is coated with an anodic oxide film; wherein parts of the anodic oxide film at different positions with respect to the thickness of the anodic oxide film have different hardnesses, respectively, and the difference in Vickers hardness between a part having the highest hardness and a part having the lowest hardness is Hv 5 or above.

[0012] The anodized aluminum alloy material has a high hardness, durability and low polluting property.

[0013] In the anodized aluminum alloy material in the first aspect of the present invention, the hardness of the part having the lowest hardness of the anodic oxide film is Hv 365 or above, which leads to improvement of plasma resistance.

[0014] The aluminum alloy forming the anodized aluminum alloy material has a Mg content between 0.1 and 2.0%, a Si content between 0.1 and 2.0%, a Mn content between 0.1 and 2.0%, and an Fe, a Cr and a Cu content of 0.03% or below and contains Al and unavoidable impurities as other components, the anodized aluminum alloy material is coated with the anodic oxide film, parts of the anodic oxide film at different positions with respect to the thickness of the anodic oxide film have different hardnesses, respectively, and the difference in Vickers hardness between a part having the highest hardness and the part having the lowest hardness of the anodic oxide film is Hv 5 or above. Therefore, the anodized aluminum alloy material has a high hardness, durability and low polluting property.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0015] The present invention will be described in terms of preferred embodiments thereof.

[0016] Composition of Aluminum Alloy Forming Anodized Aluminum Alloy Material

[0017] An anodized aluminum alloy material according to the present invention is formed of an aluminum alloy having a Mg content between 0.1 and 2.0%, a Si content between 0.1 and 2.0%, a Mn content between 0.1 and 2.0%, and an Fe, a Cr and a Cu content of 0.03% or below and containing Al and unavoidable impurities as other components, and is coated with an anodic oxide film. Parts of the anodic oxide film at different positions with respect to the thickness of the anodic oxide film have different hardnesses, respectively, and the difference in Vickers hardness between a part having the highest hardness and a part having the lowest hardness is Hv 5 or above. Thus the anodized aluminum alloy material has a high hardness, durability and low polluting property.

[0018] Reasons for determining the foregoing composition will be described.

[0019] The inventors of the present invention placed restrictions on the Fe, the Cr and the Cu content of the aluminum alloy so that a workpiece of a semiconductor or the like may not be contaminated. Effect of limiting the Fe content at a low level on increasing the hardness of the anodic oxide film and ensuring plasma resistance was utilized positively and studies were made to find out measures for preventing the growth of cracks formed in the anodic oxide film to the aluminum alloy body of the anodized aluminum alloy material. It was found through the studies that the growth of cracks formed in the anodic oxide film to the aluminum alloy body of the anodized aluminum alloy material can be prevented by properly determining process conditions for forming the anodic oxide film such that parts of the anodic oxide film at different positions with respect to the thickness of the anodic oxide film have different hardnesses, respectively, and the difference in Vickers hardness between a part having the highest hardness and a part having the lowest hardness is Hv 5 or above. Thus the penetration of a gas through the anodic oxide film to the aluminum alloy material was suppressed and general durability was ensured. Details of a mechanism of the composition capable of solving the foregoing problems have not been elucidated. However, it is inferred that stress causing a crack to grow is absorbed by a part having a low hardness of the anodic oxide film and, consequently, the crack cannot grow to the aluminum alloy body of the anodized aluminum alloy material.

[0020] The present invention will be described in detail.

[0021] Components of Aluminum Alloy

[0022] Although details of a mechanism is not clearly known, it is inferred that an anodic oxide film is strengthened when a Mg_2Si compound, and an Al—Mn—Si compound or an Al—Mn compound are combined with Mg, Si and Mn contained in an aluminum alloy.

[0023] Mg Content: 0.1 to 2.0%

[0024] Magnesium (Mg) is an element necessary for producing a Mg_2Si compound. A Mg_2Si compound is produced scarcely and a desired effect on improving the durability of the anodic oxide film cannot be achieved when the Mg content is below 0.1%. Coarse grains of a Mg_2Si compound are formed to obstruct formation of a normal anodic oxide film when the Mg content is above 2.0%. Therefore, a proper Mg content is between 0.1 and 2.0%, preferably, 0.8%.

[0025] Si Content: 0.1 to 2.0%

[0026] Silicon (Si), as well as Mg, is an element necessary for producing a Mg_2Si compound. A Mg_2Si compound is produced scarcely and a desired effect on improving the durability of the anodic oxide film cannot be achieved when the Si content is below 0.1%. Coarse grains of a Mg_2Si compound are formed to obstruct formation of a normal anodic oxide film when the Si content is above 2.0%. Therefore, a proper Si content is between 0.1 and 2.0%, preferably, 1.2%.

[0027] Mn Content: 0.1 to 2.0%

[0028] Manganese (Mn) is an element necessary for producing an Al—Mn—Si compound or an Al—Mn compound. An Al—Mn—Si compound or an Al—Mn compound is produced scarcely and a desired effect on improving the durability of the anodic oxide film cannot be achieved when the Mn content is below 0.1%. Coarse grains of the compound are formed to obstruct formation of a normal anodic oxide film when the Mn content is above 2.0%. Therefore, a proper Mn content is between 0.1 and 2.0%, preferably, 1.6%.

[0029] Fe, Cr and Cu Contents: 0.03% or Below Each

[0030] Electricity for an anodizing process is used for ionizing Al and for generating oxygen through the electrolysis of water. If the ratio of an amount of electricity for producing oxygen is high, the ratio of an amount of electricity for the ionization of Al decreases is low, aluminum oxide cannot be efficiently produced and film formation rate decreases. When the aluminum alloy contains Fe, Cr and Cu, generation of oxygen starts from those elements and the ratio of the amount of electricity for oxygen generation increases and, consequently, the film forming rate decreases. If each of the Fe, the Cr and the Cu content is above 0.03%, Fe, Cr and Cu are emitted from the aluminum alloy body and the anodic oxide film into a gas and a workpiece of a semiconductor or the like is contaminated. Therefore, each of the Fe, the Cr and the Cu content is 0.03% or below, preferably, 0.01% or below.

[0031] Al and Unavoidable Impurities as Other Elements

[0032] Substantially, Al is only the other element. However, the aluminum alloy contains, in addition to Fe, Cr and Cu, unavoidable impurities including Ni, Zn, B, Ca, Na and K in unavoidably low contents. Preferably, the total of the unavoidable impurity contents other than the Fe, the Cr and the Cu content is 0.1% or below.

[0033] A crystalline pattern is formed in the anodic oxide film and anodic oxide film has an irregular color tone if the aluminum alloy grains are coarse. Titanium (Ti) may be added to the aluminum alloy to prevent the growth of coarse aluminum alloy grains. An excessively low Ti content does not have a grain size control effect. An excessively high Ti content causes pollution. When Ti is added to the aluminum alloy, a lower limit Ti content is 0.01%, preferably, 0.015%, and an upper limit Ti content is 0.03%, preferably, 0.025%.

[0034] Method of Manufacturing Aluminum Alloy Material

[0035] A method of manufacturing an aluminum alloy material will be described.

[0036] An aluminum alloy ingot having the foregoing composition is made by an ordinary casting process, such as a continuous casting process, a semi-continuous casting process (DC casting process) or the like. Then, the aluminum alloy ingot is subjected to a homogenizing heat treatment, namely, a soaking process. An anodic oxide film excellent in durability is formed by processing the aluminum alloy ingot by the soaking process at a temperature, namely, homogenizing temperature or soaking temperature, of 500° C. or above. An anodic oxide film having still more excellent in durability can be formed by processing the aluminum alloy ingot by the homogenizing treatment at a homogenizing temperature above 550° C. Burning occurs to deteriorate the surface quality of the aluminum alloy ingot when the homogenizing temperature is above 600° C. Therefore, it is recommended that the homogenizing temperature is in the range of 500° C. (preferably, a temperature not lower than 550° C.) to 600° C. although the effect of the homogenizing temperature on the formation of the anodic oxide film is not yet ascertained, it is inferred that the homogenizing temperature participates in producing an Al—Mn—Si compound or an Al—Mn compound as mentioned above.

[0037] The aluminum alloy ingot processed by the homogenizing heat treatment is processed by a proper plastic working process, such as a rolling process, a forging process or an extrusion process, to obtain an aluminum alloy material. Then, the aluminum alloy material is subjected to a solution process, a quenching process and an artificial aging process

(hereinafter, referred to also simply as "aging process"). Then, the aluminum alloy material is formed in a suitable shape by machining to obtain an aluminum alloy material. An aluminum alloy slab obtained by processing the aluminum alloy ingot may be subjected to the solution process, the quenching process and the aging process to obtain an aluminum alloy material. The solution process, the quenching process and the aging process may be, for example, a solution process at a temperature between 515° C. and 550° C., a water quenching process and an aging process at 170° C. for 8 h or at 155° C. to 165° C. for 18 h forming an ordinary T6 process.

[0038] Anodic Oxide Film

[0039] An anodic oxide film coating the aluminum alloy material will be described. An anodic oxide film forming method is executed by properly determining conditions for electrolysis including the composition and concentration of an electrolyte, voltage, current density, waveforms of current and voltage, and temperature for electrolysis. Electrolysis for anodization needs to use an anodizing solution containing at least one of elements including C, S, N, P and B. For example, it is effective to use an aqueous solution containing at least one of oxalic acid, formic acid, sulfamic acid, phosphoric acid, phosphorous acid, boric acid, nitric acid or its compound, and phthalic acid or its compound. There is not any particular limit to the thickness of the anodic oxide film. The thickness of the anodic oxide film is between about 0.1 and about 200 μm , preferably, between 0.5 and 70 μm , more desirably, between about 1 and about 50 μm .

[0040] As mentioned above, parts of the anodic oxide film at different positions with respect to the thickness of the anodic oxide film have different hardnesses, respectively, and the difference in Vickers hardness between a part having the highest hardness and a part having the lowest hardness is Hv 5 or above. Therefore, the anodic oxide film has a high hardness, and is capable of suppressing the growth of cracks and excellent in crack resistance. Since the anodic oxide film is excellent in crack resistance, penetration of gases through the anodic oxide film to the aluminum alloy body is suppressed and general durability is ensured. If the difference in Vickers hardness between a part having the highest hardness and a part having the lowest hardness is below Hv 5, the behavior of the anodic oxide film is equal to that of an anodic oxide film having a substantially uniform thickness with respect to a direction parallel to the width, it is difficult for the anodic oxide film to suppress the growth of cracks. Consequently, the anodic oxide film has low crack resistance and low corrosive gas resistance.

[0041] According to the present invention, the anodic oxide film should have at least two parts at different positions with respect to the thickness of the anodic oxide film having different hardnesses. The number of such parts is not limited to any number, provided that the number is two or greater. The hardness of the anodic oxide film may discontinuously change or may continuously change in a slope.

[0042] From the viewpoint of suppressing the growth of cracks created in the anodic oxide film, it is considered that the part having the lowest hardness has the lowest possible Vickers hardness. However it is desirable, from the viewpoint of ensuring resistance to the abrasive effect of the physical energy of plasma, that the part has a hardness of Hv 365 or above.

[0043] An aluminum alloy material coated with the anodic oxide film (hereinafter, referred to as "anodized aluminum alloy material") is suitable for forming members to be used in

a high-temperature corrosive atmosphere. The anodized aluminum alloy material is particularly suitable for forming a vacuum chamber for a plasma processing apparatus included in a semiconductor device manufacturing system or the like, and parts placed in the vacuum chamber, such as electrodes, which are exposed to a corrosive gas in a high-temperature atmosphere and are required to have a low contaminating property of contaminating workpieces.

[0044] An anodic oxide film having parts at different positions with respect to the thickness of the anodic oxide film respectively having different hardnesses can be formed by a method that changes the temperature of an anodizing solution intermittently or continuously during an anodizing process, or a method that interrupts an anodizing process using an anodizing solution, takes out the aluminum alloy material from the anodizing solution, and resumes an anodizing process using an anodizing solution of a different composition and/or a different temperature. Those methods can form an anodic oxide film having parts at different positions with respect to the thickness respectively having different hardnesses. An anodizing solution of a lower temperature is more effective in suppressing the chemical dissolution of an anodic oxide film during the anodizing process and in forming a hard anodic oxide film.

[0045] As mentioned above, when the Fe content of an aluminum alloy is reduced to 0.03% or below with a view to suppress the contamination of a workpiece, such as a semiconductor wafer, the Fe content of an anodic oxide film can be reduced to 500 ppm or below. The Fe content of an anodic oxide film can be reduced to 150 ppm or below when the Fe content of the aluminum alloy is reduced to 0.01% or below.

[0046] As mentioned above the anodized aluminum alloy material has a high hardness and is satisfactory in durability (crack resistance and corrosive gas resistance) and low contaminating property.

EXAMPLES

[0047] Examples of the present invention will be described. Examples described herein do not place any limit to the present invention and changes that may be made therein without departing from foregoing and the following gist are within the technical scope of the present invention.

[0048] Aluminum alloy ingots of 220 mm in width, 250 mm in length and 100 mm in thickness having the compositions of examples of the present invention, namely, Samples Nos. 1, 2, 4 and 5, and comparative examples, namely, samples Nos. 3 and 6 to 14 shown in Table 1 were formed by casting and were cooled at a cooling rate in the range of 10 to 15° C./s. The aluminum alloy ingots were cut and ground to obtain aluminum alloy slabs of 220 mm in width, 150 mm in length and 60 mm in thickness. The aluminum alloy slabs were processed by a soaking process at 540° C. for 4 h. The soaked aluminum alloy slabs of 60 mm in thickness were subjected to a hot rolling process to obtain aluminum alloy plates of 6 mm in thickness. Sample alloy plates were obtained by processing the aluminum alloy plates by a solution treatment at a temperature in the range of 510° C. to 520° C. for 30 min, a water quenching process, and an aging process at a temperature in the range of 160° C. to 180° C. for 8 h. Specimens of 25 mm×35 mm (rolling direction) and 3 mm in thickness were cut out from the alloy plates. The surfaces of the specimens were ground in a surface roughness of Ra 1.6.

TABLE 1

Specimen No.		Content (% by mass)						Hardness difference	Durability		Polluting property			
		Mg	Si	Mn	Fe	Cr	Cu		Corroded area ratio (%)	Judgment	Fe content (ppm)	Cr content (ppm)	Cu content (ppm)	Judgment
1	Ex.	0.8	1.2	1.6	0.008	0.009	0.007	10	0	☉	150	190	130	☉
2	Ex.	0.8	1.2	1.6	0.008	0.009	0.007	5	2	○	150	190	130	☉
3	Comp. ex.	0.8	1.2	1.6	0.008	0.009	0.007	4	10	X	160	180	150	☉
4	Ex.	0.1	0.1	0.1	0.029	0.028	0.027	10	3	○	490	480	480	○
5	Ex.	1.9	2.0	1.8	0.027	0.028	0.028	10	3	○	470	480	490	○
6	Comp. ex.	0.09	0.8	1.1	0.006	0.008	0.009	10	11	X	120	170	190	☉
7	Comp. ex.	2.1	0.8	1.0	0.007	0.009	0.008	10	18	X	130	180	170	☉
8	Comp. ex.	1.0	0.08	0.7	0.009	0.007	0.008	10	9	X	170	150	160	☉
9	Comp. ex.	1.0	2.1	0.8	0.008	0.006	0.009	10	20	X	160	130	180	☉
10	Comp. ex.	0.9	1.1	0.09	0.008	0.009	0.006	10	10	X	150	180	130	☉
11	Comp. ex.	1.1	0.9	2.1	0.009	0.008	0.007	10	19	X	180	160	140	☉
12	Comp. ex.	0.9	1.0	0.9	0.031	0.007	0.008	10	0	☉	520	140	180	X
13	Comp. ex.	1.0	1.0	0.9	0.008	0.032	0.009	10	0	☉	170	530	190	X
14	Comp. ex.	1.0	0.9	0.9	0.007	0.009	0.031	10	0	☉	140	190	510	X

Second anodic oxide film												
Specimen No.		First anodic oxide film					Anodizing solution		Tempera-		Thick-	Hard-
		Anodizing solution	Temperature (° C.)	Voltage (V)	Thickness (μm)	Hardness (Hv)			ture (° C.)	Voltage (V)		
1	Oxalic acid solution (Concentration: 25 g/l)	10	60	15	380	Oxalic acid solution (Concentration: 25 g/l)	5	60	15	390		
2	Oxalic acid solution (Concentration: 25 g/l)	8	60	15	385	Oxalic acid solution (Concentration: 25 g/l)	5	60	15	390		
3	Oxalic acid solution (Concentration: 25 g/l)	7	60	15	386	Oxalic acid solution (Concentration: 25 g/l)	5	60	15	390		
4	Oxalic acid solution (Concentration: 25 g/l)	10	60	15	365	Oxalic acid solution (Concentration: 25 g/l)	5	60	15	375		
5	Oxalic acid solution (Concentration: 25 g/l)	10	60	15	365	Oxalic acid solution (Concentration: 25 g/l)	5	60	15	375		
6	Oxalic acid solution (Concentration: 25 g/l)	10	60	15	380	Oxalic acid solution (Concentration: 25 g/l)	5	60	15	390		
7	Oxalic acid solution (Concentration: 25 g/l)	10	60	15	380	Oxalic acid solution (Concentration: 25 g/l)	5	60	15	390		
8	Oxalic acid solution (Concentration: 25 g/l)	10	60	15	380	Oxalic acid solution (Concentration: 25 g/l)	5	60	15	390		
9	Oxalic acid solution (Concentration: 25 g/l)	10	60	15	380	Oxalic acid solution (Concentration: 25 g/l)	5	60	15	390		
10	Oxalic acid solution (Concentration: 25 g/l)	10	60	15	380	Oxalic acid solution (Concentration: 25 g/l)	5	60	15	390		
11	Oxalic acid solution (Concentration: 25 g/l)	10	60	15	380	Oxalic acid solution (Concentration: 25 g/l)	5	60	15	390		
12	Oxalic acid solution (Concentration: 25 g/l)	10	60	15	360	Oxalic acid solution (Concentration: 25 g/l)	5	60	15	370		
13	Oxalic acid solution (Concentration: 25 g/l)	10	60	15	380	Oxalic acid solution (Concentration: 25 g/l)	5	60	15	390		
14	Oxalic acid solution (Concentration: 25 g/l)	10	60	15	380	Oxalic acid solution (Concentration: 25 g/l)	5	60	15	390		

(Note)

Examples are abbreviated to Exs. and Comparative examples to Comp. exs.

[0049] Each of the specimens was immersed in a 10% NaOH solution of 60° C. for 2 min, the specimen was rinsed with water, the specimen was immersed in a 20% HNO₃ solution of 20° C. for 2 min, and then the specimen was rinsed

with water to clean the surface thereof. Then, a first anodic oxide film was formed on a surface of the specimen and a second anodic oxide film was formed on the first anodic oxide film by an anodizing process. Process conditions for the anod-

izing process are shown in Table 1. The first and the second anodic oxide film were formed in a thickness of 15 μm using a processing solution having an oxalic concentration of 25 g/L (the letter "L" represents "liter"). Bath voltage was fixed at 60 V. The difference between the anodizing conditions respectively for the forming the first and the second anodic oxide film was only the temperature of the processing solution. The temperature of the processing solution for forming the first anodic oxide film was higher than that for forming the second anodic oxide film.

[0050] The Fe, the Cr and the Cu content of the anodized aluminum alloy specimens (hereinafter referred to simply as "specimens") were measured, the hardness of the anodic oxide films was measured, and the durability of the anodic oxide films was tested.

[0051] Measurement of Fe, Cr and Cu Contents of Anodic Oxide Film

[0052] Contaminating properties of the specimens were evaluated. The specimen was immersed in 100 ml of a 7% hydrochloric acid solution to dissolve the anodic oxide film to the extent that the aluminum alloy body is not exposed. The weight W (g) of the dissolved anodic oxide film was determined by calculating the difference in weight between the weight of the hydrochloric acid solution before the dissolution of the anodic oxide film and that of the same after the dissolution of the anodic oxide film. Then, the Fe, the Cr and the Cu content of the hydrochloric acid solution were determined through the ICP analysis of the hydrochloric acid solution, and the respective weights W_{Fe} , W_{Cr} and W_{Cu} (g) of Fe, Cr and Cu contained in 100 ml of the hydrochloric acid were calculated. Then, the Fe, the Cr and the Cu content of the anodic oxide film, namely, W_{Fe}/W , W_{Cr}/W and W_{Cu}/W , were calculated. The contaminating property of the specimen was evaluated by the Fe, the Cr and the Cu content of the anodic oxide film on the basis of the following criterion. Results of evaluation are shown in Table 1.

[0053] Criterion for Contaminating Property Evaluation

[0054] Double circle: All the Fe, the Cr and the Cu content are 300 ppm or below

[0055] Circle: At least one of the Fe, the Cr and the Cu content is above 300 ppm and 500 ppm or below and other elements are 300 ppm or below

[0056] Cross: At least one of the Fe, the Cr and the Cu content is above 500 ppm

[0057] Results of Evaluation of Polluting Property

[0058] As shown in Table 1, some of the Fe, the Cr and the Cu content of the anodic oxide films of the specimens Nos. 12 to 14 of the comparative examples was above 500 ppm. All of the Fe, the Cr and the Cu content of the specimens Nos. 1, 2, 4 and 5 of the examples and the specimens Nos. 3 and 6 to 11 of the comparative examples were satisfactorily as low as 500 ppm or below. As shown in Table 1, all of the Fe, the Cr and the Cu content of the specimens Nos. 1 and 2 of the examples and the specimens Nos. 3 and 6 to 11 of the comparative examples were very low values of 300 ppm or below and those examples and comparative examples were very satisfactory.

[0059] Measurement of Hardness of Anodic Oxide Film

[0060] Each specimen was embedded in a resin, a cross section of the specimen including sections of the anodic oxide film and the aluminum alloy body was polished. The hardness of the polished section of the anodic oxide film was measured by a measuring method specified in Z2244 (1998), JIS.

[0061] Results of Measurement

[0062] In each of the specimens Nos. 1, 2, 4 and 5 of the examples and the specimens Nos. 3 and 6 to 14 of the comparative examples, the second anodic oxide film has a hardness higher than that of the first anodic oxide film. Such a hardness difference between the first and the second anodic oxide film was caused by a condition that the temperature of the anodizing solution used for forming the second anodic oxide film was lower than that of the anodizing solution used for forming the first anodic oxide film. The difference in hardness between the first and the second anodic oxide film of the specimen No. 2 of the example was Hv 5. Such a hardness difference was caused by a condition that the temperature of the anodizing solution used for forming the second anodic oxide film was 5° C. and that of the anodizing solution used for forming the first anodic oxide film was 8° C. The difference in hardness between the first and the second anodic oxide film of the specimen No. 3 of the comparative example was Hv 4. Such a hardness difference was caused by a condition that the temperature of the anodizing solution used for forming the second anodic oxide film was 5° C. and that of the anodizing solution used for forming the first anodic oxide film was 10° C. Thus the anodic oxide film can be formed in an optional hardness by controlling the temperature of the anodizing solution. As shown in Table 1, the respective hardnesses of the anodic oxide films excluding the anodic oxide film of the specimen No. 12 of the comparative example were Hv 365 or above. Therefore, the plasma resistance of the anodic oxide films excluding the anodic oxide film of the specimen no. 12 of the comparative example is satisfactory.

[0063] Test of Durability of Anodic Oxide Film

[0064] A durability test included a crack resistance test at a first stage and a corrosive gas resistance test at a second stage. In the crack resistance test, a specimen was heated at 450° C. for 1 h in a test vessel of an atmospheric atmosphere, and then the specimen taken out from the test vessel was dipped in water of 27° C. for quenching. The specimen tested by the crack resistance test was subjected to two corrosive gas resistance test cycles. Each corrosive gas resistance test cycle held the specimen in a 5% Cl_2 —Ar gas atmosphere of 400° C. for 4 h. Then, the corroded area ratio of the surface of the specimen was calculated by using and expression: (Corroded area ratio) $\{(\text{Area of corroded parts})/(\text{Area of the surface of the specimen})\} \times 100$. The specimens were evaluated on the basis of the following criterion. Results of evaluation are shown in Table 1.

[0065] Criterion for Durability Evaluation

[0066] Double circle: Corroded area ratio 0%

[0067] Circle: Corroded area ratio: 0 to 3%

[0068] Cross: Corroded area ratio: Above 3%

[0069] Results of Durability Evaluation

[0070] As shown in Table 1, the specimens Nos. 3 and 6 to 11 of the comparative examples were unacceptable. The specimens Nos. 1, 2, 4 and 5 of the examples and the specimens Nos. 12 to 14 of the comparative examples were satisfactory in durability. As shown in Table 1, the specimen No. 1

of the example and the specimen Nos. 12 to 14 of the comparative examples were very satisfactory in durability.

[0071] It is known from the synthetic conclusion based on the measured data on the Fe, the Cr and the Cu content of the anodic oxide films, the measured data on the hardness of the anodic oxide films, and the results of the durability tests of the anodic oxide films that only the specimens Nos. 1, 2, 4 and 5 of the examples meet all the criteria. The specimens Nos. 1, 2, 4 and 5 of the examples meeting all the criteria have a high hardness and are satisfactory in both durability and low polluting property.

What is claimed is:

1. An anodized aluminum alloy material formed of an aluminum alloy having a Mg content between 0.1 and 2.0% by mass, a Si content between 0.1 and 2.0% by mass, a Mn

content between 0.1 and 2.0% by mass, and an Fe, a Cr and a Cu content of 0.03% by mass or below and containing Al and unavoidable impurities as other components, and coated with an anodic oxide film;

wherein parts of the anodic oxide film at different positions with respect to thickness of the anodic oxide film have different hardnesses, respectively, and difference in Vickers hardness between a part having the highest hardness and a part having the lowest hardness is Hv 5 or above.

2. The anodized aluminum alloy material according to claim 1, wherein the hardness of the part having the lowest hardness of the anodic oxide film is Hv 365 or above.

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