

DESCRIPTION

LAMINATE AND METHOD FOR PRODUCING SAME

5 **Technical Field**

[0001]

The present invention relates to a laminate and a method for producing the same. More specifically, the present invention relates to a laminate suitable as a constituent member of devices such as semiconductor production devices, and a method for producing the laminate.

Background Art

[0002]

15 In a semiconductor production process, special halogen gases which are strongly reactive and corrosive such as fluorine, hydrogen chloride, boron trichloride, nitrogen trifluoride, chlorine trifluoride, and hydrogen bromide (these may be hereinafter referred to as "corrosive gas"), have conventionally been used in a dry etching step and in the cleaning of production devices for example.

[0003]

However, when the above corrosive gas reacts with the moisture contained in an atmosphere and is hydrolyzed,

products such as hydrogen fluoride, oxalic acid, and hydrogen chloride are generated. The products are problematic since they easily corrode metallic surfaces of constituent members such as valves, couplings, piping, and reaction chambers during the use of the corrosive gas.

[0004]

In order to increase corrosion resistance, methods of plating a metallic base material with a nickel-phosphorus alloy to form a fluorinated passive film of nickel have conventionally been performed (see for example Patent Literature 1 to Patent Literature 3). However, such methods were insufficient in some cases.

[0005]

Further, pinholes on a plating surface may be a reason why corrosion progresses. There seem to be several factors why pinholes occur, for example such that hydrogen gas generated by a plating reaction forms bubbles during the formation of a plating film to inhibit film formation, or such that impurities (such as an oxide film, contamination, and oil) remaining on a base material are not eliminated in a pretreatment step, resulting in the inhibition of film formation. In response to the above, Patent Literature 4 discloses an approach in which a hard alloy plating layer is formed on gold plating to increase abrasion resistance and

prevent discoloration and corrosion due to a reaction such as oxidation or sulfurization attributable to gas or moisture.

Citation List

5 Patent Literature

[0006]

Patent Literature 1: JP 2954716 B2

Patent Literature 2: JP 3094000 B2

Patent Literature 3: JP 2004-360066 A

10 Patent Literature 4: JP 2581021 B2

Summary of Invention

[0006a]

In a first aspect, the present disclosure refers to a
15 laminate comprising

a metallic base material,

a first nickel-containing plating film layer formed on
the metallic base material,

a gold plating film layer formed on the first nickel-
20 containing plating film layer,

a second nickel-containing plating film layer formed on
the gold plating film layer, and

a nickel fluoride film layer formed on the second
nickel-containing plating film layer.

[0006b]

In another aspect, the present disclosure refers to a method for producing a laminate, comprising

a step (A) of forming a first nickel-containing plating
5 film layer on a metallic base material,

a step (B) of forming a gold plating film layer on the first nickel-containing plating film layer,

a step (C) of forming a second nickel-containing plating film layer on the gold plating film layer, and

10 a step (D) of forming a nickel fluoride film layer on the second nickel-containing plating film layer.

[0006c]

In a further aspect, the present disclosure refers to a constituent member of a semiconductor production device, made
15 up of the laminate disclosed herein.

Technical Problem

[0007]

As a result of a study by the present inventors, the
20 methods of forming a fluorinated passive film of nickel on a nickel-phosphorus alloy plating surface as disclosed in Patent Literature 1 to Patent Literature 3 were found to involve insufficient hydrochloric acid corrosion resistance in some cases, due to the occurrence of corrosion starting

from pinholes in nickel-phosphorus alloy plating. The method disclosed in Patent Literature 4 had a problem that remarkably increased corrosion resistance cannot be expected since the outermost surface layer is alloy plating.

[0008]

In view of the above, an object of the present invention is to provide a metallic material which can be employed as a constituent member of a semiconductor production device and excels in corrosion resistance, particularly corrosion resistance to acids.

Solution to Problem

[0009]

10 The present invention relates to the following [1] to [14] for example.

 [1] A laminate comprising a metallic base material, a first nickel-containing plating film layer formed on the metallic base material, a gold plating film layer formed on the first nickel-containing plating film layer, a second nickel-containing plating film layer formed on the gold plating film layer, and a nickel fluoride film layer formed on the second nickel-containing plating film layer.

[0010]

20 [2] The laminate described in [1], in which pinholes in the gold plating film layer are sealed with a metal which is a nickel simple substance, and pinholes in the first and second nickel-containing plating film layers are sealed with a metal which is a gold simple substance.

[3] The laminate described in [1] or [2], in which the metallic base material comprises at least one metal selected from the group consisting of stainless steel, iron, aluminum, aluminum alloys, copper, and copper alloys.

5 [0011]

[4] The laminate described in any one of [1] to [3], having a nickel strike layer between the metallic base material and the first nickel-containing plating film layer, and between the gold plating film layer and the second
10 nickel-containing plating film layer.

[5] The laminate described in any one of [1] to [4], in which the first nickel-containing plating film layer comprises a nickel-phosphorus alloy plating layer having a phosphorus concentration of 8% by mass or higher and lower
15 than 10% by mass, and the second nickel-containing plating film layer comprises a nickel-phosphorus alloy plating layer having a phosphorus concentration of 10% by mass or higher and 12% by mass or lower.

[0012]

20 [6] The laminate described in any one of [1] to [5], in which the gold plating film layer comprises a displacement gold plating film layer and a reduction gold plating film layer in this order from the first nickel-containing plating film layer.

[7] The laminate described in any one of [1] to [6], in which the nickel fluoride film layer has a thickness of 70 nm or greater.

[0013]

5 [8] A method for producing a laminate, comprising a step (A) of forming a first nickel-containing plating film layer on a metallic base material, a step (B) of forming a gold plating film layer on the first nickel-containing plating film layer, a step (C) of forming a second nickel-
10 containing plating film layer on the gold plating film layer, and a step (D) of forming a nickel fluoride film layer on the second nickel-containing plating film layer.

[0014]

 [9] The method for producing a laminate described in
15 [8], comprising a step (X) between the step (C) and the step (D), in which the laminate obtained in the step (C) is subjected to a heat treatment under the condition of a temperature being 250°C or higher in order to seal pinholes in the gold plating film layer with a metal which is a nickel
20 simple substance and seal pinholes in the first and second nickel-containing plating film layers with a metal which is a gold simple substance.

[0015]

[10] The method for producing a laminate described in

[8] or [9], in which the step (D) is performed in an atmosphere having a fluorine gas concentration of 8% by volume or higher at a temperature of 250°C or higher.

[11] The method for producing a laminate described in
5 any one of [8] to [10], comprising a step of subjecting the metallic base material to a nickel strike treatment under the condition of a current density being 3 to 20 A/dm² before the step (A) and before the step (C).

[0016]

10 [12] The method for producing a laminate described in any one of [8] to [11], in which the step (A) comprises a step of forming a nickel-phosphorus alloy plating layer having a phosphorus concentration of 8% by mass or higher and lower than 10% by mass, and the step (C) comprises a step of
15 forming a nickel-phosphorus alloy plating layer having a phosphorus concentration of 10% by mass or higher and 12% by mass or lower.

[0017]

[13] The method for producing a laminate described in
20 any one of [8] to [12], in which the step (B) comprises a step (b1) of forming a displacement gold plating film layer, and a step (b2) of forming a reduction gold plating film layer after the step (b1).

[14] A constituent member of a semiconductor production

device, which is made up of the laminate described in any one of [1] to [7].

Advantageous Effects of Invention

5 [0018]

The present invention is capable of providing laminates having excellent corrosion resistance, particularly excellent corrosion resistance to acids.

Brief Description of Drawings

[0019]

[Fig. 1] Schematic drawings showing a laminate before and after a sealing treatment ((a) before the sealing treatment, (b) after the sealing treatment)

15

Description of Embodiments

[0020]

An embodiment of the present invention is specifically described below.

20

A laminate of an embodiment of the present invention comprises a metallic base material, a first nickel-containing plating film layer formed on the metallic base material, a gold plating film layer formed on the first nickel-containing plating film layer, a second nickel-containing plating film

layer formed on the gold plating film layer, and a nickel fluoride film layer formed on the second nickel-containing plating film layer.

[0021]

5 For the laminate of the embodiment of the present invention, it is preferred that pinholes in the gold plating film layer are sealed with a metal which is a nickel simple substance, and pinholes in the first and second nickel-containing plating film layers are sealed with a metal which
10 is a gold simple substance.

[0022]

A method for producing the laminate of the embodiment of the present invention comprises a step (A) of forming a first nickel-containing plating film layer on a metallic base
15 material, a step (B) of forming a gold plating film layer on the first nickel-containing plating film layer, a step (C) of forming a second nickel-containing plating film layer on the gold plating film layer, and a step (D) of forming a nickel fluoride film layer on the second nickel-containing plating
20 film layer.

[0023]

In addition, the method for producing the laminate of the embodiment of the present invention preferably comprises a step (X) between the step (C) and the step (D), in which

the laminate obtained in the step (C) is subjected to a heat treatment under the condition of the temperature being 250°C or higher for 2 hours or longer in order to seal pinholes in the gold plating film layer with a metal which is a nickel simple substance and seal pinholes in the first and second nickel-containing plating film layers with a metal which is a gold simple substance.

[0024]

[Metallic base material]

10 Metallic base materials used in the embodiment of the present invention have at least a surface made up of a metal. The metallic base materials are not particularly limited, and examples thereof are metals generally used in constituent members of semiconductor production devices, preferably including stainless steel, iron, aluminum, aluminum alloys, copper, and copper alloys.

[0025]

In order to increase adhesion to a nickel-containing plating film layer, the metallic base materials may be subjected to a pretreatment for the step (A) such as degreasing, acid cleaning, or a nickel strike treatment depending on the base materials. The nickel strike treatment is a preliminary plating treatment using a nickel-containing plating bath, in which a current density is preferably 3 to

20 A/dm², and more preferably 6 to 10 A/dm². The nickel strike treatment time is preferably 1 minute or longer and 5 minutes or shorter.

[0026]

5 [First nickel-containing plating film layer]

A first nickel-containing plating film layer is formed on the metallic base material by the step (A). When the metallic base material is subjected to a nickel strike treatment, a nickel strike layer is included between the
10 metallic base material and the first nickel-containing plating film layer.

[0027]

From the viewpoint of increased corrosion resistance, the nickel-containing plating film layer preferably contains
15 phosphorus, and preferably comprises a nickel-phosphorus alloy plating layer having a phosphorus concentration of 8% by mass or higher and lower than 10% by mass.

[0028]

The first nickel-containing plating film layer has a
20 nickel content of preferably 80% by mass or greater, more preferably 85% to 95% by mass, and particularly preferably 90% to 92% by mass in relation to 100% by mass of the entirety of the nickel-containing plating film layer. Due to the nickel content within the above range, the proportion of

phosphorus in the film layer increases, which enables the exhibition of excellent corrosion resistance.

[0029]

<Step (A)>

5 The first nickel-containing plating film layer may be formed on a metallic base material using an electroless plating bath comprising a nickel salt, and a phosphorus compound as a reducer. Examples of nickel salts are nickel sulfate, nickel chloride, nickel acetate, and nickel
10 carbonate. Examples of phosphorus compounds are sodium hypophosphite and potassium hypophosphite.

[0030]

 The film formation rate of the first nickel-phosphorus alloy plating layer is preferably 20 to 30 $\mu\text{m}/\text{h}$ (hour), and
15 more preferably 22 to 25 $\mu\text{m}/\text{h}$ (hour). The first nickel-phosphorus-containing plating film layer has a film thickness of preferably 5 μm or greater, and more preferably 7 to 25 μm . From the viewpoints of film properties of resisting pinhole formation and cost efficiency, the film thickness is
20 still more preferably from 9 to 20 μm .

[0031]

[Gold plating film layer]

 The gold plating film layer is formed on the nickel-containing plating film layer by the step (B).

The gold content in the gold plating film is, relative to 100% by mass of the entirety of the gold plating film layer, preferably 90% by mass or greater, more preferably 99% by mass or greater, and particularly preferably 99.9% by mass or greater. Due to the gold content within the above range, corrosion resistance of laminates according to the present invention is stabilized. The gold content is obtained by a method for quantifying impurities, namely by dissolving gold plating in aqua regia to measure the gold content by atomic absorption spectrometry and inductively coupled plasma (ICP) atomic emission spectrometry.

[0032]

From the viewpoints of film properties of resisting pinhole formation and cost efficiency, the thickness of the gold plating film is preferably from 0.1 μm to 2 μm , more preferably 0.2 to 1.5 μm , and particularly preferably 0.3 to 0.8 μm . It is publicly known based on conventional art that the thicker the precious metal plating film is, the more the number of pinholes is reduced, and high corrosion resistance is expected to be achievable by increasing the thickness of a precious metal plating film. Considering the high price thereof, however, it is preferred to select an appropriate thickness.

[0033]

<Step (B)>

Methods for forming the gold plating film layer are not particularly limited and an electroless gold plating method is preferred. In an electroless gold plating method, it is preferred to perform displacement gold plating and thereafter reduction gold plating. Namely, the step (B) preferably comprises a step (b1) of forming a displacement gold plating film layer, and a step (b2) of forming a reduction gold plating film layer after the step (b1).

10 [0034]

In displacement gold plating, nickel is dissolved from a nickel film releasing electrons, which reduce gold ions in the solution, and the reduced gold ions in the solution are deposited as a gold plating film. In reduction gold plating, gold ions in the solution are reduced by electrons released due to an oxidation reaction by a reducer, and thereby a gold plating film is deposited.

[0035]

Examples of electroless gold plating solutions are plating baths containing components such as gold potassium cyanide, gold chloride, gold sulfite, and gold thiosulfate. Examples of reducers are sodium hydroxide, dimethylamine borane, hexamethylenetetramine, and chain polyamines comprising an alkyl group having 3 or more carbon atoms and

multiple amino groups.

[0036]

The gold plating film layer may be formed by performing displacement gold plating preferably at a temperature of 50 to 90°C for 3 to 7 minutes, more preferably at a temperature of 65 to 75°C for 3 to 7 minutes, and by performing reduction gold plating preferably at a temperature of 55 to 65°C for 7 to 15 minutes, more preferably at a temperature of 58 to 62°C for 7 to 15 minutes.

10 [0037]

[Second nickel-containing plating film layer]

A second nickel-containing plating film layer is formed on the gold plating film layer by the step (C). When the gold plating film layer is subjected to nickel strike treatment, a nickel strike layer is included between the gold plating film layer and the second nickel-containing plating film layer.

[0038]

From the viewpoint of increased corrosion resistance, the nickel-containing plating film layer preferably contains phosphorus, and preferably comprises a nickel-phosphorus alloy plating layer having a phosphorus concentration of 10% by mass or higher and 12% by mass or lower.

[0039]

The second nickel-containing plating film layer has a

nickel content of preferably 80% by mass or greater, more preferably 85% to 95% by mass, and particularly preferably 90% to 92% by mass in relation to 100% by mass of the entirety of the nickel-containing plating film layer. Due to the nickel content within the above range, the proportion of phosphorus in the film layer increases, which enables the exhibition of excellent corrosion resistance. In addition, when electroless nickel-phosphorus alloy plating films having different phosphorus concentrations are laminated, film formation proceeds while pinhole defects are formed in different positions. For this reason, disturbance hardly reaches the base material directly, and increased corrosion resistance is expected.

[0040]

15 <Step (C)>

The second nickel-containing plating film layer may be formed on a metallic base material using an electroless plating bath comprising a nickel salt and a phosphorus compound as a reducer. Examples of the nickel salts are nickel sulfate, nickel chloride, nickel acetate, and nickel carbonate. Examples of the phosphorus compounds are sodium hypophosphite and potassium hypophosphite.

[0041]

The film formation rate of the second nickel-phosphorus

alloy plating layer is preferably 10 to 15 $\mu\text{m}/\text{h}$ (hour), and more preferably 11 to 13 $\mu\text{m}/\text{h}$ (hour). The second nickel-phosphorus alloy plating film layer has a film thickness of preferably 5 μm or greater, and more preferably 7 to 25 μm .

5 From the viewpoints of film properties of resisting pinhole formation and cost efficiency, the film thickness is still more preferably from 10 to 20 μm .

[0042]

[Sealing treatment]

10 A sealing treatment is performed by sealing pinholes in the gold plating film layer with a metal which is a nickel simple substance, and by sealing pinholes in the first and second nickel-containing plating film layers with a metal which is a gold simple substance.

15 [0043]

<Step (X)>

In the step (X), the laminate obtained in the step (C) is subjected to a heat treatment between the step (C) and the later-described step (D) to cause metal thermal diffusion.

20 Thereby pinholes in the gold plating film layer are sealed with a metal which is a nickel simple substance, and pinholes in the first and second nickel-containing plating film layers are subjected to a sealing treatment with a metal which is a gold simple substance. The presence of gold and nickel simple

substances can be confirmed by energy dispersive X-ray spectroscopy (EDS).

The heat conditions are preferably at a temperature of 250°C or higher for 2 hours or longer, and more preferably at
5 a temperature of 300 to 350°C for 2 to 6 hours.

[0044]

[Nickel fluoride film layer]

A nickel fluoride film layer is formed on the second nickel-containing plating film layer. The nickel fluoride
10 film layer is a passive film. The nickel fluoride film layer as a passive film is formed by subjecting a surface of the second nickel-containing plating film layer to a fluorination treatment in the step (D), on the nickel-containing plating film layer.

15 [0045]

The thickness of the nickel fluoride film layer is preferably 70 nm or greater, more preferably 80 to 200 nm, and still more preferably 100 to 150 nm. Due to a thickness of the nickel fluoride film layer within the above range,
20 adhesion between the gold plating film layer and the second nickel-containing plating film layer is increased.

[0046]

<Step (D)>

In the step (D), a surface of the nickel-containing

plating film layer, which has undergone the steps (A) to (C) and the step (X) if necessary, is fluorinated with fluorine gas to form a nickel fluoride film layer.

[0047]

5 The step (D) is preferably performed in an atmosphere having a fluorine gas concentration of 8% by volume or higher, more preferably 10% by volume or higher. The film formation temperature is preferably 250°C or higher, and more preferably 300°C or higher. The fluorination treatment time
10 is preferably 2 hours or longer. Examples of gases accompanying fluorine gas are inert gases such as nitrogen gas. In the embodiment of the present invention, a fluorinated passive film made up of a thick film of nickel fluoride is obtained under the above reaction conditions. By
15 adjusting the thickness of the nickel alloy plating film, reaction temperature, and reaction time in accordance with the use of a member, the film thickness of the nickel fluoride film is adjustable in an intended way. The above reaction temperature means a temperature obtained by
20 measuring a temperature of a gas atmosphere in a reactor with a thermocouple.

Examples

[0048]

The present invention is more specifically described below with reference to, but not limited to, examples. The film thickness of each layer (excluding a nickel fluoride film layer) of a laminate was calculated based on the increased weight, layer area, and a known density. The film thickness of a nickel fluoride film layer was calculated by a later-described method which uses X-ray photoelectron spectroscopy (XPS).

[0049]

10 [Example 1]

 <Step (A)>

 A surface of stainless steel (SUS316L) was subjected to a pretreatment comprising degreasing, acid cleaning, and a nickel strike treatment. On the surface of the stainless steel having undergone the nickel strike treatment, a first nickel-containing plating film layer (film thickness: 10 μ m) having a phosphorus content of 8% by mass or greater and lower than 10% by mass in the formed film was formed using an electroless nickel-phosphorus plating chemical "NIMUDEN (trade name) NSX" (produced by C. Uyemura & Co., Ltd.) under the conditions of a plating temperature being 90°C and a pH value being 4.5 to 4.8, for a plating time of 25 minutes.

[0050]

 <Step (B)>

Using 2 types of electroless gold plating solutions
"Flash Gold NC (displacement type)" and "Self Gold OTK-IT
(reduction type)" (both produced by Okuno Pharmaceutical Co.,
Ltd.) in this order, a treatment at a displacement plating
5 temperature of 70°C for 5 minutes and a treatment at a
reduction plating temperature of 60°C for 10 minutes were
each performed in this order to form a gold plating film
layer having a total thickness of 0.6 μm on the first nickel-
containing plating film layer formed in the step (A).

10 [0051]

<Step C>

A surface of the gold plating film layer formed in the
step (B) was subjected to a nickel strike treatment in the
same manner as described in the step (A). On a surface of the
15 gold plating film layer having undergone the nickel strike
treatment, a second nickel-containing plating film layer
(film thickness: 10 μm) having a phosphorus content of 10% by
mass or greater and 12% by mass or lower in the formed film
was formed using an electroless nickel-phosphorus plating
20 chemical "NIMUDEN (trade name) HDX" (produced by C. Uyemura &
Co., Ltd.) for a plating time of 50 minutes.

[0052]

<Step (X)>

The stainless steel having the first nickel-containing

plating film layer, gold plating film layer, and second nickel-containing plating film layer formed in the steps (A), (B), and (C) was placed inside an atmospheric pressure gas-phase flow reactor, the temperature inside the reactor was
5 increased to 300°C, and this state was maintained for 2 hours.

[0053]

After heating, the stainless steel was analyzed by energy dispersive X-ray spectroscopy (EDS). It was confirmed
10 that pinholes in the first and second nickel-containing plating film layers were sealed with a metal which is a gold simple substance and that pinholes in the gold plating film layer were sealed with a metal which is a nickel simple substance.

15 [0054]

<Step (D)>

After the step (X), the atmosphere inside the atmospheric pressure gas-phase flow reactor was replaced with nitrogen gas, followed by the introduction of 100% by volume
20 of oxygen gas to completely replace the nitrogen gas with oxygen gas, and this state was maintained for 12 hours. Subsequently, the oxygen gas was replaced with nitrogen gas, followed by the introduction of 10% by volume of fluorine gas (the remaining 90% by volume was nitrogen gas), and this

state was maintained for 12 hours to form a nickel fluoride film layer. Further, nitrogen gas was supplied for 12 hours to stabilize the formed film. With respect to the obtained stainless steel having a nickel fluoride film as an outermost surface layer, the presence of nickel fluoride was confirmed based on the ratio of the amount of F to the amount of Ni detected by X-ray photoelectron spectroscopy (XPS). From the sputtering time and known sputtering rate of 2.4 nm/min (in terms of SiO₂) regarding F and Ni, the thickness of the nickel fluoride film was obtained to be 103 nm.

[0055]

[Example 2]

The step (A) was performed in the same manner as described in Example 1 and thereafter the step (B) in Example 1 was performed in the same manner as described in Example 1 except for changing the reduction gold plating treatment time to 20 minutes in order to form a gold plating film layer having a thickness of 1.2 μm . Thereafter, the steps (C), (X), and (D) were performed in the same manner as described in Example 1. The thickness of the nickel fluoride film was obtained in the same manner as described in Example 1, and the thickness was 103 nm.

[0056]

[Example 3]

An aluminum alloy (A5052) was used instead of the stainless steel (SUS316L) in Example 1 and a pretreatment comprising degreasing, an activation treatment, acid cleaning, and a zinc replacement treatment was performed.

5 Thereafter, the steps (A), (B), (C), (X), and (D) were performed in the same manner as described in Example 1. The thickness of the nickel fluoride film was obtained in the same manner as described in Example 1, and the thickness was 103 nm. The activation treatment was performed using an acid
10 mixture of ammonium acid fluoride and nitric acid as a treating agent at room temperature for 30 seconds. The acid cleaning was performed using nitric acid as a cleaning agent at room temperature for 25 seconds. The zinc replacement treatment was performed using a zincate bath as a treating
15 agent at room temperature for 25 seconds. In addition, the acid cleaning and zinc replacement treatment were each performed twice under the above conditions.

[0057]

[Comparative Example 1]

20 A surface of stainless steel (SUS316L) was subjected to a pretreatment comprising degreasing, acid cleaning, and a nickel strike treatment. On a surface of the stainless steel having undergone the nickel strike treatment, a first nickel-containing plating film layer having a phosphorus content of

8% by mass or greater and lower than 10% by mass in the formed film was formed using an electroless nickel-phosphorus plating chemical "NIMUDEN (trade name) NSX" (produced by C. Uyemura & Co., Ltd.) under the conditions of a plating temperature being 90°C and a pH value being 4.5 to 4.8, at a film formation rate of 10 µm/25 minutes. Subsequently, a second nickel-containing plating film layer having a phosphorus content of 10% by mass or greater and 12% by mass or lower in the formed film was formed using an electroless nickel-phosphorus plating chemical "NIMUDEN (trade name) HDX" (produced by C. Uyemura & Co., Ltd.) at a film formation rate of 10 µm/50 minutes. Thereby, nickel-containing plating film layers having a total thickness of 20 µm were formed on the stainless steel having undergone the nickel strike treatment.

The step (D) was thereafter performed in the same manner as described in Example 1. Thereby, the nickel-containing plating film layers and a nickel fluoride film layer were formed on a surface of the stainless steel having undergone the nickel strike treatment.

[0058]

[Comparative Example 2]

In Comparative Example 1, an aluminum alloy (A5052) was used as the metallic base material instead of stainless steel (SUS316L), a pretreatment comprising degreasing, an

activation treatment, acid cleaning, and a zinc replacement treatment was performed, and thereafter electroless nickel-phosphorus alloy plating film layers and a nickel fluoride film layer were formed in the same manner as described in

5 Comparative Example 1.

[0059]

[Comparative Example 3]

In Example 1, only the steps (A), (B), and (C) were performed, that is, the steps (X) and (D) were not performed,
10 to form a first nickel-containing plating film layer, a gold plating film layer, and a second nickel-containing plating film layer on stainless steel.

[0060]

[Evaluation]

15 A hydrochloric acid corrosion resistance test was performed on the films formed on the surfaces of the metallic base materials obtained in the above Examples 1 to 3 and Comparative Examples 1 to 3. The evaluation results are summarized in Table 1.

20 [0061]

<Hydrochloric acid corrosion resistance test>

A test piece in a size of 15 mm (length) x 15 mm (width) x 1 mm (thickness) was immersed in a 35% by mass hydrochloric acid solution at a temperature of 25°C for 5

hours. Based on the reduced amount of mass [mg/dm²] before and after the immersion, hydrochloric acid corrosion resistance was evaluated in accordance with the following criteria.

5 (Evaluation criteria)

A: less than 0.1 mg/dm²

B: 0.1 mg/dm² or greater and less than 3.0 mg/dm²

C: 3.0 mg/dm² or greater and less than 10.0 mg/dm²

D: 10.0 mg/dm² or greater

[0062]

[Table 1]

Table 1

	Example 1	Example 2	Example 3	Comparative Example 1	Comparative Example 2	Comparative Example 3
Metallic base material	SUS	SUS	Al	SUS	Al	SUS
First nickel-containing plating film layer [μm]	10	10	10	10	10	10
Second nickel-containing plating film layer [μm]	10	10	10	10	10	10
Gold plating film layer [μm]	0.6	1.2	0.6	-	-	0.6
Nickel fluoride film layer [nm]	103	103	103	103	103	-
Hydrochloric acid corrosion resistance	B	A	B	C	C	D

[0063]

In Table 1, SUS means stainless steel (SUS316L) and Al means an aluminum alloy (A5052).

5 **Reference Signs List**

[0064]

- | | | |
|----|---|---|
| | 1 | Metallic base material |
| | 2 | First nickel-containing plating film layer |
| | 3 | Gold plating film layer |
| 10 | 4 | Second nickel-containing plating film layer |
| | 5 | Nickel fluoride film layer |
| | 6 | Pinhole |
| | 7 | Location where pinhole was subjected to sealing treatment |

15

CLAIMS

[Claim 1]

A laminate comprising
a metallic base material,
5 a first nickel-containing plating film layer formed on
the metallic base material,
a gold plating film layer formed on the first nickel-
containing plating film layer,
a second nickel-containing plating film layer formed on
10 the gold plating film layer, and
a nickel fluoride film layer formed on the second
nickel-containing plating film layer.

[Claim 2]

The laminate according to claim 1, wherein pinholes in
15 the gold plating film layer are sealed with a metal which is
a nickel simple substance, and
pinholes in the first and second nickel-containing
plating film layers are sealed with a metal which is a gold
simple substance.

20 [Claim 3]

The laminate according to claim 1 or 2, wherein the
metallic base material comprises at least one metal selected
from the group consisting of stainless steel, iron, aluminum,
aluminum alloys, copper, and copper alloys.

[Claim 4]

The laminate according to any one of claims 1 to 3,
having a nickel strike layer between the metallic base
material and the first nickel-containing plating film layer,
5 and between the gold plating film layer and the second
nickel-containing plating film layer.

[Claim 5]

The laminate according to any one of claims 1 to 4,
wherein the first nickel-containing plating film layer
10 comprises a nickel-phosphorus alloy plating layer having a
phosphorus concentration of 8% by mass or higher and lower
than 10% by mass, and the second nickel-containing plating
film layer comprises a nickel-phosphorus alloy plating layer
having a phosphorus concentration of 10% by mass or higher
15 and 12% by mass or lower.

[Claim 6]

The laminate according to any one of claims 1 to 5,
wherein the gold plating film layer comprises a displacement
gold plating film layer and a reduction gold plating film
20 layer in this order from the first nickel-containing plating
film layer.

[Claim 7]

The laminate according to any one of claims 1 to 6,
wherein the nickel fluoride film layer has a thickness of 70

nm or greater.

[Claim 8]

A method for producing a laminate, comprising
a step (A) of forming a first nickel-containing plating
5 film layer on a metallic base material,
a step (B) of forming a gold plating film layer on the
first nickel-containing plating film layer,
a step (C) of forming a second nickel-containing
plating film layer on the gold plating film layer, and
10 a step (D) of forming a nickel fluoride film layer on
the second nickel-containing plating film layer.

[Claim 9]

The method for producing a laminate according to claim
8 comprising a step (X) between the step (C) and the step
15 (D), wherein the laminate obtained in the step (C) is
subjected to a heat treatment under the condition of a
temperature being 250°C or higher in order to seal pinholes
in the gold plating film layer with a metal which is a nickel
simple substance and seal pinholes in the first and second
20 nickel-containing plating film layers with a metal which is a
gold simple substance.

[Claim 10]

The method for producing a laminate according to claim
8 or 9, wherein the step (D) is performed in an atmosphere in

which a fluorine gas concentration is 8% by volume or higher and a temperature is 250°C or higher.

[Claim 11]

The method for producing a laminate according to any
5 one of claims 8 to 10, comprising a step of subjecting the metallic base material to a nickel strike treatment under the condition of a current density of 3 to 20 A/dm² before the step (A) and before the step (C).

[Claim 12]

10 The method for producing a laminate according to any one of claims 8 to 11,

wherein the step (A) comprises a step of forming a nickel-phosphorus alloy plating layer having a phosphorus concentration of 8% by mass or higher and lower than 10% by
15 mass, and

the step (C) comprises a step of forming a nickel-phosphorus alloy plating layer having a phosphorus concentration of 10% by mass or higher and 12% by mass or lower.

20 [Claim 13]

The method for producing a laminate according to any one of claims 8 to 12, wherein the step (B) comprises a step (b1) of forming a displacement gold plating film layer, and a step (b2) of forming a reduction gold plating film layer

after the step (b1).

[Claim 14]

A constituent member of a semiconductor production
device, made up of the laminate according to any one of
5 claims 1 to 7.

LAMINATE AND METHOD FOR PRODUCING SAME**ABSTRACT**

The object of the present invention is to provide a metallic material which can be employed as a constituent member of a semiconductor production device and has excellent corrosion resistance, particularly excellent corrosion resistance to acids. A laminate according to the present invention comprises a metallic base material, a first nickel-containing plating film layer formed on the metallic base material, a gold plating film layer formed on the first nickel-containing plating film layer, a second nickel-containing plating film layer formed on the gold plating film layer, and a nickel fluoride film layer formed on the second nickel-containing plating film layer.

[Fig. 1]