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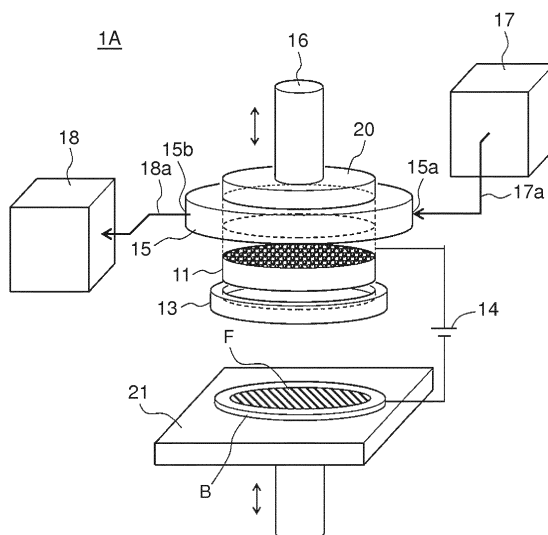
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(54) **FILM-FORMING METAL SOLUTION AND METAL FILM-FORMING METHOD**

(57) A film-forming metal solution for supplying metal ions to a solid electrolyte membrane in film formation is provided. In the film formation, the solid electrolyte membrane is disposed between an anode and a substrate as a cathode, and the solid electrolyte membrane is brought into contact with the substrate and a voltage is placed between the anode and the substrate to precipitate a metal on a surface of the substrate from the metal ions

contained in the solid electrolyte membrane, so that a metal film of the metal is formed on the surface of the substrate. The film-forming metal solution contains a solvent, and the metal dissolved in the solvent in an ionic state. A hydrogen ion concentration of the film-forming metal solution is within a range of 0 to $10^{-7.85}$ mol/L at 25°C.

FIG. 1



Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The invention relates to a film-forming metal solution for forming a nickel film, and a metal film-forming method of forming a metal film using the film-forming metal solution. More specifically, the invention relates to a film-forming metal solution suitable for forming a metal film on a surface of a substrate by bringing a solid electrolyte membrane into contact with the substrate, and a metal film-forming method of forming a metal film using the film-forming metal solution.

2. Description of Related Art

[0002] In the course of producing an electronic circuit substrate or the like, a nickel film is conventionally formed on a surface of a substrate to form a nickel circuit pattern. Proposed techniques of forming such metal films include a technique of forming, on a surface of a semiconductor substrate made of silicon (Si) or the like, a metal film by plating such as electroless plating (see, for example, Japanese Patent Application Publication No. 2010-037622 (JP 2010-037622 A)), and a technique of forming a metal film by physical vapor deposition (PVD) such as sputtering.

[0003] However, plating such as electroless plating creates the need for aqueous cleaning of a substrate after the plating and the need for treatment of waste liquid resulting from the aqueous cleaning. When a film is formed on a surface of a substrate by PVD such as sputtering, internal stress is generated in the formed metal film. This imposes a limit on an increase in the film thickness. In particular, when sputtering is employed, a film may be formed only under high vacuum.

[0004] In view of this, for example, a film-forming apparatus, as illustrated in FIG. 4, including at least an anode 11, a solid electrolyte membrane 13 and an electric power supply (not illustrated) is proposed (see, for example, WO2013/125643). The anode 11 is made of a porous material. The solid electrolyte membrane 13 is disposed between the anode 11 and a substrate B, which serves as a cathode, such that an aqueous solution containing metal ions comes into contact with the anode 11-side portion of the solid electrolyte membrane 13. The electric power supply places a voltage between the anode 11 and the substrate B.

[0005] A housing 15 of the film-forming apparatus has a reservoir 19 in which the aqueous solution containing the metal ions is stored. The anode 11 and the solid electrolyte membrane 13 are disposed such that the aqueous solution containing the metal ions stored in the reservoir 19 can be supplied to the solid electrolyte membrane 13 via the anode 11.

[0006] With the film-forming apparatus described above, a metal film F made of metal is formed on a surface of the substrate B. Specifically, the metal film F is formed on the surface of the substrate B when the electric power supply places a voltage between the anode 11 and the substrate B, so that a metal is precipitated on the surface of the substrate B from the metal ions contained in the solid electrolyte membrane 13.

[0007] When the technique described in WO 2013/125643 is employed, however, hydrogen gas may be generated between the solid electrolyte membrane 13 and the substrate B, and the thus generated hydrogen gas may be accumulated between the solid electrolyte membrane 13 and the substrate B. The accumulated hydrogen gas remains, as illustrated in FIG. 4, in the form of bubbles between the solid electrolyte membrane 13 and the substrate B, which has been brought into contact with the solid electrolyte membrane 13 under pressure. Thus, the metal precipitation may be inhibited at the locations where the hydrogen gas bubbles are formed. As a result, non-precipitated portions (voids) where a metal is not precipitated are formed in the metal film F, and such voids make the metal film F non-uniform.

SUMMARY OF THE INVENTION

[0008] The invention provides a film-forming metal solution with which generation of hydrogen gas between a solid electrolyte membrane and a substrate placed in contact with each other is inhibited, and a metal film-forming method of forming a metal film using the film-forming metal solution.

[0009] As a result of earnest studies, the present inventors presumed that when a solvent in which a metal is dissolved in an ionic state is water, hydrogen ions (free hydrogen) present due to the self-ionization of the water are reduced when the metal is precipitated on a surface of a substrate that serves as a cathode, resulting in generation of hydrogen gas. Based on this presumption, the present inventors have obtained a novel finding that using a solvent having a lower hydrogen ion concentration than that of water makes it possible to inhibit generation of hydrogen gas more reliably than in a case where water is used as a solvent.

[0010] The invention is made on the basis of this novel finding obtained by the present inventors. A first aspect of the invention relates to a film-forming metal solution for supplying metal ions to a solid electrolyte membrane in film formation in which the solid electrolyte membrane is disposed between an anode and a substrate as a cathode, and the solid electrolyte membrane is brought into contact with the substrate and a voltage is placed between the anode and the

substrate to precipitate a metal on a surface of the substrate from the metal ions contained in the solid electrolyte membrane to form a metal film of the metal on the surface of the substrate. The film-forming metal solution contains a solvent, and the metal dissolved in the solvent in an ionic state. A hydrogen ion concentration of the film-forming metal solution is within a range of 0 to $10^{-7.85}$ mol/L at 25°C.

[0011] According to the first aspect of the invention, the total amount of hydrogen ions (protons) that migrate from the anode side to the cathode side of the solid electrolyte membrane is decreased by maintaining the hydrogen ion concentration of the film-forming metal solution within the above-described range. Thus, it is possible to inhibit generation of hydrogen gas between the solid electrolyte membrane and the substrate placed in contact with each other.

[0012] A hydrogen ion concentration of 0 mol/L means that the film-forming metal solution contains no hydrogen ions, and the upper limit value of the hydrogen ion concentration, $10^{-7.85}$ mol/L (at 25°C), is lower than a hydrogen ion concentration of 10^{-7} mol/L, attained at the time of self-ionization of water. It has been found, as a result of experiments made by the present inventors, that when the hydrogen ion concentration exceeds $10^{-7.85}$ mol/L (at 25°C), a uniform metal film is not formed due to generation of hydrogen gas.

[0013] In the invention, when a metal salt used as a solute contains no hydrogen, a hydrogen ion concentration of the film-forming metal solution is equal to a hydrogen ion concentration of the solvent. Because metal salts of most of metals used to form films contain no hydrogen, the hydrogen ion concentration of the film-forming metal solution is equal to the hydrogen ion concentration of the solvent.

[0014] Such a solvent preferably has a lower hydrogen ion concentration than that of water at the time of self-ionization, and examples of the solvent include an aprotic solvent and an alcoholic solvent. In these solvents, a metal is present in an ionic state (namely, a metal can be dissolved in these solvents in an ionic state).

[0015] The solvent may be an alcoholic solvent containing at least one selected from methanol, ethanol and propanol (1-propanol or 2-propanol), or a solvent containing the alcoholic solvent and water.

[0016] According to this aspect, the hydrogen ion concentrations of methanol, ethanol and propanol are respectively $10^{-8.35}$ mol/L, $10^{-8.55}$ mol/L and $10^{-8.25}$ mol/L, all of which are lower than the above-described upper limit concentration of $10^{-7.85}$ mol/L (at 25°C), and therefore hydrogen gas is less likely to be generated between the solid electrolyte membrane and the substrate. When methanol, ethanol or propanol is used, a metal such as nickel, tin or copper can be dissolved in the solvent in an ionic state. As long as the hydrogen ion concentration is $10^{-7.85}$ mol/L or less (at 25°C), the alcoholic solvent may contain water.

[0017] The metal to be dissolved in the solvent may have a higher ionization tendency than that of hydrogen. When a metal having a higher ionization tendency than that of hydrogen is used, hydrogen is easily generated during precipitation of the metal. Thus, it is particularly effective to limit the hydrogen ion concentration as in the aspect of the invention. Thus, hydrogen gas is less likely to be generated during precipitation of the metal, and hence a uniform metal film is formed.

[0018] Among metal species to be precipitated, a metal having a higher oxidation-reduction potential than that of hydrogen (such as copper or silver) has a lower ionization tendency than that of hydrogen, and hence is easily precipitated during precipitation. However, even when such a metal is used, hydrogen gas may be generated during precipitation under certain film-forming conditions. Thus, even when such a metal is used, the above aspect of the invention offers the effect of inhibiting generation of hydrogen gas.

[0019] The metal having a higher ionization tendency than that of hydrogen is nickel. As is obvious from experiments made by the present inventors, a uniform nickel film is obtained by using a solution containing nickel ions and having a hydrogen ion concentration that falls within the above-described range.

[0020] A second aspect of the invention relates to a metal film-forming method for forming a metal film using the film-forming metal solution described above. According to the metal film-forming method, a solid electrolyte membrane is disposed between an anode and a substrate as a cathode, and the solid electrolyte membrane is brought into contact with the substrate and a voltage is placed between the anode and the substrate to precipitate a metal on a surface of the substrate from metal ions contained in the solid electrolyte membrane to form a metal film of the metal on the surface of the substrate.

[0021] In this case, while the metal ions are supplied to the solid electrolyte membrane by bringing the film-forming metal solution into contact with the solid electrolyte membrane, a voltage is placed between the anode and the substrate to form the metal film on the surface of the substrate.

[0022] According to this aspect, it is possible to form a metal film while inhibiting generation of hydrogen gas, which may occur when a metal film is formed by precipitating a metal from metal ions with a solid electrolyte membrane and a substrate placed in contact with each other.

[0023] According to the aspects of the invention, it is possible to inhibit generation of hydrogen gas between the solid electrolyte membrane and the substrate placed in contact with each other.

BRIEF DESCRIPTION OF THE DRAWINGS

[0024] Features, advantages, and technical and industrial significance of exemplary embodiments of the invention will

be described below with reference to the accompanying drawings, in which like numerals denote like elements, and wherein:

FIG. 1 is a schematic conceptual diagram of a metal film-forming apparatus according to an embodiment of the invention;

FIG. 2 is a schematic sectional view for describing a metal film-forming method performed by the metal film-forming apparatus illustrated in FIG. 1;

FIG. 3A is a photograph of a nickel film obtained in Example 2;

FIG. 3B is a photograph of a nickel film obtained in Comparative Example 2; and

FIG. 4 is a diagram for describing a problem in forming a film using a conventional film-forming apparatus including a solid electrolyte membrane.

DETAILED DESCRIPTION OF EMBODIMENTS

[0025] Hereinafter, a metal film-forming apparatus capable of appropriately performing a metal film-forming method according to an embodiment of the invention will be described.

[0026] FIG. 1 is a schematic conceptual diagram of a metal film-forming apparatus 1A (hereinafter, referred simply to as "film-forming apparatus 1A") according to the embodiment of the invention. FIG. 2 is a schematic sectional view for describing a metal film-forming method performed by the film-forming apparatus 1A to form a metal film F illustrated in FIG. 1.

[0027] As illustrated in FIG. 1, the film-forming apparatus 1A according to the invention precipitates a metal from metal ions to form, on a surface of a substrate B, a metal film made of the precipitated metal. The substrate B in the present embodiment is a substrate made of a metal material such as aluminum, or a surface-treated resin or silicon substrate on which a metal primary coating is formed.

[0028] The film-forming apparatus 1A includes at least an anode 11 made of metal, a solid electrolyte membrane 13, and an electric power supply 14. The solid electrolyte membrane 13 is disposed on a surface of the anode 11, at a position between the anode 11 and the substrate B that serves as a cathode. The electric power supply 14 places a voltage between the anode 11 and the substrate B, which serves as the cathode.

[0029] The anode 11 is housed in a housing (metal ion supplying portion) 15 that supplies, to the anode 11, a solution L containing metal ions for film formation (hereinafter, referred to as "metal solution"). The housing 15 has a perforated portion that vertically passes through the housing 15, and the anode 11 is housed in the inner space of the housing 15. The solid electrolyte membrane 13 has a recessed portion that covers a bottom surface of the anode 11. The solid electrolyte membrane 13 covers the lower opening of the perforated portion of the housing 15 with a lower portion of the anode 11 housed in the solid electrolyte membrane 13.

[0030] In the perforated portion of the housing 15, there is disposed a contact pressurizing portion (metal punch) 20 that is in contact with a top surface of the anode 11 to pressurize the anode 11. The contact pressurizing portion 20 pressurizes the solid electrolyte membrane 13 via the anode 11, so that the surface of the substrate B is pressurized with the solid electrolyte membrane 13. Specifically, the contact pressurizing portion 20 pressurizes the surface of the anode 11 corresponding to a film-forming region E on the surface of the substrate B where the metal film F is to be formed, such that the film-forming region E is uniformly pressurized.

[0031] In the present embodiment, the bottom surface of the anode 11 has a size that coincides with that of the film-forming region E of the substrate B, and the top surface and the bottom surface of the anode 11 are in the same size. Thus, when the (whole) top surface of the anode 11 is pressurized with the contact pressurizing portion 20 using a thrust exerted by a pressurizing device 16 (described later), (the whole of) the film-forming region E of the substrate B is uniformly pressurized with the (whole) bottom surface of the anode 11 via the solid electrolyte membrane 13.

[0032] In addition, a solution tank 17 is connected to one side of the housing 15 via a supply pipe 17a, and a waste liquid tank 18 is connected to the other side of the housing 15 via a waste liquid pipe 18a. The metal solution L is stored in the solution tank 17, and waste liquid, that is, the used metal solution L, is collected into the waste liquid tank 18.

[0033] The supply pipe 17a is connected to a supply passage 15a of the housing 15, through which the metal solution L is supplied to the anode 11. The waste liquid pipe 18a is connected to a discharge passage 15b of the housing 15, through which the metal solution L is discharged into the waste liquid tank 18. As illustrated in FIG. 2, the anode 11 made of a porous material is disposed in a passage that connects the supply passage 15a and the discharge passage 15b of the housing 15 to each other.

[0034] Due to this structure, the metal solution L stored in the solution tank 17 is supplied through the supply pipe 17a into the housing 15. In the housing 15, the metal solution L flows through the supply passage 15a and then flows from the supply passage 15a into the anode 11. The metal solution L that has passed through the anode 11 flows through the discharge passage 15b to be delivered to the waste liquid tank 18 through the waste liquid pipe 18a.

[0035] In addition, the pressurizing device 16 is connected to the contact pressurizing portion 20. The pressurizing

device 16 presses the solid electrolyte membrane 13 against the film-forming region E of the substrate B by moving the anode 11 toward the substrate B. Examples of the pressurizing device 16 include a hydraulic cylinder and a pneumatic cylinder. The film-forming apparatus 1A further includes a base 21 on which the substrate B is fixed. The base 21 is used to adjust the alignment of the substrate B with respect to the anode 11.

[0036] The anode 11 is made of a porous material that allows the metal solution L to pass therethrough and that supplies metal ions to the solid electrolyte membrane 13. The porous material is not limited to any particular porous materials as long as (1) the porous material has corrosion resistance against the metal solution L, (2) the porous material has an electrical conductivity high enough to serve as an anode, (3) the porous material allows the metal solution L to pass therethrough, and (4) the porous material can be pressurized by the pressurizing device 16 via the contact pressurizing portion 20 described above. Examples of the porous material include metal foams, such as a titanium foam, having a lower ionization tendency (or a higher electrode potential) than that of plating metal ions and made of open-cell foams having open pores.

[0037] When a metal foam is used, the metal foam is not limited to any particular metal foams as long as the metal foam satisfies the condition (3) described above. However, a metal foam having a porosity of approximately 50 to 95% by volume, a pore diameter of approximately 50 to 600 μm and a thickness of approximately 0.1 to 50 mm is preferably used.

[0038] The solid electrolyte membrane 13 is not limited to any particular solid electrolyte membranes as long as the solid electrolyte membrane 13 can be impregnated with the metal ions when the solid electrolyte membrane 13 is brought into contact with the metal solution L and a metal derived from the metal ions can be precipitated on the surface of the substrate B in response to application of a voltage. Examples of the material of the solid electrolyte membrane 13 include fluorine resins such as Nafion® manufactured by DuPont, hydrocarbon resins, polyamic acid resins, and resins having an ion exchange function such as SELEMION (including CMV, CMD and CMF series) manufactured by Asahi Glass Co., Ltd.

[0039] In the present embodiment, a porous material is used as the anode 11 of the apparatus for forming the metal film F. However, as long as metal ions can be supplied to the solid electrolyte membrane 13, a gap may be formed between an anode and a solid electrolyte membrane and a metal solution may be supplied into the gap, as described later.

[0040] Hereinafter, a metal film-forming method for forming a metal film using the film-forming apparatus 1A will be described. First, as illustrated in FIG. 1 and FIG. 2, the substrate B is placed on the base 21, the alignment of the substrate B with respect to the anode 11 is adjusted, and the temperature of the substrate B is adjusted. Next, the solid electrolyte membrane 13 is disposed on a surface of the anode 11 made of a porous material, and the solid electrolyte membrane 13 is brought into contact with the substrate B.

[0041] Next, the anode 11 is moved toward the substrate B by the pressurizing device 16, so that the solid electrolyte membrane 13 is pressed against the film-forming region E of the substrate B. Thus, the solid electrolyte membrane 13 is pressurized via the anode 11, and hence the solid electrolyte membrane 13 uniformly conforms to the surface of the film-forming region E of the substrate B. In other words, while the solid electrolyte membrane 13 is kept in contact with (pressed against) the substrate B by using, as a back-up material, the anode 11 pressurized by the contact pressurizing portion 20, the metal film F having a more uniform thickness is formed.

[0042] Next, the electric power supply 14 places a voltage between the anode 11 and the substrate B, which serves as the cathode, so that the metal is precipitated on the surface of the substrate B from the metal ions contained in the solid electrolyte membrane 13. The anode 11 is in direct contact with the contact pressurizing portion 20 made of metal, and thus there is electrical continuity between the anode 11 and the contact pressurizing portion 20. Thus, the electric power supply 14 can place a voltage between the anode 11 and the substrate B.

[0043] In this case, a metal film is formed while the metal solution L is caused to flow through the anode 11. Using the anode 11 made of a porous material allows the metal solution L to pass through the anode 11. Hence, the metal solution L is supplied, together with the metal ions, to the solid electrolyte membrane 13. Thus, in the course of forming a metal film, the metal solution L is constantly and stably supplied into the anode 11 made of a porous material. The metal solution L thus supplied passes through the anode 11 to come into contact with the solid electrolyte membrane 13 disposed adjacent to the anode 11, and thus the solid electrolyte membrane 13 is impregnated with the metal ions.

[0044] When a voltage is placed between the anode 11 and the substrate B, which serves as the cathode, the metal ions contained in the solid electrolyte membrane 13 migrate from the anode 11 side to the substrate B side, and then the metal is precipitated, on the surface of the substrate B, from the metal ions contained in the solid electrolyte membrane 13. As a result, the metal film F is formed on the surface of the substrate B.

[0045] In this way, the film-forming region E of the substrate B is uniformly pressurized with the solid electrolyte membrane 13, and thus the metal film F is formed on the substrate B while the solid electrolyte membrane 13 uniformly conforms to the film-forming region E of the substrate B. As a result, the uniform metal film F having a uniform thickness with less variations is formed on the surface of the film-forming region E of the substrate B.

[0046] The metal solution L contains a solvent and a metal (metal ions) dissolved in the solvent in an ionic state. In the present embodiment, a hydrogen ion concentration of the metal solution is within a range of 0 to $10^{-7.85}$ mol/L at 25°C.

[0047] When the hydrogen ion concentration of the metal solution L is maintained within the above-described range, the total amount of hydrogen ions (protons) that migrate from the anode side to the cathode side of the solid electrolyte membrane 13 is decreased. Thus, it is possible to inhibit generation of hydrogen gas between the solid electrolyte membrane 13 and the substrate B placed in contact with each other.

[0048] A solvent having a hydrogen ion concentration of 0 mol/L is a solvent that contains no hydrogen ions. Examples of such a solvent include polar aprotic solvents such as tetrahydrofuran (THF), acetonitrile, N,N-dimethylformamide (DMF) and dimethyl sulfoxide. Because these solvents have polarities, these solvents can contain a metal such as nickel, tin or copper (described later) in an ionic state.

[0049] Examples of a solvent of a metal solution having a hydrogen ion concentration of $10^{-7.85}$ mol/L or less (at 25°C) include alcoholic solvents. A solvent obtained by adding water to an alcoholic solvent may be used as long as the solvent satisfies the above-described condition on a hydrogen ion concentration.

[0050] Examples of alcoholic solvents that can contain a metal such as nickel, tin or copper in an ionic state include methanol, ethanol, propanol (1-propanol or 2-propanol) and a solvent obtained by mixing at least two of these solvents together. Even when a considerably small amount of water is added to such an alcoholic solvent, water molecules and alcoholic molecules are integrated with each other to inhibit generation of free hydrogen in the solvent.

[0051] A hydrogen ion concentration of a metal solution containing nickel, tin or copper is substantially equal to a hydrogen ion concentration of an alcoholic solvent (or an alcoholic solvent containing water).

[0052] A metal to be dissolved in a solvent in an ionic state is charged into the solvent in the form of ionizable metal salt and is then dissolved in the solvent in an ionic state. Examples of such a metal include cobalt, iron, nickel, tin, copper and silver. Among these metals, nickel and tin, which have a higher ionization tendency than that of hydrogen, are preferably used.

[0053] When such a metal is used, the metal having a higher ionization tendency than that of hydrogen is precipitated on the surface of the substrate B by placing a voltage between the anode 11 and the substrate B. As a result, hydrogen gas is less likely to be generated in the course of forming the metal film F, and thus a uniform metal film F is obtained.

[0054] The invention will be described below with reference to the following examples.

Example 1

[0055] Nickel chloride (metal salt) was dissolved in methanol (solvent) to prepare a 0.1 M nickel solution (metal solution). A solid electrolyte (manufactured by DuPont; Nation N117) and a porous nickel plate were stacked on a copper substrate, and the 0.1 M nickel solution was supplied to the porous nickel plate. Then, the porous nickel plate was electrically connected to the copper substrate, and a constant voltage of 2.4 V was applied for 60 seconds. In this way, a nickel film was formed on the copper substrate.

Example 2

[0056] A nickel film was formed in a manner similar to that in Example 1. The difference from Example 1 is that ethanol was used as a solvent.

Example 3

[0057] A nickel film was formed in a manner similar to that in Example 1. The difference from Example 1 is that propanol (1-propanol) was used as a solvent.

Example 4

[0058] A nickel film was formed in a manner similar to that in Example 1. The difference from Example 1 is that a mixed liquid of methanol and water (a mixed liquid containing 90% methanol by volume and 10% water by volume) was used as a solvent.

Comparative Example 1

[0059] A nickel film was formed in a manner similar to that in Example 1. The difference from Example 1 is that a mixed liquid of methanol and water (a mixed liquid containing 85% methanol by volume and 15% water by volume) was used as a solvent.

Comparative Example 2

[0060] A nickel film was formed in a manner similar to that in Example 1. The difference from Example 1 is that water was used as a solvent.

Comparative Example 3

[0061] A nickel film was formed in a manner similar to that in Example 1. The difference from Example 1 is that butanol (1-butanol) was used as a solvent.

Visual check of films

[0062] The nickel films obtained in Examples 1 to 4 and Comparative Examples 1 to 3 were visually checked. The results are shown in Table 1. Table 1 also shows calculated values (theoretical values) of hydrogen ion concentrations of the film-forming metal solutions (solvents) at 25°C in Examples 1 to 4 and Comparative Examples 1 to 3.

Table 1

	Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2	Comparative Example 3
Type of solvent (volume ratio)	Methanol	Ethanol	Propanol	Methanol and water (90 : 10)	Methanol and water (85 : 15)	Water	Butanol
Hydrogen ion concentration (mol/L)	10 ^{-8.35}	10 ^{-8.55}	10 ^{-8.25}	10 ^{-7.85}	10 ^{-7.72}	10 ^{-7.00}	10 ^{-8.35}
Metal precipitation	Observed	Observed	Observed	Observed	Observed	Observed	Not observed
Uniform precipitation	Uniform	Uniform	Uniform	Uniform	Non-uniform	Non-uniform	-
Metal precipitation Observed:	Uniform precipitation Uniform:						
Precipitation of metal was visually observed	Precipitated metal had uniformly glossy appearance						
Metal precipitation Not observed:	Uniform precipitation Non-uniform:						
Precipitation of metal was not visually observed	Precipitated metal failed to have uniformly glossy appearance						

Results

[0063] As a result of visual check of the nickel film obtained in each of Examples 1 to 4, precipitation of nickel was observed and the color tone of the precipitated nickel was uniform, and hence it was confirmed that a uniform nickel film was obtained. FIG. 3A is a photograph of the nickel film obtained in Example 2.

[0064] As a result of visual check of the nickel film obtained in Comparative Example 1, precipitation of nickel was observed, but the color tone of the precipitated nickel was in a patchy pattern, which reveals the presence of voids.

[0065] As a result of visual check of the nickel film obtained in Comparative Example 2, the color tone of the nickel film was in a patchy pattern, which reveals the presence of voids. The patchy pattern was more conspicuous than that in Comparative Example 1 (see FIG. 3B).

[0066] The reason why the results of Comparative Examples 1 and 2 were obtained is presumed as follows. In Comparative Examples 1 and 2, the amount of free hydrogen was larger than that in Examples 1 to 4. Thus, hydrogen ions (protons) were reduced when a voltage was placed between the anode and the substrate. As a result, hydrogen gas was generated between the solid electrolyte membrane and the substrate. Thus, the hydrogen gas was accumulated between the solid electrolyte membrane and the substrate to disturb the precipitation of nickel, and voids (non-precipitated portions) were generated, resulting in formation of a film in a patchy pattern.

[0067] In Comparative Example 3, nickel chloride did not dissolve in the solvent, and precipitation of a nickel film was not observed. The reason for this may be as follows. As the amount of carbon in a molecule constituting the solvent is increased, the polarity of the molecule is lowered, and hence nickel cannot dissolve in the solvent in an ionic state.

[0068] While the embodiment of the invention has been described in detail, the invention is not limited to the above-described embodiment but may be implemented in various other embodiments within the scope of the invention.

[0069] In the above-described embodiment, the anode made of a porous material is used. However, a porous material need not be used as the anode as long as nickel ions are appropriately supplied to the solid electrolyte membrane. For example, a nickel solution may be supplied to a gap between the anode and the solid electrolyte membrane.

Claims

1. A film-forming metal solution for supplying metal ions to a solid electrolyte membrane in film formation in which the solid electrolyte membrane is disposed between an anode and a substrate as a cathode, and the solid electrolyte membrane is brought into contact with the substrate and a voltage is placed between the anode and the substrate to precipitate a metal on a surface of the substrate from the metal ions contained in the solid electrolyte membrane to form a metal film of the metal on the surface of the substrate, **characterized in that:**

the film-forming metal solution contains a solvent, and the metal dissolved in the solvent in an ionic state; and a hydrogen ion concentration of the film-forming metal solution is within a range of 0 to $10^{-7.85}$ mol/L at 25°C.

2. The film-forming metal solution according to claim 1, wherein the solvent is an alcoholic solvent containing at least one selected from methanol, ethanol and propanol, or a solvent containing the alcoholic solvent and water.

3. The film-forming metal solution according to claim 1 or 2, wherein the metal has a higher ionization tendency than an ionization tendency of hydrogen.

4. The film-forming metal solution according to claim 3, wherein the metal is nickel.

5. A metal film-forming method for forming a metal film using the film-forming metal solution according to any one of claims 1 to 4, **characterized in that**, while the metal ions are supplied to the solid electrolyte membrane by bringing the film-forming metal solution into contact with the solid electrolyte membrane, a voltage is placed between the anode and the substrate to form the metal film on the surface of the substrate.

FIG. 1

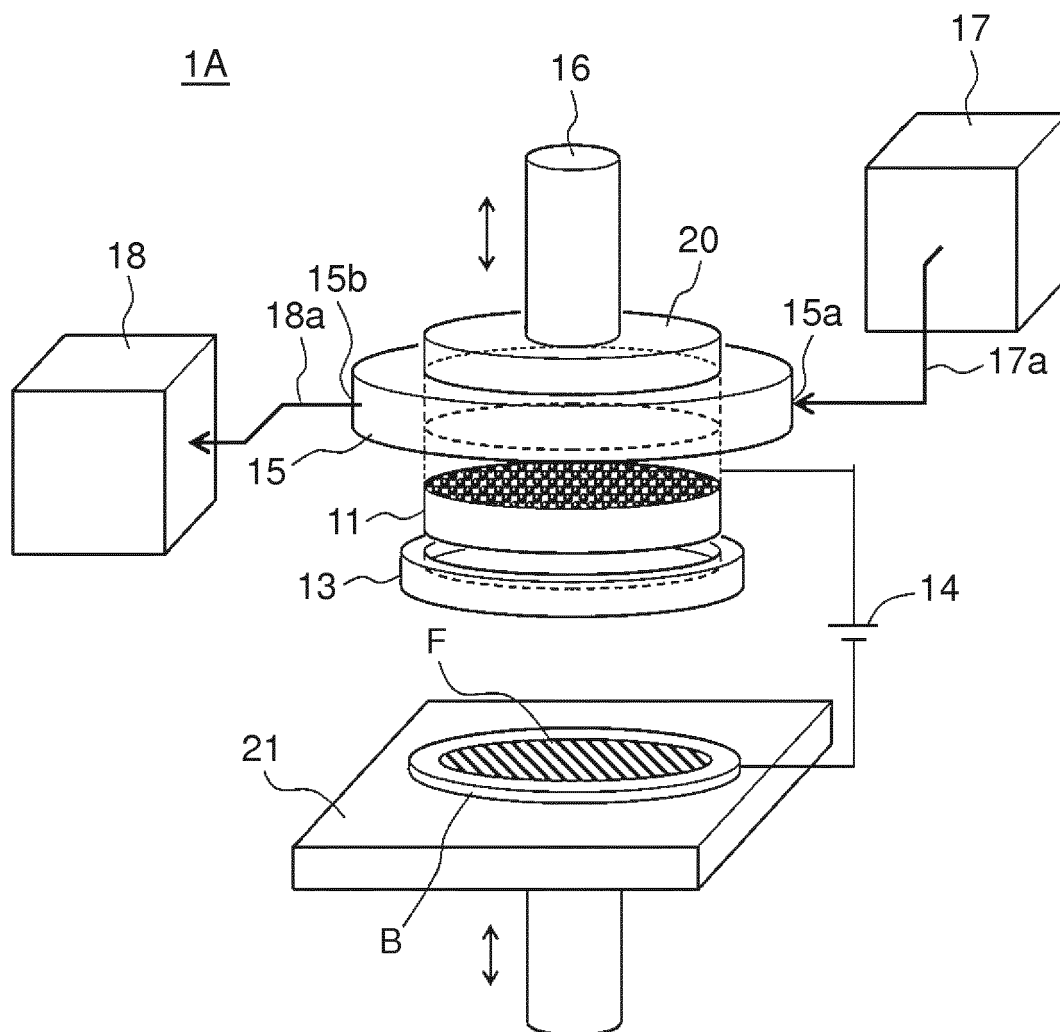


FIG. 2

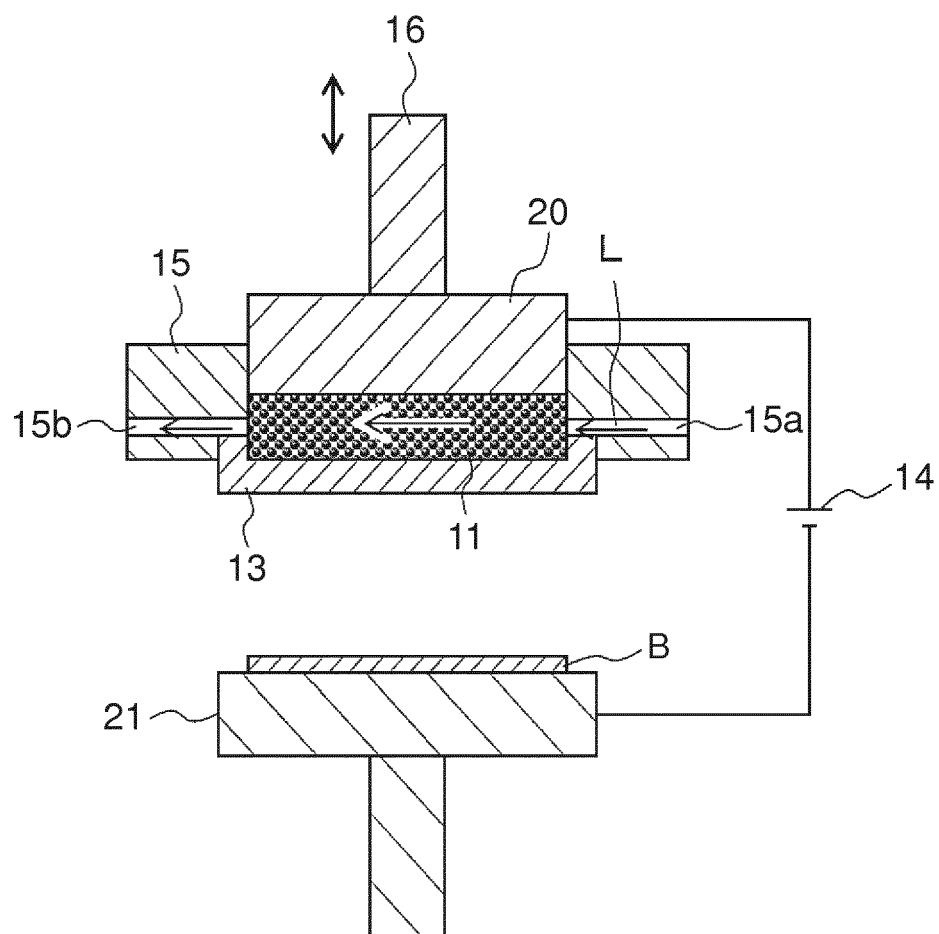


FIG. 3A

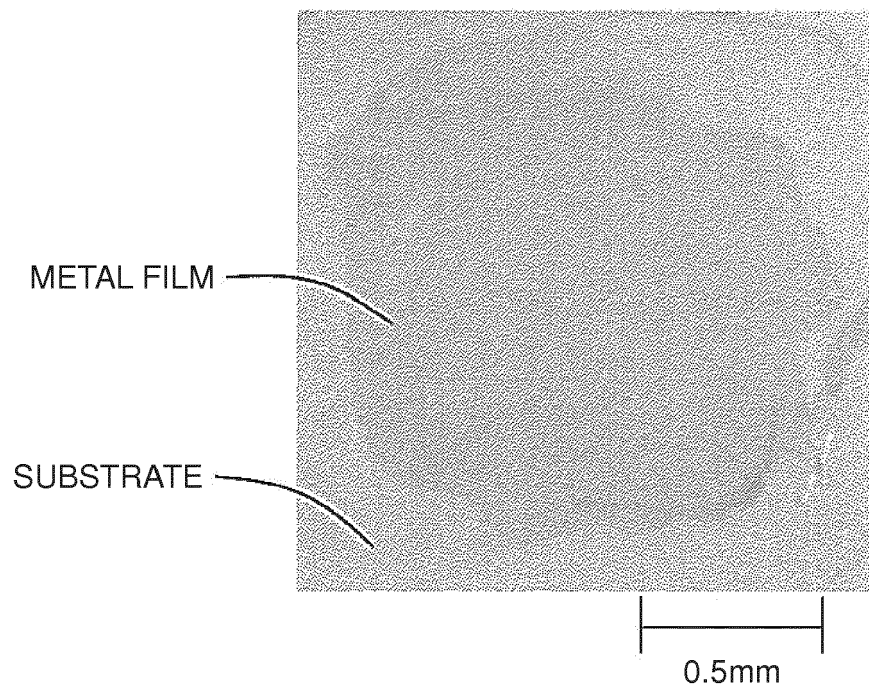


FIG. 3B

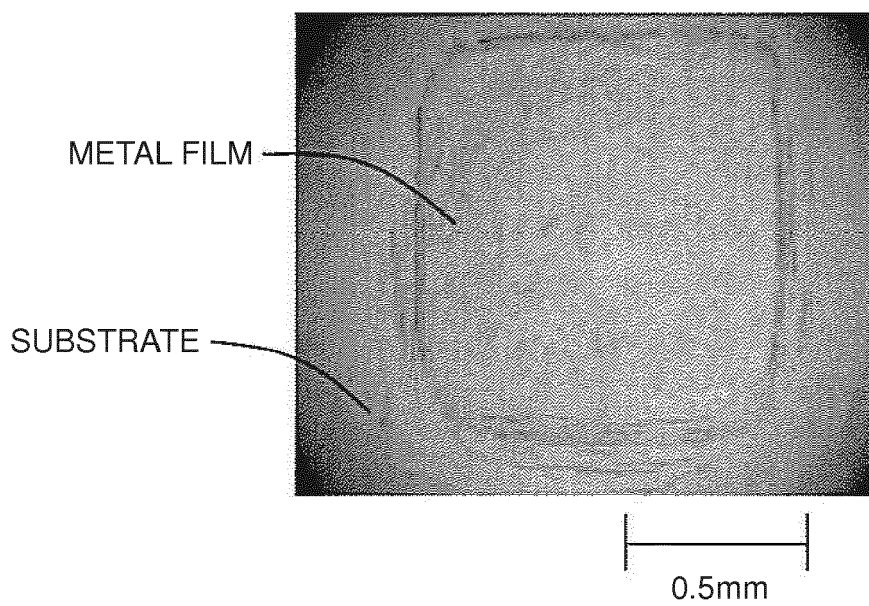
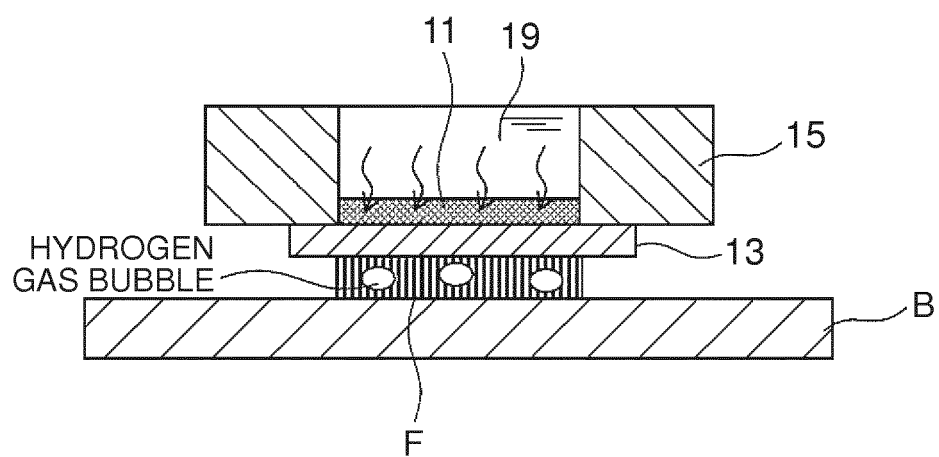


FIG. 4
RELATED ART





EUROPEAN SEARCH REPORT

Application Number
EP 15 17 7944

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