(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 891 730 A1

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
08.07.2015 Bulletin 2015/28

(21) Application number: **12883907.3**

(22) Date of filing: **31.08.2012**

(51) Int Cl.:
C25D 21/11 *(2006.01)* ***C25D 3/66*** *(2006.01)*

(86) International application number:
PCT/JP2012/072093

(87) International publication number:
WO 2014/033890 (06.03.2014 Gazette 2014/10)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME

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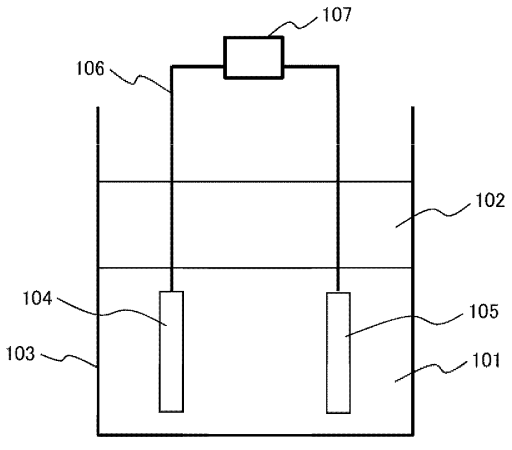
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(54) NONAQUEOUS ELECTROPLATING METHOD AND NONAQUEOUS ELECTROPLATING APPARATUS

(57) An object of the invention is to provide a nonaqueous electroplating method which can electroplate base metals and alloys including base metals safely and soundly with high efficiency even in the air atmosphere (in an atmosphere which is open to the air), as well as a nonaqueous electroplating apparatus enabling the method and having high operation performance. The nonaqueous electroplating method according to the invention is a method which electroplates a plating object with a nonaqueous plating solution, wherein the nonaqueous plating solution includes a halide of a metal to be plated (a metal halide) and an organic compound forming an ion pair against the metal halide, a hydrophobic liquid which phase-separates from the nonaqueous plating solution and which has a specific gravity smaller than the nonaqueous plating solution is further used, and an upper surface of the nonaqueous plating solution is liquid-sealed by the hydrophobic liquid.

[FIG. 1]



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Description

Technical Field

[0001] The present invention relates to an electroplating method using a nonaqueous plating solution, and a nonaqueous electroplating apparatus for carrying out the method.

Background Art

[0002] For electroplating processes for metals, aqueous solutions have been used as plating solutions in many cases. Aqueous plating solutions are low-volatile and easily-controlled, and their effluent processing is comparatively easy. Therefore, aqueous electroplating has been deemed as a low-cost process.

[0003] Meanwhile, types of metal elements which can be electrochemically deposited by using water as a solvent for a plating solution were limited. Metal elements such as aluminum (Al), titanium (Ti) and magnesium (Mg), which are expected to serve as functional metal thin films, have a high affinity for oxygen, and their oxidation-reduction potentials are lower compared with a reduction decomposition potential of water (the standard electrode potentials are negative). Therefore, it was difficult to electroplate these metal species from aqueous solutions.

[0004] In order to electroplate metals (base metals) whose oxidation-reduction potentials are negative or alloy films including them, electroplating using organic solvents, molten salts or the like having a wider stable potential region (potential window), in which they are not electrolyzed, compared with water (so-called nonaqueous electroplating) has been studied. For example, in aluminum plating, that obtained by dissolving aluminum chloride ($AlCl_3$) and lithium aluminum hydride ($LiAlH_4$), or $AlCl_3$ and lithium hydride (LiH) in an ether (e.g. diethyl ether or tetrahydrofuran), and the like have been known as organic solvent-based plating solutions. However, there was a problem in which these plating solutions required scrupulous attention to handling, since they are ignitable or highly flammable.

[0005] Therefore, electroplating using, as highly safe solvents (e.g. solvents having characteristics such as high chemical stability, incombustibility and low vapor pressures), molten salts which exist as liquids in a room-temperature level (so-called ionic liquids) has been studied. For example, Patent Literature 1 (JP-A-5-51785) discloses an electric aluminum plating solution obtained by including 0.1 to 50 g/L of polystyrene or polymethylstyrene in a plating solution which is obtained by mixing and melting an aluminum halide (A) and at least one type of a compound (B) selected from the group consisting of monoalkylpyridinium halides, dialkylpyridinium halides, 1-alkylimidazolium halides, and 1,3-dialkylimidazolium halides, at a molar ratio where "A:B=1:1 to 3:1". According to Patent Literature 1, an aluminum film exhibiting a smooth and fine lustrous surface can be formed at an ordinary or low temperature with high workability without danger of an explosion or ignition.

[0006] Moreover, Patent Literature 2 (JP-A-1-132791) discloses an electric aluminum plating apparatus in which a plating bath, which includes a molten salt plating solution of aluminum chloride and butylpyridinium chloride, or a plating solution obtained by adding an organic solvent to the plating solution, as well as an anode, is formed into a closed type where the upper side of the plating bath is openable and closable, a storage tank for the plating solution is also formed into a closed type, inert inlets are provided in both the bath, both the bath and the tank are connected to one another via a circulation pipe, and a barrel is rotatably supported to a cathode of an aluminum shaft inside the plating bath. According to Patent Literature 2, the plating solution is never oxidized in the plating apparatus since the plating bath and the storage tank are designed as closed types, and both the bath and the tank are connected to one another via a circulation pipe such that the total plating solution can be delivered to the storage tank.

[0007] Furthermore, Non Patent Literature 1 has reported studies on electrocrystallization of nickel (Ni), cobalt (Co) and their aluminum alloys. In Non Patent Literature 1, it is shown that nanoscale electroplating of Ni, Co and their Al alloys from ionic electrolytes (room-temperature molten salts or ionic liquids) having a wider electrochemical window compared to aqueous electrolytes is possible.

Citation List

Patent Literature

[0008]

PTL 1: JP-A-5-51785
PTL 2: JP-A-1-132791

Non Patent Literature

[0009] NPL 1: W. Freyland, C.A. Zell, S.Zein El Abedin, F. Endres: "Nanoscale electrodeposition of metals and semiconductors from ionic liquids", Electrochimica Acta 48 (2003) 3053-3061.

Summary of Invention

Technical Problem

[0010] As described above, since chemical stability of nonaqueous electroplating solutions is generally low, there is a problem in which, when the plating solutions come into contact with water or oxygen in the atmosphere, they are likely to be oxidized/decomposed, their current efficiencies are deteriorated, and appearances of the resulting plating films are deteriorated. In particular, in plating solutions using aluminum chloride, aluminum chloride itself undergoes a chemical reaction with water (for example, water in the atmosphere) to generate hydrogen chloride. Therefore, from the perspectives of not only stability of the electroplating but also working safety, there is a difficulty in their handling that the plating solutions cannot substantially be exposed to the atmosphere.

[0011] It is considered that the plating solution described in Patent Literature 1 is safe even when coming into contact with oxygen or water. However, in terms of maintenance of stability of the plating solution and plating properties, it is considered that the plating solution is desirably used in an oxygen-free dry atmosphere (in dry nitrogen or argon). That is, it can be said that traditional laboriousness in its handling is still present in a point that the plating solution is desirably unexposed to the atmosphere.

[0012] Furthermore, in the electric aluminum plating apparatus described in Patent Literature 2, the plating bath, where electroplating is carried out, has a closed structure in which an inert atmosphere is generated with dry nitrogen, argon or the like. Therefore, in addition to operation of taking a plating object in and out, a manipulation in which, after all the plating solution is transferred to the storage tank, the plating bath is opened is required even in operation of slight adjustment of positions of the electrodes. Consequently, there is a problem in which the plating apparatus is inferior in its operating performance.

[0013] In addition, Non Patent Literature 1 is an academic paper which discusses a mechanism of electrocrystallization from ionic liquids, and do not particularly discuss about handleability of electroplating solutions, methods for electroplating aluminum alloys, and electroplating apparatuses.

[0014] Because of the above-described background, concerning electroplating of metals (base metals), whose oxidation-reduction potentials are negative, or alloy films including them, an electroplating method and an electroplating apparatus which combine high safety, high workability and soundness of the film have strongly been sought. Accordingly, an object of the invention is to provide a nonaqueous electroplating method which can electroplate base metals and alloys including base metals safely and soundly with high efficiency even in the air atmosphere (in an atmosphere which is open to the air), as well as a nonaqueous electroplating apparatus enabling the method and having high operation performance.

Solution to Problem

[0015] (I) According to one aspect of the invention, provided is a nonaqueous electroplating method, including: electroplating a plating object with a nonaqueous plating solution, wherein the nonaqueous plating solution includes a halide of a metal to be plated (a metal halide) and an organic compound forming an ion pair against the metal halide, a hydrophobic liquid which phase-separates from the nonaqueous plating solution and which has a specific gravity smaller than the nonaqueous plating solution is further used, and an upper surface of the nonaqueous plating solution is liquid-sealed by the hydrophobic liquid.

[0016] The following modifications or changes can be added to the above-described nonaqueous electroplating method (I) according to the invention.

(i) The plating object passes through a layer of the hydrophobic liquid which liquid-seals the nonaqueous plating solution, and is immersed in the nonaqueous plating solution, thereby being subjected to electroplating, and then, the plating object passes through the layer of the hydrophobic liquid, and is taken therefrom.

(ii) The hydrophobic liquid includes at least one of a liquid paraffin and a silicone oil.

(iii) The organic compound includes at least one of a dialkylimidazolium salt, a pyridinium salt, an aliphatic phosphonium salt, and a quaternary ammonium salt.

(iv) In the nonaqueous plating solution, a molar concentration of the metal halide is between 1-fold and 3-fold higher than a molar concentration of the organic compound.

(v) The metal halide contains at least an aluminum halide.

(vi) The metal halide includes two or more types of metal halides.

[0017] (II) According to another aspect of the invention, provided is a nonaqueous electroplating apparatus which subjects a plating object to electroplating, wherein the electroplating is carried out by the above-described nonaqueous electroplating method according to the invention.

[0018] (III) According to still another aspect of the invention, provided is a nonaqueous electroplating apparatus which subjects a plating object to electroplating, including:

a plating bath whose upper face is open to subject the plating object to electroplating by insertion and removal of the plating objet; a plating solution-storage tank for storing a nonaqueous plating solution which includes a halide of a metal to be plated (a metal halide) and an organic compound forming an ion pair against the metal halide; a hydrophobic liquid-storage tank for storing a hydrophobic liquid which has a specific gravity smaller than the nonaqueous plating solution and which phase-separates from the nonaqueous plating solution;
a plating solution-circulating pipe and a plating solution-circulating pump for connecting the plating solution-storage tank and the plating bath to one another to circulate the nonaqueous plating solution; and
a hydrophobic liquid-circulating pipe and a hydrophobic liquid-circulating pump for connecting the hydrophobic liquid-storage tank and the plating bath to one another to circulate the hydrophobic liquid.

[0019] The following modifications or changes can be added to the above-described nonaqueous electroplating apparatus (III) according to the invention.
(vii) The nonaqueous electroplating apparatus further includes: a first liquid temperature-controlling system for controlling a temperature of the nonaqueous plating solution, in a portion of the plating bath which comes into contact with the nonaqueous plating solution; and a second liquid temperature-controlling system for controlling a temperature of the hydrophobic liquid, in a portion of the plating bath which comes into contact with hydrophobic liquid.
(viii) The nonaqueous electroplating apparatus further includes: a third liquid temperature-controlling system for controlling a temperature of the nonaqueous plating solution, in the plating solution-storage tank; and a fourth liquid temperature-controlling system for controlling a temperature of the hydrophobic liquid, in the hydrophobic liquid-storage tank.

Advantageous Effects of Invention

[0020] According to the invention, a nonaqueous electroplating method which can electroplate base metals and alloys including base metals safely and soundly with high efficiency even in the air atmosphere (in an atmosphere which is open to the atmosphere) can be provided. Furthermore, a nonaqueous electroplating apparatus for carrying out the method can be provided.

Brief Description of Drawings

[0021]

[FIG. 1] FIG. 1 is a schematic diagram showing one example of the nonaqueous electroplating method according to the invention.
[FIG. 2] FIG. 2 is a schematic diagram showing another example of the nonaqueous electroplating method according to the invention.
[FIG. 3] FIG. 3 is a schematic diagram showing one example of the nonaqueous electroplating apparatus according to the invention.

Description of Embodiments

[0022] Hereinafter, embodiments of the invention will be described with reference to the figures, etc. However, the invention is not considered to be limited to embodiments mentioned herein, and appropriate combinations or modifications are possible without departing from the technical idea of the invention.

(Nonaqueous electroplating method)

[0023] FIG. 1 is a schematic diagram showing one example of the nonaqueous electroplating method according to the invention. As shown in FIG. 1, by using a nonaqueous plating solution 101 and a hydrophobic liquid 102 which phase-separates from the nonaqueous plating solution 101 and which has a specific gravity smaller than the nonaqueous plating solution 101, the nonaqueous electroplating of the invention is carried out in a state where the upper surface of

the nonaqueous plating solution 101 is liquid-sealed by the hydrophobic liquid 102. The nonaqueous plating solution 101 is shielded from the atmosphere by liquid-sealing of the nonaqueous plating solution 101 with the hydrophobic liquid 102. This prevents water in the atmosphere from penetrating the nonaqueous plating solution 101, and, penetration of oxygen thereto can also be suppressed. As a result, nonaqueous plating can be carried out by use of a plating bath 103 whose upper face is open to the atmosphere (i.e. under the air atmosphere).

[0024] As to a plating object 104 and a counter electrode 105, their entire bodies are immersed/disposed in the nonaqueous plating solution 101, and they are connected to a power supply 107 via lead wires 106. By electrification, the entire body of the plating object 104 is covered by a plating film.

[0025] For the counter electrode 105, an insoluble electrode (e.g., platinum, or titanium-platinum) may be used, or a soluble electrode including a metal to be plated may be used. When a soluble electrode is used, metal ions consumed in plating are automatically supplied, and a concentration of metal ions in the plating solution can be kept within a certain range. In particular, when continuously conducting plating, metal ions are automatically supplied depending on an electrified amount, and therefore, a soluble electrode is preferably used.

[0026] When disposing the plating object 104 in the nonaqueous plating solution 101, the plating object 104 passes through a layer of the hydrophobic liquid 102, and is immersed in the nonaqueous plating solution 101. Therefore, there are acting effects that, even when an aqueous plating pretreatment solution or pure water for washing the plating pretreatment solution remains on the surface of the plating object 104, their water content is eliminated by the hydrophobic liquid 102 while passing through the layer of the hydrophobic liquid 102.

[0027] The nonaqueous plating solution 101 includes a halide of a metal to be plate (metal halide) and an organic compound forming an ion pair with the metal halide. As metal halides used in the invention, chlorides or bromides of base metals (metals having negative standard electrode potentials, e.g. tin, nickel, cobalt, chrome, zinc, aluminum, and the like) can favorably be used. The metal halide used therein is preferably an anhydrous salt. In addition, the invention is not limited to electroplating of base metals, and may be utilized for not only electroplating of alloys including base metals but also electroplating of precious metals (metals having positive standard electrode electric potentials, e.g. copper, gold, and the like). Further, for the metal halide, halides of two or more types of different metal species may be mixed and used therefor.

[0028] As the organic compound (an organic compound forming a ion pair with the above-described metal halides) used in the invention, at least one of a dialkylimidazolium salt, a pyridinium salt, an aliphatic phosphonium salt, and a quaternary ammonium salt can favorably be used. More specifically, as for the dialkylimidazolium salt, for example, 1-ethyl-3-methylimidazolium chloride, 1-ethyl-3-methylimidazolium bromide, 1-ethyl-3-methylimidazolium iodide, 1-butyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium bromide, 1-butyl-3-methylimidazolium iodide, and the like can be mentioned. As for the pyridinium salt, for example, methylpyridinium chloride, methylpyridinium bromide, methylpyridinium iodide, ethylpyridinium chloride, ethylpyridinium bromide, ethylpyridinium iodide, butylpyridinium chloride, butylpyridinium bromide, butylpyridinium iodide, and the like can be mentioned. As for the aliphatic phosphonium salt, ethyltributylphosphonium chloride, ethyltributylphosphonium bromide, ethyltributylphosphonium iodide, methyltributylphosphonium chloride, methyltributylphosphonium bromide, methyltributylphosphonium iodide, and the like can be mentioned. As for the quaternary ammonium salt, tetraethylammonium bromide, trimethylethylammonium chloride, tetrabutylammonium chloride, and the like can be mentioned.

[0029] It is preferable that the above-described organic compound and metal halide are mixed and molted at a molar ratio where "1:1 ≤ organic compound:metal halide ≤ 1:3", more preferably, "1:1.5 ≤ organic compound:metal halide ≤ 1:3." When the molar concentration of the metal halide is equal to or lower than the molar concentration of the organic compound, the plating deposition rate is significantly decreased, resulting in deterioration of deposition uniformity in plating. On the other hand, when the molar concentration of the metal halide is more than 3 times as high as the molar concentration of the organic compound, the viscosity of the nonaqueous plating solution 101 increases, resulting in a decrease of the current efficiency in plating.

[0030] When halides of two or more types of different metal species are mixed and used as the metal halide (i.e. in a case of alloy plating), the organic compound and the metal halides are preferably mixed and molten at a molar ratio where "1:1 ≤ organic compound:total metal halides ≤ 1:3." In a precise sense, the ratio of metal species mixed therein depends on a deposition efficiency (deposition ratio) of each metal species. However, the ratio almost agrees with a compositional ratio of an alloy to be plated.

[0031] It is preferable that the hydrophobic liquid 102 used in the invention phase-separates from the nonaqueous plating solution 101 (in other words, having low compatibility with the nonaqueous plating solution 101), and has a specific gravity smaller than the nonaqueous plating solution 101. In particular, the specific gravity is preferably smaller than 1, and, for example, a liquid paraffin or silicone oil can favorably be used.

[0032] In addition, the hydrophobic liquid 102 is liquid at an ordinary temperature (20°C to 25°C), and is a liquid which phase-separates from water. As for the viscosity thereof, as long as it is a viscosity sufficient to agitate the hydrophobic liquid at an ordinary temperature, such a viscosity is acceptable. However, the hydrophobic liquid rather preferably has a low viscosity. The average molecular weight of the hydrophobic liquid 102 is not particularly limited as long as it satisfies

with the above-mentioned requirements. For example, the average molecular weight is preferably 200 to 1000.

[0033] The plating treatment temperature is preferably 20°C to 80°C, more preferably 25°C to 60°C in view of workability. For electrifying conditions, plating is preferably carried out at a current density of 0.01 A/dm^2 to 10 A/dm^2 on direct or pulse current. According to this, the current efficiency will be high, and a uniform plating film can be formed. When the current density is too high, decomposition of compounds, ununiformity of the plating film, and a reduction in the current efficiency will occur, and therefore, such a high current density is not preferable. In addition, the current efficiency is preferably 30% or more, more preferably 80% or more in view of production efficiency.

[0034] FIG. 2 is a schematic diagram showing another example of the nonaqueous electroplating method according to the invention. As shown in FIG. 2, the nonaqueous electroplating method of this embodiment differs from the foregoing embodiment (see FIG. 1) in that portions of a plating object 204 and a counter electrode 205 are each immersed/disposed in a nonaqueous plating solution 101. By electrification, a plating film is deposited selectively on the portion of the plating object 204 which is immersed in the nonaqueous plating solution 101. By using the plating method of this embodiment, the plating object 204 can easily and partially/selectively be covered by a plating film without conducting masking with an insulating tape or the like. Other acting effects are the same as the foregoing embodiment.

(Nonaqueous electroplating apparatus)

[0035] FIG. 3 is an outline schematic diagram showing one example of the nonaqueous electroplating apparatus according to the invention. As shown in FIG. 3, the nonaqueous electroplating apparatus 300 of the invention includes a plating bath 303 whose upper face is open to the atmosphere, and the nonaqueous plating solution 101 and the hydrophobic liquid 102 are contained in the plating bath 303, and the nonaqueous plating solution 101 is liquid-sealed by the hydrophobic liquid 102, thereby being shielded from the atmosphere.

[0036] The nonaqueous electroplating apparatus 300 further includes a plating solution-storage tank 306 for storing the nonaqueous plating solution 101, a hydrophobic liquid-storage tank 307 for storing the hydrophobic liquid 102, plating solution-circulating pipes 308 and plating solution-circulating pumps 309 for connecting the plating solution-storage tank 306 and the plating bath 303 to one another to circulate the nonaqueous plating solution 101, and hydrophobic liquid-circulating pipes 310 and hydrophobic liquid-circulating pumps 311 for connecting the hydrophobic liquid-storage tank 307 and the plating bath 303 to one another to circulate the hydrophobic liquid 102. The outward and return paths of the plating solution-circulating pipes 308 are connected to the bottom of the plating bath 303. While the return path of the hydrophobic liquid-circulating pipes 310 is connected to the bottom of the plating bath 303, the outward path of the hydrophobic liquid-circulating pipes 310 is connected to the upper part (a domain where the layer of the hydrophobic liquid 102 is formed when the nonaqueous plating solution 101 and the hydrophobic liquid 102 are contained in the plating bath 303) of the plating bath 303.

[0037] When the nonaqueous plating solution 101 is contained in the plating bath 303, the hydrophobic liquid 102 is first supplied through the outward path of the hydrophobic liquid-circulating pipes 310 which is connected to the upper part of the plating bath 303, and then, the nonaqueous plating solution 101 is supplied through the outward path of the plating solution-circulating pipes 308 which is connected to the bottom part of the plating bath 303. According to this, the nonaqueous plating solution 101 can be introduced into the plating bath 303 without exposing the nonaqueous plating solution 101 to the atmosphere. When the nonaqueous plating solution 101 is discharged from the plating bath 303, the nonaqueous plating solution 101 is first discharged from the return path of the plating solution-circulating pipes 308 which is connected to the bottom of the plating bath 303, and then, the hydrophobic liquid 102 is discharged from the return path of the hydrophobic liquid-circulating pipes 310 which is connected to the bottom of the plating bath 303. According to this, in the same manner as introduction of the nonaqueous plating solution 101, the nonaqueous plating solution 101 can be discharged from the plating bath 303 without exposing the nonaqueous plating solution 101 to the atmosphere. Additionally, by simultaneously carrying out supply and discharge of the nonaqueous plating solution 101 with the plating solution-circulating pipes 308 and the plating solution-circulating pumps 309, circulation of the nonaqueous plating solution 101 is enabled.

[0038] FIG. 3 shows a case where a long continuous object is used as a plating object 304. The plating object 304 passes through the layer of the hydrophobic liquid 102, and is immersed in the nonaqueous plating solution 101, thereby being subjected to electroplating. Then, the plating object 304 passes through the layer of the hydrophobic liquid 102, and is taken therefrom. Conductor rolls 312 are disposed above the opening face of the plating bath 303, and a sink roll 313 is disposed in a domain where the nonaqueous plating solution 101 inside the plating bath 303 is contained. Furthermore, counter electrodes 305 are disposed, parallel to the plating object 304, in a domain where the nonaqueous plating solution 101 inside the plating bath 303 is contained, such that the counter electrodes 305 are opposed to the plating object 304. The shape or the number of counter electrodes 305 is not particularly limited. For example, each of the counter electrodes 305 may be a parallel plate, or may be a cylinder. The plating object 304 is wrapped around the conductor rolls 312 and the sink roll 313, and electrification during transfer of the plating object 304 is carried out.

[0039] It is preferable that the plating solution temperature is properly controlled depending on a type of the nonaqueous

plating solution 101 used herein. In order to precisely and stably control the temperature of the nonaqueous plating solution 101, it is preferable that the temperatures of the nonaqueous plating solution 101 and the hydrophobic liquid 102 are the same. Therefore, it is preferable that a first liquid temperature-controlling system 314 for controlling the temperature of the nonaqueous plating solution 101 is disposed in a domain inside the plating bath 303 where the nonaqueous plating solution 101 is contained (apart which comes to contact with the nonaqueous plating solution 101) and that a second liquid temperature-controlling system 315 for controlling the temperature of the hydrophobic liquid 102 is disposed in a domain inside the plating bath 303 where the layer of the hydrophobic liquid 102 is contained (a part which comes to contact with the hydrophobic liquid 102).

[0040] In addition, for the same reason mentioned above, it is preferable that a third liquid temperature-controlling system 316 for controlling the temperature of the nonaqueous plating solution 101 is disposed in the plating solution-storage tank 306, and that a fourth liquid temperature-controlling system 317 for controlling the temperature of the hydrophobic liquid 102 is disposed in the hydrophobic liquid-storage tank 307. By prospectively adjusting, to desired liquid temperatures, the temperatures of the nonaqueous plating solution 101 and the hydrophobic liquid 102 inside both the storage tanks, control of the liquid temperatures inside the plating bath 303 can efficiently be carried out when supplying them to the plating bath 303.

Examples

[0041] Hereinafter, contents of the invention will be described in more detail by showing specific examples below. However, the following examples show specific examples of contents of the invention, and the invention is not limited to the examples. Additionally, various changes and modifications made by a person skilled in the art are possible within technical ideas disclosed in the description.

(Example 1)

[0042] Anhydrous aluminum chloride ($AlCl_3$, manufactured by Wako Pure Chemical Industries, Ltd.) was used as a metal halide, and 1-ethyl-3-methylimidazolium chloride (EMIMCl manufactured by KANTO CHEMICAL CO., INC.) was used as an organic compound, and these compounds were mixed at a molar ratio where "EMIMCl:$AlCl_3$= 1:2" to obtain a nonaqueous plating solution. Preparation of the nonaqueous plating solution was carried out inside a glove box (temperature: 25°C, relative humidity: 5%) under an argon atmosphere. 60 mL of the prepared nonaqueous plating solution was charged to a 100 mL glass beaker.

[0043] Then, a liquid paraffin (manufactured by KANTO CHEMICAL CO., INC.) was used as a hydrophobic liquid. 40 mL of the liquid paraffin was poured into the beaker, in which the foregoing nonaqueous plating solution was contained, thereby liquid-sealing the nonaqueous plating solution with the hydrophobic liquid. This was used as an evaluation solution of Example 1.

[0044] In order to examine influences of exposure to the atmosphere (influences of water content in the air), an air-atmosphere glove box, to which the air having an adjusted humidity and an adjusted relative humidity (the temperature: 25°C, the relative humidity: 60%) had been introduced, was prepared. The adjustment of the temperature and the humidity of the air to be introduced was carried out by passing the air through a gas-washing bottle containing pure water, followed by using a humidity-adjusting machine (EFA5-100-A manufactured by GL Sciences Inc.). The evaluation solution of Example 1 was transferred from the glove box under the argon atmosphere to the glove box under the air atmosphere, and was exposed to the temperature/humidity-controlled air (wet air) for a predetermined time.

[0045] Electroplating was carried out in the following manner. A copper foil (purity: 99.9%, length × breadth × thickness = 20 mm × 35 mm × 0.1 mm) was used as a plating object, and an aluminum plate (purity: 99.9%, length × breadth × thickness = 25 mm × 35 mm × 2 mm) was used as a counter electrode. The plating object and the counter electrode, to which lead wires were each connected, were opposed to one another inside the beaker at an interval of 30 mm, and were thus immersed in the evaluation solution. Both the lead wires were connected to a constant-current power supply, and electroplating was carried out (the current density = -1 A/dm^2, the plating time = 30 minutes, the temperature of the plating solution = 25°C). After completion of the electroplating, the plated object was washed with acetone and pure water, and was dried with nitrogen gas. The resulting object was used as a test material for measurements.

[0046] Evaluation solutions which had been exposed to the temperature/humidity-controlled air (wet air) for 2 hours, 12 hours and 24 hours were used to carry out the above-described electroplating, and a current efficiency was calculated for each evaluation solution. A deposition amount of the plated aluminum was obtained by measurement. The obtained deposition amount was compared with a deposition amount calculated based on a current value of a Coulombmeter, and a proportion (percentage) of the actual deposition amount to the calculated deposition amount was obtained as a current efficiency. The constitution of the plating solution and current efficiencies of the electroplating using the plating solution are shown in Table 1 below.

(Comparative Example 1)

[0047] An evaluation solution for Comparative Example 1 was prepared, and each test material was produced in the same manner as above Example 1 except that any hydrophobic liquid was not used. Both the constitution of the plating solution and calculation results of current efficiencies are described in Table 1.
[Table 1]

Table 1 Constitutions of plating solutions and current efficiencies of electroplating carried out with the plating baths

	Nonaqueous plating solutions		Hydrophobic liquids	Current efficiencies (%)		
	Meatal halides	Organic compounds		Exposure 2 hours	Exposure 12 hours	Exposure 24 hours
Example 1	$AlCl_3$ 67 mol%	EMIMCl 33 mol%	Liquid paraffin	100	100	99
Example 2	$AlCl_3$ 67 mol%	EMIMCl 33 mol%	Silicone oil	100	100	100
Example 3	$AlCl_3$ 67 mol%	BPCl 33 mol%	Liquid paraffin	96	96	95
Example 4	$AlCl_3$ 60 mol%	TBACl 40 mol%	Liquid paraffin	40	39	38
Example 5	$AlCl_3$ 60 mol%	MTBPCl 40 mol%	Liquid paraffin	30	30	30
Example 6	$AlCl_3$ 60 mol% $NiCl_2$ 10 mol%	EMIMCl 30 mol%	Liquid paraffin	96	95	95
Example 7	$ZnCl_2$ 67 mol%	EMIMCl 33 mol%	Liquid paraffin	51	52	52
Comparative Example 1	$AlCl_3$ 67 mol%	EMIMCl 33 mol%	None	56	0	0
Comparative Example 2	$AlCl_3$ 67 mol%	BPCl 33 mol%	None	82	21	0
Comparative Example 3	$AlCl_3$ 60 mol%	TBACl 40 mol%	None	20	0	0
Comparative Example 4	$AlCl_3$ 67 mol%	MTBPCl 33 mol%	None	18	0	0
Comparative Example 5	$AlCl_3$ 60 mol% $NiCl_2$ 10 mol%	EMIMCl 30 mol%	None	51	0	0
Comparative Example 6	$ZnCl_2$ 67 mol%	EMIMCl 33 mol%	None	40	0	0

[0048] As shown in Table 1, in Comparative Example 1 where the nonaqueous plating solution was not liquid-sealed with a hydrophobic liquid, the current efficiency decreased to 56% by 2 hours of the wet-air exposure, and the current efficiency was 0% at 12 hours or later of the wet-air exposure (aluminum itself stopped depositing). That is, it was confirmed that the nonaqueous plating solution was significantly deteriorated by water contents in the air. In addition, in Comparative Example 1, occurrence of white smoke, which was considered hydrogen chloride gas, was observed in

connection with the wet-air exposure of the nonaqueous plating solution.

[0049] To the contrary, in Example 1 relating to the invention, since the nonaqueous plating solution was liquid-sealed with the liquid paraffin, almost no changes in current efficiencies associated with the wet-air exposure were observed, and, for example, the current efficiency was in an excellent state where it indicated 99% even in 24 hours of the wet-air exposure. In addition, any occurrence of white smoke was not observed in Example 1 where even the wet-air exposure was carried out.

(Example 2)

[0050] An evaluation solution for Example 2 was prepared, and each test material was produced in the same manner as Example 1 except that a silicone oil (KF-96L-1cs manufactured by Shin-Etsu Chemical Co., Ltd.) was used as a hydrophobic liquid. Both the constitution of the plating solution and calculation results of current efficiencies are described in Table 1. As shown in Table 1, since the nonaqueous plating solution was liquid-sealed with the silicone oil also in Example 2, almost no changes in current efficiencies associated with the wet-air exposure were observed, and, for example, the current efficiency was in an excellent state where it indicated 100% even in 24 hours the wet-air exposure. In addition, any occurrence of white smoke was also not observed during the wet-air exposure. From this result, it was confirmed that a silicone oil was also effective as a hydrophobic liquid.

(Example 3)

[0051] Anhydrous aluminum chloride ($AlCl_3$, manufactured by Wako Pure Chemical Industries, Ltd.) was used as a metal halide, and butylpyridinium chloride (BPCL manufactured by KANTO CHEMICAL CO., INC.) was used as an organic compound, and these compounds were mixed at a molar ratio where "$BPCl:AlCl_3$ = 1:1.5" to prepare a nonaqueous plating solution. Except for that, an evaluation solution for Example 3 was prepared, and each test material was produced in the same manner as Example 1. Both the constitution of the plating solution and calculation results of current efficiencies are described in Table 1.

(Comparative Example 2)

[0052] An evaluation solution for Comparative Example 2 was prepared, and each test material was produced in the same manner as above Example 3 except that any hydrophobic liquid was not used. Both the constitution of the plating solution and calculation results of current efficiencies are described in Table 1.

[0053] As shown in Table 1, in Comparative Example 2 where the nonaqueous plating solution was not liquid-sealed with a hydrophobic liquid, a tendency in which the current efficiency decreased with an increase in the time for the wet-air exposure was recognized. The current efficiency decreased to 82% by 2 hours of the wet-air exposure, the current efficiency decreased to 21% by 12 hours of the wet-air exposure, and further, the current efficiency reached 0% at 24 hours of the wet-air exposure where deposition of aluminum was not observed. To the contrary, almost no changes in the current efficiency associated with the wet-air exposure were observed in Example 3, and, it was confirmed that an excellent state of the current efficiency was maintained, for example, even at 24 hours of the wet-air exposure where the current efficiency indicated 95%.

(Example 4)

[0054] Anhydrous aluminum chloride ($AlCl_3$, manufactured by Wako Pure Chemical Industries, Ltd.) was used as a metal halide, and tetrabutylammonium chloride (TBACl manufactured by KANTO CHEMICAL CO., INC.) was used as an organic compound, and these compounds were mixed at a molar ratio where "$TBACl:AlCl_3$ = 1:1.5" to prepare a nonaqueous plating solution. Additionally, as for conditions for electroplating, "the current density = -0.1 A/dm^2, and the plating time = 300 minutes." Except for these conditions, an evaluation solution for Example 4 was prepared, and each test material was produced in the same manner as Example 1. Both the constitution of the plating solution and calculation results of current efficiencies are described in Table 1.

(Comparative Example 3)

[0055] An evaluation solution for Comparative Example 3 was prepared, and each test material was produced in the same manner as above Example 4 except that any hydrophobic liquid was not used. Both the constitution of the plating solution and calculation results of current efficiencies are described in Table 1.

[0056] As shown in Table 1, in Comparative Example 3 where the nonaqueous plating solution was not liquid-sealed with a hydrophobic liquid, the current efficiency was as low as 20% at 2 hours of the wet-air exposure. Further, the

current efficiency was 0% at 12 hours and later of the wet-air exposure where no deposition of aluminum was observed. On the other hand, in Example 4, almost no changes in the current efficiency were observed even when time for the wet-air exposure was increased, although the current efficiency of Example 4 was lower than Examples 1 to 3. In addition, as to a factor for such a low current efficiency in Example 4, it is considered that a dissolution amount of $AlCl_3$ in the nonaqueous plating solution was slightly small and that an amount of aluminum complexes contributing deposition of aluminum was insufficient. Also, a possibility that the viscosity of the nonaqueous plating solution was relatively high, affecting the electric conductivity, can be considered.

(Example 5)

[0057] Anhydrous aluminum chloride ($AlCl_3$, manufactured by Wako Pure Chemical Industries, Ltd.) was used as a metal halide, and methyltributylphosphonium chloride (MTBPCl manufactured by Nippon Chemical Industrial Co. , Ltd.) was used as an organic compound, and these compounds were mixed at a molar ratio where "MTBPCl:$AlCl_3$ = 1:1.5" to obtain a nonaqueous plating solution. Except for that, an evaluation solution for Example 5 was prepared, and each test material was produced in the same manner as Example 4. Both the constitution of the plating solution and calculation results of current efficiencies are described in Table 1.

(Comparative Example 4)

[0058] An evaluation solution for Comparative Example 4 was prepared, and each test material was produced in the same manner as above Example 5 except that any hydrophobic liquid was not used. Both the constitution of the plating solution and calculation results of current efficiencies are described in Table 1.

[0059] As shown in Table 1, in Comparative Example 4 where the nonaqueous plating solution was not liquid-sealed with a hydrophobic liquid, the current efficiency was as low as 18% at 2 hours of the wet-air exposure. Further, the current efficiency was 0% at 12 hours or later of the wet-air exposure where no deposition of aluminum was observed. On the other hand, in Example 5, the current efficiency did not change even when the time for the wet-air exposure was increased. In addition, as to a factor for such a low current efficiency in Example 5, it is considered that the dissolution amount of $AlCl_3$, the solution viscosity, and/or the electric conductivity for the nonaqueous plating solution were associated with the low current efficiency in the same manner as Example 4.

(Example 6)

[0060] Anhydrous aluminum chloride ($AlCl_3$, manufactured by Wako Pure Chemical Industries, Ltd.) and anhydrous nickel chloride ($NiCl_2$ manufactured by KANTO CHEMICAL CO., INC.) were used as a metal halide, and 1-ethyl-3-methylimidazolium chloride (EMIMCl manufactured by KANTO CHEMICAL CO.,INC.) was used as an organic compound, and these compounds were mixed at a molar ratio where "EMIMCl:$AlCl_3$:$NiCl_2$ = 1:2:0.33" to prepare a nonaqueous plating solution. Except for that, an evaluation solution for Example 6 was prepared, and each test material was produced in the same manner as Example 1. Both the constitution of the plating solution and calculation results of current efficiencies are described in Table 1. In addition, as to calculations for current efficiencies, the calculations were carried out supposing that aluminum was deposited singularly.

(Comparative Example 5)

[0061] An evaluation solution for Comparative Example 5 was prepared, and each test material was produced in the same manner as above Example 6 except that any hydrophobic liquid was not used. Both the constitution of the plating solution and calculation results of current efficiencies are described in Table 1.

[0062] As shown in Table 1, in Comparative Example 5 where the nonaqueous plating solution was not liquid-sealed with the hydrophobic liquid, the current efficiency was as low as 51% at 2 hours of the wet-air exposure. Further, the current efficiency was 0% at 12 hours and later of the wet-air exposure, and any deposition of aluminum was not observed. To the contrary, in Example 6, almost no changes in the current efficiency with an increase in the time of the wet-air exposure were observed, and, for example, it was confirmed that an excellent state of the current efficiency was maintained even at 24 hours of the wet-air exposure where the current efficiency indicated 95%.

(Example 7)

[0063] Zinc chloride ($ZnCl_2$, manufactured by KANTO CHEMICAL CO., INC.) was used as a metal halide, and 1-ethyl-3-methylimidazolium chloride (EMIMCl manufactured by KANTO CHEMICAL CO., INC.) was used as an organic compound, and these compounds were mixed at a molar ratio where "EMIMCl : $ZnCl_2$ = 1:2" to prepare a nonaqueous plating

solution. A liquid paraffin (manufactured by KANTO CHEMICAL CO., INC.) was used as a hydrophobic liquid. As for other conditions, an evaluation solution for Example 7 was prepared in the same manner as Example 1.

[0064] Electroplating was carried out in the following manner. A nickel foil (purity: 99%, length × breadth × thickness = 20 mm × 35 mm × 0.1 mm) was used as a plating object, and a zinc plate (purity: 99.9%, length × breadth × thickness = 25 mm × 35 mm × 2 mm) was used as a counter electrode. The plating object and the counter electrode, to which lead wires were each connected, were opposed to one another inside the beaker at an interval of 30 mm, and were thus immersed in the evaluation solution. Also, a zinc wire (purity: 99.9%, diameter = 1 mm) was immersed in the evaluation solution as a reference electrode. The plating object, the counter electrode and the reference electrode were connected to an electrochemical measurement system (HZ-5000, HOKUTO DENKO CORPORATION) via lead wires, and constant-potential electroplating was carried out (the potential = 0.15 V, the conduction amount = 10 c, the plating solution temperature = 70°C). After completion of electroplating, the plated object was washed with acetone and pure water, and was dried with nitrogen gas, thus obtaining a test material for measurements. Calculations for current efficiencies were carried out in the same manner as Example 1. Both the constitution of the plating solution and calculation results of current efficiencies are described in Table 1.

(Comparative Example 6)

[0065] An evaluation solution for Comparative Example 6 was prepared, and each test material was produced in the same manner as above Example 7 except that any hydrophobic liquid was not used. Both the constitution of the plating solution and calculation results of current efficiencies are described in Table 1.

[0066] As shown in Table 1, in Comparative Example 6 where the nonaqueous plating solution was not liquid-sealed with a hydrophobic liquid, the current efficiency was as low as 40% at 2 hours of the wet-air exposure. Further, the current efficiency was 0% at 12 hours or later of the wet-air exposure where any deposition of zinc was not observed. To the contrary, in Example 7, almost no changes in the current efficiency with an increase in the time for the wet-air exposure were confirmed.

(Example 8)

[0067] Electroplating was carried out in the same manner as Example 1 except that a copper foil (purity: 99.9%, length × breadth × thickness = 20 mm × 35 mm × 0.1 mm) was used as a plating object, and that the plating object which was in a wet state by washing with pure water was inserted into/disposed inside the plating solution. As a result, even when the plating object in a wet state with pure water was inserted into the plating solution, white smoke by hydrogen chloride gas did not occur. In addition, the formed plating film exhibited a silver-white and uniform appearance, and the same results as Example 1 was obtained for current efficiencies. It is considered that, when the plating object passed through the hydrophobic liquid (the liquid paraffin in this case), water attached to the surface of the plating object was eliminated, thereby causing the above results.

(Comparative Example 7)

[0068] Electroplating was carried out in the same manner as above-described Example 8 except that any hydrophobic liquid was not used. When the plating object wet with pure water was immersed in the nonaqueous plating solution, pure water and the nonaqueous plating solution underwent a chemical reaction, and white smoke by hydrogen chloride gas was caused. In addition, the formed plating film exhibited a darkened appearance.

(Example 9)

[0069] Aluminum plating was carried out by using an electroplating apparatus having a structure as shown in FIG. 3. In the same manner as Example 1, a mixture obtained by mixing anhydrous aluminum chloride ($AlCl_3$ manufactured by Wako Pure Chemical Industries, Ltd.) and 1-ethyl-3-methylimidazolium chloride (EMIMCl manufactured by KANTO CHEMICAL CO., INC.) at a molar ratio where "EMIMCl : $AlCl_3$ = 1 : 2" was used as a nonaqueous plating solution. A liquid paraffin (manufactured by KANTO CHEMICAL CO., INC.) was used as a hydrophobic liquid. The temperature of the nonaqueous plating solution and the temperature of the hydrophobic liquid were each controlled to 30°C by first and second liquid temperature-controlling systems. An aluminum plate of a purity of 99.9% was used for the counter electrode, and a long steel strip was used as a plating object. Continuous plating for 12 hours was carried out where "the current density = -1 A/dm^2." Consequently, an appearance of the formed plating film was uniform from the beginning to the end.

(Comparative Example 8)

[0070] Continuous plating for 12 hours was carried out in the same manner as above Example 9 except that the hydrophobic liquid was not used. As a result, as the plating time passed, an appearance of the formed plating film turned black, and any deposition of aluminum was not recognized from the point when 9 hours passed.

[0071] As is clear from the above explanations, it was proved that, according to the nonaqueous electroplating method and the nonaqueous electroplating apparatus of the invention, a contact between the nonaqueous plating solution and the atmosphere can be prevented by liquid-sealing the nonaqueous solution with the hydrophobic liquid, and that base metals and alloys including base metals can safely and soundly be electroplated with high efficiency even under the air atmosphere (in an atmosphere open to the air atmosphere).

Reference Signs List

[0072] 101···A nonaqueous plating solution, 102···A hydrophobic liquid, 103, 303···A plating bath, 104, 204, 304···A plating object, 105, 205, 305···A counter electrode, 106···A lead wire, 107···A power supply, 306···A plating solution-storage tank, 307···A hydrophobic liquid-storage tank, 308···A plating solution-circulating pipe, 309···A plating solution-circulating pump, 310···A hydrophobic liquid-circulating pipe, 311···A hydrophobic liquid-circulating pump, 312···A conductor roll, 313··· A sink roll, 314··· A first liquid temperature-controlling system, 315··· A second liquid temperature-controlling system, 316··· A third liquid temperature-controlling system, 317··· A fourth liquid temperature-controlling system.

Claims

1. A nonaqueous electroplating method, comprising: electroplating a plating object with a nonaqueous plating solution, wherein
the nonaqueous plating solution comprises a halide of a metal to be plated (a metal halide) and an organic compound forming an ion pair against the metal halide,
a hydrophobic liquid which phase-separates from the nonaqueous plating solution and which has a specific gravity smaller than the nonaqueous plating solution is further used, and
an upper surface of the nonaqueous plating solution is liquid-sealed by the hydrophobic liquid.

2. The nonaqueous electroplating method according to claim 1, wherein the plating object passes through a layer of the hydrophobic liquid which liquid-seals the nonaqueous plating solution, and is immersed in the nonaqueous plating solution, thereby being subjected to electroplating, and then, the plating object passes through the layer of the hydrophobic liquid, and is taken therefrom.

3. The nonaqueous electroplating method according to claim 1 or 2, wherein the hydrophobic liquid comprises at least one of a liquid paraffin and a silicone oil.

4. The nonaqueous electroplating method according to any one of claims 1 to 3, wherein the organic compound includes at least one of a dialkylimidazolium salt, a pyridinium salt, an aliphatic phosphonium salt, and a quaternary ammonium salt.

5. The nonaqueous electroplating method according to any one of claims 1 to 4, wherein, in the nonaqueous plating solution, a molar concentration of the metal halide is between 1-fold and 3-fold higher than a molar concentration of the organic compound.

6. The nonaqueous electroplating method according to any one of claims 1 to 5, wherein the metal halide contains at least an aluminum halide.

7. The nonaqueous electroplating method according to any one of claims 1 to 6, wherein the metal halide comprises two or more types of metal halides.

8. A nonaqueous electroplating apparatus which subjects a plating object to electroplating, wherein the electroplating is carried out by the nonaqueous electroplating method according to any one of claims 1 to 7.

9. A nonaqueous electroplating apparatus which subjects a plating object to electroplating, comprising:

a plating bath whose upper face is open to subject the plating object to electroplating by insertion and removal of the plating objet;
a plating solution-storage tank for storing a nonaqueous plating solution which comprises a halide of a metal to be plated (a metal halide) and an organic compound forming an ion pair against the metal halide;
a hydrophobic liquid-storage tank for storing a hydrophobic liquid which has a specific gravity smaller than the nonaqueous plating solution and which phase-separates from the nonaqueous plating solution;
a plating solution-circulating pipe and a plating solution-circulating pump for connecting the plating solution-storage tank and the plating bath to one another to circulate the nonaqueous plating solution; and
a hydrophobic liquid-circulating pipe and a hydrophobic liquid-circulating pump for connecting the hydrophobic liquid-storage tank and the plating bath to one another to circulate the hydrophobic liquid.

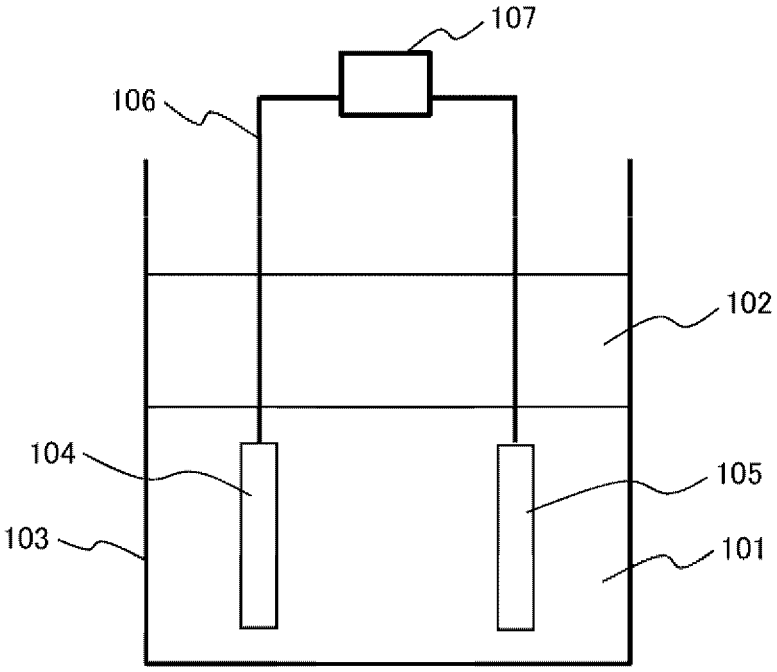
10. The nonaqueous electroplating apparatus according to claim 9, further comprising:

a first liquid temperature-controlling system for controlling a temperature of the nonaqueous plating solution, in a portion of the plating bath which comes into contact with the nonaqueous plating solution; and
a second liquid temperature-controlling system for controlling a temperature of the hydrophobic liquid, in a portion of the plating bath which comes into contact with the hydrophobic liquid.

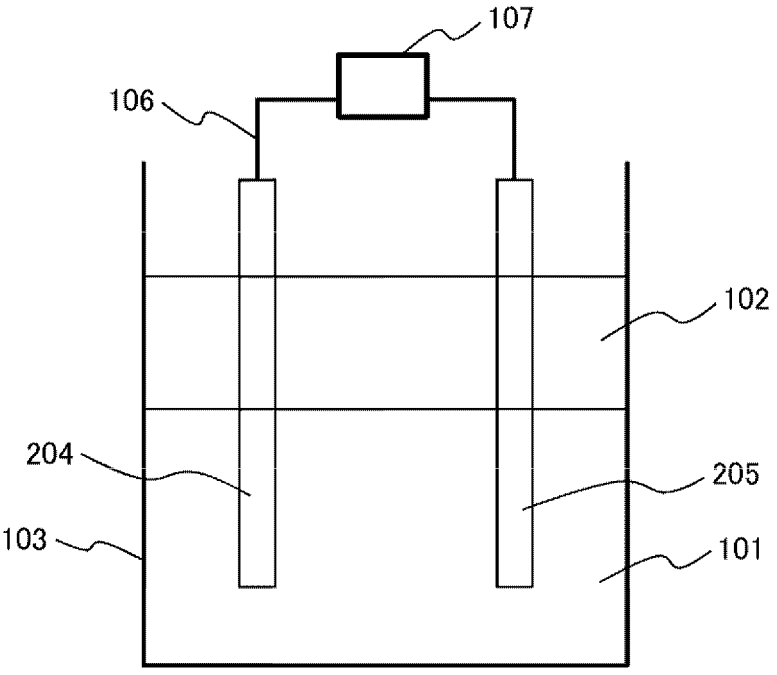
11. The nonaqueous electroplating apparatus according to claim 9 or 10, further comprising:

a third liquid temperature-controlling system for controlling a temperature of the nonaqueous plating solution, in the plating solution-storage tank; and
a fourth liquid temperature-controlling system for controlling a temperature of the hydrophobic liquid, in the hydrophobic liquid-storage tank.

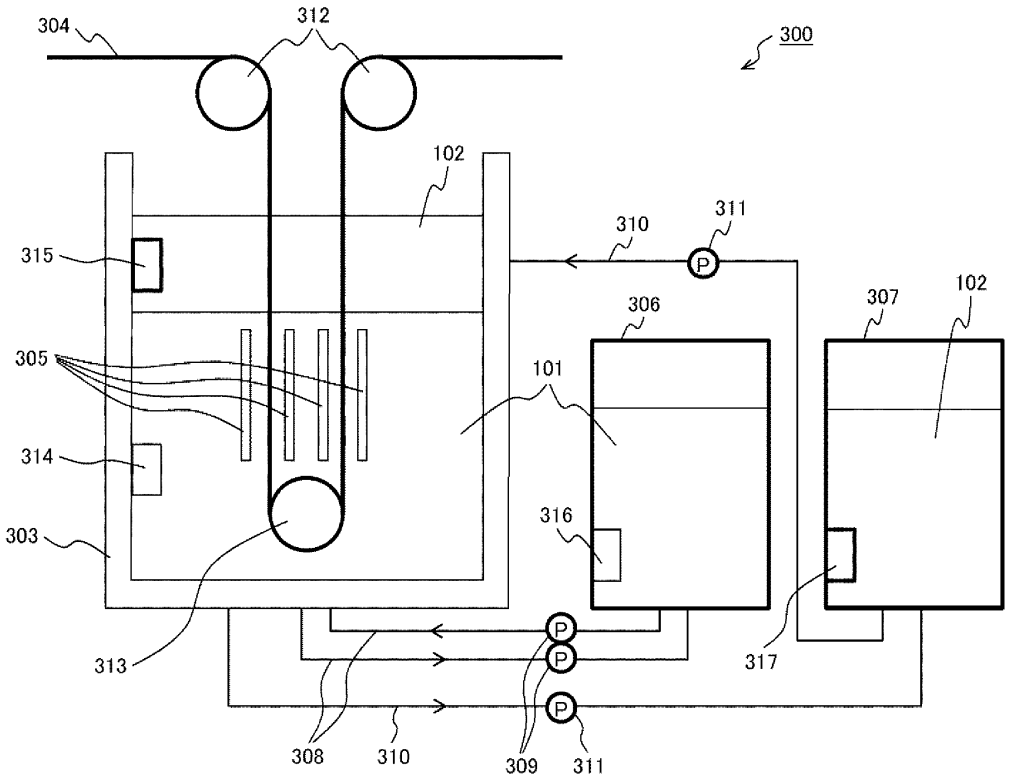
[FIG. 1]



[FIG. 2]



[FIG. 3]


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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/072093

A. CLASSIFICATION OF SUBJECT MATTER
C25D21/11(2006.01)i, *C25D3/66*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C25D21/11, C25D3/66

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2012
Kokai Jitsuyo Shinan Koho	1971-2012	Toroku Jitsuyo Shinan Koho	1994-2012

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Microfilm of the specification and drawings annexed to the request of Japanese Utility Model Application No. 182594/1981(Laid-open No. 87868/1983) (Nippon Paint Co., Ltd.), 14 June 1983 (14.06.1983), claims (Family: none)	1-11
A	JP 5-126122 A (Nisshin Steel Co., Ltd.), 21 May 1993 (21.05.1993), paragraph [0014] (Family: none)	1-11

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search 02 October, 2012 (02.10.12)	Date of mailing of the international search report 09 October, 2012 (09.10.12)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/072093

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 1-132791 A (Nisshin Steel Co., Ltd.), 25 May 1989 (25.05.1989), claims; page 1, lower right column, line 18 to page 2, upper left column, line 8 (Family: none)	1-11

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 5051785 A **[0005] [0008]**
- JP 1132791 A **[0006] [0008]**

Non-patent literature cited in the description

- **W. FREYLAND ; C.A. ZELL ; S.ZEIN EL ABEDIN ; F. ENDRES.** Nanoscale electrodeposition of metals and semiconductors from ionic liquids. *Electrochimica Acta,* 2003, vol. 48, 3053-3061 **[0009]**