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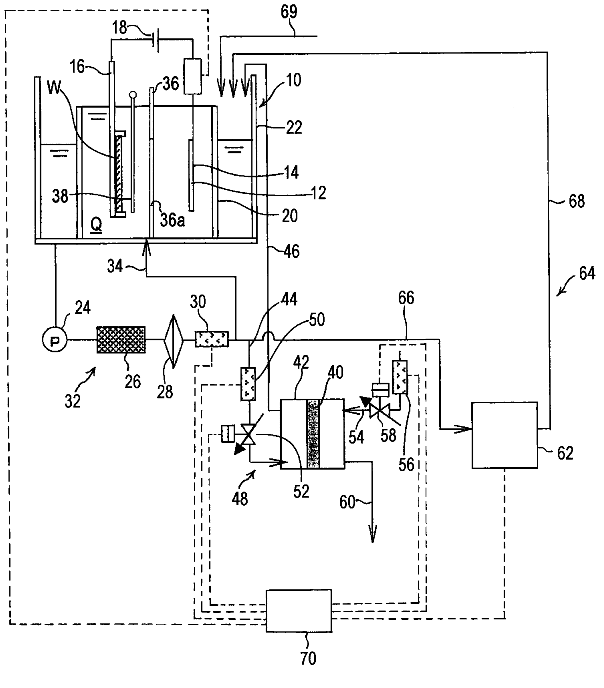
(54) Plating apparatus and plating solution management method

(57) A plating apparatus plates a substrate with Sn alloy to form an Sn alloy film on a surface of the substrate. The apparatus includes: a plating bath for retaining a plating solution therein, the substrate being immersed in the plating solution in a position opposite to an insoluble anode; a plating solution dialysis line for extracting the plating solution from the plating bath and returning the plating solution to the plating bath; a dialysis cell provided in the plating solution dialysis line and configured to remove a free acid from the plating solution by dialysis using an anion exchange membrane; a free acid concentration analyzer; and a controller for controlling a flow rate of the plating solution flowing through the plating solution dialysis line based on the concentration of the free acid measured by the free acid concentration analyzer.

FIG. 1



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Description

BACKGROUND OF THE INVENTION

Field of the Invention:

[0001] The present invention relates to a plating apparatus useful for forming a plating film of an Sn alloy, such as lead-free Sn-Ag having good soldering properties, on a substrate surface, and to a management method of a plating solution for use in the plating apparatus.

Description of the Related Art:

[0002] As is known in the art, a plating film of an Sn alloy (e.g., Sn-Ag), formed on a substrate surface by electroplating, can be used for lead-free solder bumps. An insoluble anode is typically used as an electrode in plating the substrate surface with the Sn alloy. The Sn alloy plating film is formed on the substrate surface by applying a voltage between the insoluble anode and the substrate surface, which are disposed opposite to each other and immersed in a plating solution. The insoluble anode is also typically used as an electrode when plating the substrate surface with Sn-Cu or Sn-Bi which is the Sn alloy.

[0003] A known method of successively carrying out plating of substrates with the Sn alloy, such as Sn-Ag, uses a plating solution containing: (i) a salt or complex formed from the reaction of Sn ion (Sn^{2+}) and an acid or a complexing agent (e.g., tin methanesulfonate) capable of forming a water-soluble salt or complex with Sn ion (Sn^{2+}); and (ii) a salt or complex formed from the reaction of Ag ion (Ag^{+}) and an acid or a complexing agent (e.g., silver methanesulfonate) capable of forming a water-soluble salt or complex with Ag ion (Ag^{+}). In this method, the salt(s) or complex(es) is supplied to the plating solution so as to replenish the plating solution with those metal ions (Sn ions and Ag ions) which have been consumed with the progress of plating (see Japanese Patent No. 4698904).

[0004] Such a metal ion replenishing method has a problem that, because the metal ion and the free acid (e.g., methanesulfonic acid) are separated from each other and the metal ions are consumed by the plating process, a concentration of the free acid in the plating solution gradually increases as the plating process progresses. In order to solve such a problem, there has been proposed a method in which the free acid is removed from a part of the plating solution using an ion-exchange resin, electrodialysis, or diffusion dialysis (see Japanese Laid-Open Patent Publication No. H1-312099).

[0005] Another proposed method using the insoluble anode involves subjecting a plating solution, which is being circulated, to diffusion dialysis to remove the free acid from the plating solution, thereby controlling a pH of the plating solution (see Japanese Laid-Open Patent Publication No. S57-29600). Japanese Laid-Open Patent Publication No. S59-28584 discloses optimization of liquid supply to an electrolytic cell or a dialysis cell, and Japanese Patent Laid-Open Publication No. H9-75681 discloses recovery of an acid using the diffusion dialysis while causing water to flow in a direction opposite to a flow direction of a raw liquid.

[0006] The method described in the aforementioned Japanese Laid-Open Patent Publication No. S57-29600 removes the free acid from the plating solution by dialysis so as to control the pH of the plating solution without measuring the concentration of the free acid in the plating solution. It is therefore possible that when plating of substrates is carried out successively while replenishing the plating solution with metal ions, a too large amount of the free acid may be removed, resulting in a too low concentration of the free acid in the plating solution, or conversely, a too small amount of the free acid may be removed, resulting in a too high concentration of the free acid in the plating solution. Use of the plating solution having a too low or too high concentration of the free acid could result in a poor appearance of a plating film and/or non-uniform film thickness. Such plating solution must be discarded and as a result process costs increase. The same holds true for the other prior art techniques disclosed in the above documents.

SUMMARY OF THE INVENTION

[0007] The present invention has been made in view of the above situation. It is therefore an object of the present invention to provide a plating apparatus and a plating solution management method which can use a plating solution for a longer period of time by controlling a concentration of free acid in the plating solution within a preferable range.

[0008] In order to achieve the object, the present invention provides a plating apparatus for plating a substrate with Sn alloy to form an Sn alloy film on a surface of the substrate, including: a plating bath for retaining a plating solution therein and having an insoluble anode disposed in the plating solution, the substrate being immersed in the plating solution in a position opposite to the insoluble anode; a plating solution dialysis line for extracting the plating solution from the plating bath and returning the plating solution to the plating bath; a dialysis cell provided in the plating solution dialysis line and configured to remove a free acid from the plating solution by dialysis using an anion exchange membrane; a free acid concentration analyzer configured to measure a concentration of the free acid in the plating solution; and a controller for controlling a flow rate of the plating solution flowing through the plating solution dialysis line, based on the concentration of the free acid measured by the free acid concentration analyzer.

[0009] Another aspect of the present invention provides a plating apparatus for plating a substrate with Sn alloy to form an Sn alloy film on a surface of the substrate, including: a plating bath for retaining a plating solution therein and having an insoluble anode disposed in the plating solution, the substrate being immersed in the plating solution in a position opposite to the insoluble anode; a plating solution dialysis line for extracting the plating solution from the plating bath and returning the plating solution to the plating bath; a dialysis cell provided in the plating solution dialysis line and configured to remove a free acid from the plating solution by dialysis using an anion exchange membrane; and a controller for controlling a flow rate of the plating solution flowing through the plating solution dialysis line, based on an integrated value of a quantity of electricity applied to the plating solution in the plating bath.

[0010] Still another aspect of the present invention provides a plating solution management method including: forming an Sn alloy film on a surface of a substrate by applying a voltage between an insoluble anode and the substrate disposed opposite to each other in a plating solution retained in a plating bath; measuring a concentration of a free acid in the plating solution by a free acid concentration analyzer; extracting the plating solution from the plating bath through a plating solution dialysis line and then returning the plating solution to the plating bath; and removing the free acid from the plating solution flowing through the plating solution dialysis line by a dialysis cell having an anion exchange membrane, while controlling a flow rate of the plating solution flowing through the plating solution dialysis line based on the concentration of the free acid measured by the free acid concentration analyzer.

[0011] Still another aspect of the present invention provides a plating solution management method including: forming an Sn alloy film on a surface of a substrate by applying a voltage between an insoluble anode and the substrate disposed opposite to each other in a plating solution retained in a plating bath; extracting the plating solution from the plating bath through a plating solution dialysis line and then returning the plating solution to the plating bath; and removing a free acid from the plating solution flowing through the plating solution dialysis line by a dialysis cell having an anion exchange membrane, while controlling a flow rate of the plating solution flowing through the plating solution dialysis line based on an integrated value of a quantity of electricity applied to the plating solution in the plating bath.

[0012] According to the present invention, the flow rate of the plating solution, supplied to the dialysis cell for removing the free acid from the plating solution, is controlled based on the analytical value of the concentration of the free acid in the plating solution or based on the integrated value of the quantity of electricity applied to the plating solution in the plating bath. Therefore, plating can be performed while controlling the concentration of the free acid in the plating solution in a preferable range. This makes it possible to extend a life of the plating solution and to form a plating film with good appearance and good in-plane uniformity of thickness stably over a longer period of time.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013]

FIG. 1 is a schematic view of a plating apparatus according to an embodiment of the present invention;

FIG. 2 is a schematic perspective view of a substrate holder;

FIG. 3 is a plan view of the substrate holder shown in FIG. 2;

FIG. 4 is a right side view of the substrate holder shown in FIG. 2;

FIG. 5 is an enlarged view of a portion *A* of FIG. 4;

FIG. 6 is a schematic view of the plating apparatus according to another embodiment of the present invention;

FIG. 7 is a schematic view of the plating apparatus according to yet another embodiment of the present invention;

FIG. 8 is a graph showing a relationship between an integrated value (Ah/L) of a quantity of electricity applied to a plating solution and a concentration of free acid in the plating solution (g/L), as observed when plating is carried out while performing dialysis of the plating solution, and also showing the same relationship but observed when plating is carried out without dialysis of the plating solution;

FIG. 9 is a graph showing a relationship between the integrated value (Ah/L) of the quantity of electricity applied to the plating solution and an in-plane uniformity (%) of heights of bumps (thickness of plating film) on a substrate, as observed when plating is carried out while performing dialysis of the plating solution, and also showing the same relationship but observed when plating is carried out without dialysis of the plating solution;

FIGS. 10A through 10F are diagrams each illustrating a change in a cross-sectional shape of a bump with the increase in the integrated value of the quantity of electricity applied to the plating solution, as observed when plating is carried out while performing dialysis of the plating solution;

FIGS. 11A through 11D are diagrams each illustrating a change in the cross-sectional shape of the bump with the increase in the integrated value of the quantity of electricity applied to the plating solution, as observed when plating is carried out without dialysis of the plating solution;

FIG. 12 is a graph showing a relationship between a coefficient a (= A/v) [A (m^2) represents an effective area of an anion exchange membrane, and v (L/h) represents a flow rate of the plating solution supplied to a dialysis cell] and a removal rate (%) of the free acid, as observed when plating is carried out while performing dialysis of the plating solution in the dialysis cell;

FIG. 13 is a graph showing a relationship between a ratio V/v [V (L/h) represents a flow rate of water supplied to the dialysis cell, and v (L/h) represents the flow rate of the plating solution supplied to the dialysis cell] and the removal rate (%) of the free acid, as observed when the flow rate of water supplied to the dialysis cell is constant; and

FIG. 14 is a graph showing a relationship between the ratio V/v [V (L/h) represents the flow rate of water supplied to the dialysis cell, and v (L/h) represents the flow rate of the plating solution supplied to the dialysis cell] and the removal rate (%) of the free acid, as observed when the flow rate of the plating solution supplied to the dialysis cell is constant.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0014] Preferred embodiments of the present invention will now be described in detail with reference to the drawings. The following description illustrates an example in which a plating film of Sn-Ag alloy is formed on a substrate surface by using a plating solution using tin methanesulfonate solution as a supply source of Sn ion (Sn^{2+}) and silver methanesulfonate solution as a supply source of Ag ion (Ag^+). The same reference numerals are used in FIGS. 1 through 7 to refer to the same or like elements, and duplicate descriptions thereof are omitted.

[0015] FIG. 1 is a schematic view of a plating apparatus according to an embodiment of the present invention. As shown in FIG. 1, the plating apparatus includes a plating bath 10 for retaining a plating solution Q therein, an anode holder 14 for holding an insoluble anode 12 (which may be made of titanium) and disposing it at a predetermined position in the plating bath 10 while immersing the insoluble anode 12 in the plating solution Q, and a substrate holder 16 for removably holding a substrate W and disposing it at a predetermined position, opposite to the insoluble anode 12, in the plating bath 10 while immersing the substrate in the plating solution Q.

[0016] When plating of the substrate W is performed, the insoluble anode 12 is electrically connected to a positive electrode of a plating power source 18, while a conductive layer (not shown), such as a seed layer, formed on a surface of the substrate W is coupled to a negative electrode of the plating power source 18. A plating film of Sn-Ag alloy is formed by plating on the surface of the conductive layer. This plating film can be used for production of lead-free solder bumps.

[0017] The plating bath 10 includes an inner bath 20 for storing the plating solution Q therein, and an overflow bath 22 surrounding the inner bath 20. The plating solution Q overflows a top of the inner bath 20 into the overflow bath 22. One end of a plating solution circulation line 32 is coupled to a bottom of the overflow bath 22. This plating solution circulation line 32 is provided with a pump 24, a heat exchanger (heat regulator) 26, a filter 28, and a flow meter 30. The other end of the plating solution circulation line 32 is coupled to a bottom of the inner bath 20 via a plating solution return pipe 34.

[0018] In the plating bath 10, a regulation plate 36 for regulating an electric potential distribution in the plating bath 10 is disposed between the insoluble anode 12 and the substrate holder 16 disposed in the plating bath 10. In this embodiment the regulation plate 36 is made of polyvinyl chloride, which is a dielectric material, and has a central opening 36a having such a size so as to sufficiently regulate expansion of an electric field. The regulation plate 36 has its lower end that reaches the bottom of the plating bath 10.

[0019] Located between the substrate holder 16 and the regulation plate 36 in the plating bath 10, there is provided a vertically-extending agitating paddle (agitating tool) 38 which reciprocates parallel to the substrate W, held by the substrate holder 16, to agitate the plating solution Q existing between the substrate holder 16 and the regulation plate 36. By agitating the plating solution Q by means of the agitating paddle 38, a sufficient amount of ions can be supplied uniformly to the surface of the substrate W.

[0020] A plating solution supply pipe 44 for supplying the plating solution Q to a dialysis cell 42, which has an anion exchange membrane 40 therein, is coupled to the plating solution return pipe 34 of the plating solution circulation line 32. A plating solution discharge pipe 46 extending from the dialysis cell 42 is coupled to a top of the overflow bath 22. The plating solution supply pipe 44 and the plating solution discharge pipe 46 constitute a plating solution dialysis line 48, which is coupled to the plating solution circulation line 32 and takes a part of the plating solution Q out of the plating solution circulation line 32 to allow the plating solution to circulate therethrough. The plating solution supply pipe 44 is provided with a flow meter 50 and a plating solution flow control valve 52 as a plating solution flow control mechanism. A water supply line 54 for supplying water (pure water) into the dialysis cell 42 is coupled to the dialysis cell 42. The water supply line 54 is provided with a flow meter 56 and a water flow control valve 58 as a water flow control mechanism. A drainage line 60 is coupled to the dialysis cell 42.

[0021] The plating solution Q, flowing through the plating solution dialysis line 48, is supplied into the dialysis cell 42, where a free acid (e.g., methanesulfonic acid) is removed by dialysis using the anion exchange membrane 40. The plating solution Q after dialysis is returned to the overflow bath 22. The free acid that has been removed from the plating solution Q by the dialysis diffuses in the water (the pure water) supplied into the dialysis cell 42 through the water supply line 54, and is discharged to the exterior of the dialysis cell 42 through the drainage line 60.

[0022] The anion exchange membrane 40 used in this embodiment is DSV (an effective area is 0.0172 m^2) manufactured by AGC Engineering Co., Ltd. An arbitrary number (e.g., 19) of such membranes may be incorporated in the dialysis cell 42 depending on the amount of the plating solution to be dialyzed (the amount of the free acid to be removed).

[0023] A plating solution extraction pipe 66 of a plating solution analysis line 64, which is provided with a free acid concentration analyzer 62, is coupled to the plating solution return pipe 34 of the plating solution circulation line 32. An extract discharge pipe 68 extending from the free acid concentration analyzer 62 is coupled to the top of the overflow bath 22. A part of the plating solution Q, circulating through the plating solution circulation line 32, is extracted through the plating solution extraction pipe 66 and fed to the free acid concentration analyzer 62, where the concentration of the free acid in the plating solution Q is measured. The plating solution after measurement is returned to the overflow bath 22.

[0024] A replenisher solution supply line 69 for supplying a replenisher solution is coupled to the top of the overflow bath 22. A plating solution and metal ion (i.e., tin methanesulfonate solution as a supply source of Sn ion Sn^{2+} and silver methanesulfonate solution as a supply source of Ag ion Ag^{+}) are supplied through the replenisher solution supply line 69 into the plating solution Q circulating through the plating solution circulation line 32.

[0025] Results of analysis (analytical value of the concentration of the free acid) by the free acid concentration analyzer 62 and results of measurement by the flow meters 30, 50, 56 are inputted into a controller 70. Based on outputs from the controller 70, an opening degree of the plating solution flow control valve (the plating solution flow control mechanism) 52 and an opening degree of the water flow control valve (the water flow control mechanism) 58 are adjusted so as to regulate the flow rate of the plating solution Q flowing through the plating solution dialysis line 48 into the dialysis cell 42 and the flow rate of the water flowing through the water supply line 54 into the dialysis cell 42.

[0026] As shown in FIGS. 2 through 5, the substrate holder 16 includes a first holding member (base holding member) 154 having a rectangular plate shape and made of e.g., vinyl chloride, and a second holding member (movable holding member) 158 rotatably coupled to the first holding member 154 through a hinge 156 which allows the second holding member 158 to open and close with respect to the first holding member 154. Although in this embodiment the second holding member 158 is configured to be openable and closable through the hinge 156, it is also possible to dispose the second holding member 158 opposite to the first holding member 154 and to move the second holding member 158 away from and toward the first holding member 154 to thereby open and close the second holding member 158.

[0027] The second holding member 158 includes a base portion 160 and a ring-shaped seal holder 162. The seal holder 162 is made of vinyl chloride so as to enable a retaining ring 164, which will be described later, to slide well. A substrate-side sealing member 166 is fixed to an upper surface of the seal holder 162. This substrate-side sealing member 166 is placed in pressure contact with a periphery of the surface of the substrate W to seal a gap between the substrate W and the second holding member 158 when the substrate W is held by the substrate holder 16. A holder-side sealing member 168 is fixed to a surface, facing the first holding member 154, of the seal holder 162. This holder-side sealing member 168 is placed in pressure contact with the first holding member 154 to seal a gap between the first holding member 154 and the second holding member 158. The holder-side sealing member 168 is located outwardly of the substrate-side sealing member 166.

[0028] As shown in FIG. 5, the substrate-side sealing member 166 is sandwiched between the seal holder 162 and a first mounting ring 170a which is secured to the seal holder 162 by fastening tools 169a, such as bolts. The holder-side sealing member 168 is sandwiched between the seal holder 162 and a second mounting ring 170b which is secured to the seal holder 162 by fastening tools 169b, such as bolts.

[0029] The seal holder 162 of the second holding member 158 has a stepped portion at a periphery thereof, and the retaining ring 164 is rotatably mounted to the stepped portion via a spacer 165. The retaining ring 164 is inescapably held by an outwardly projecting retaining plates 172 (see FIG. 3) mounted to a side surface of the seal holder 162. This retaining ring 164 is made of a material (e.g., titanium) having high rigidity and excellent acid and alkali corrosion resistance and the spacer 165 is made of a material having a low friction coefficient, for example PTFE, so that the retaining ring 164 can rotate smoothly.

[0030] Inverted L-shaped clampers 174, each having an inwardly projecting portion and located outside of the retaining ring 164, are provided on the first holding member 154 at equal intervals along a circumferential direction of the retaining ring 164. The retaining ring 164 has outwardly projecting portions 164b along the circumferential direction of the retaining ring 164 at positions corresponding to positions of the clampers 174. A lower surface of the inwardly projecting portion of each clamper 174 and an upper surface of each projecting portion 164b of the retaining ring 164 are tapered in opposite directions along the rotational direction of the retaining ring 164. A plurality (e.g., three) of upwardly protruding dots 164a are provided on the retaining ring 164 in predetermined positions along the circumferential direction of the retaining ring 164. The retaining ring 164 can be rotated by pushing and moving each dot 64a from a lateral direction by means of a rotating pin (not shown).

[0031] When the second holding member 158 is open, the substrate W is inserted into the central portion of the first holding member 154, and the second holding member 158 is then closed through the hinge 156. Subsequently the retaining ring 164 is rotated clockwise so that each projecting portion 164b of the retaining ring 164 slides into the inwardly projecting portion of each clamper 174. As a result, the first holding member 154 and the second holding member 158 are fastened to each other and locked by engagement between the tapered surfaces of the retaining ring 164 and the tapered surfaces of the clampers 174. The lock can be released by rotating the retaining ring 164 counterclockwise and to disengage the projecting portions 164b of the retaining ring 164 from the inverted L-shaped clampers 174. When the second holding member 158 is locked in the above-described manner, the lower end of the inner downwardly-protruding portion of the substrate-side sealing member 166 is placed in pressure contact with the periphery of the surface of the substrate W held by the substrate holder 16, while the lower end of the outer downwardly-protruding portion of the holder-side sealing member 168 is placed in pressure contact with the surface of the first holding member 154, whereby the sealing members 166 and 168 are uniformly pressed to seal the gap between the substrate W and the second holding member 158 and the gap between the first holding member 154 and the second holding member 158, respectively.

[0032] A protruding portion 182 is formed on the central portion of the first holding member 154 so as to protrude in a ring shape corresponding to a size of the substrate W. The protruding portion 182 has a support surface 180 which is placed in contact with the periphery of the substrate W to support the substrate W. The protruding portion 182 has recesses 184 arranged at predetermined positions along a circumferential direction of the protruding portion 182.

[0033] As shown in FIG. 3, a plurality of electrical conductors (electrical contacts) 186 (e.g., 12 conductors as illustrated), coupled respectively to wires extending from external contacts provided in a hand 190, are disposed in the recesses 184 of the protruding portion 182. When the substrate W is placed on the support surface 180 of the first holding member 154, ends of the electrical conductors 186 are exposed in a springy state on the surface of the first holding member 154 at positions beside the substrate W to contact lower portions of the electrical contacts 188 shown in FIG. 5.

[0034] The electrical contacts 188, to be electrically connected to the electrical conductors 186, are secured to the seal holder 162 of the second holding member 158 by fastening tools 189, such as bolts. The electrical contacts 188 each have a leaf spring-like contact portion lying outside the substrate-side sealing member 166 and projecting inwardly. This contact portion is springy and bends easily. When the substrate W is held by the first holding member 154 and the second holding member 158, the contact portions of the electrical contacts 188 make elastic contact with the peripheral surface of the substrate W supported on the support surface 180 of the first holding member 154.

[0035] The second holding member 158 is opened and closed by a not-shown pneumatic cylinder and by the weight of the second holding member 158 itself. More specifically, the first holding member 154 has a through-hole 154a, and a pneumatic cylinder is provided so as to face the through-hole 154a. The second holding member 158 is opened by extending a piston rod of the pneumatic cylinder to lift up a pressing rod through the through-hole 154a to push up the seal holder 162 of the second holding member 158. The second holding member 158 is closed by its own weight when the piston rod is retracted.

[0036] A pair of approximately T-shaped hands 190 is connected to the ends of the first holding member 154 of the substrate holder 16. These hands 190 serve as a support when the substrate holder 16 is transported and when the substrate holder 16 is held in a suspended state.

[0037] In this embodiment the opening degree of the plating solution flow control valve 52 and the opening degree of the water flow control valve 58 are adjusted based on the concentration of the free acid measured by the free acid concentration analyzer 62 so as to control the flow rate of the plating solution Q flowing through the plating solution dialysis line 48 into the dialysis cell 42 and the flow rate of water flowing through the water supply line 54 into the dialysis cell 42, thereby controlling the amount of the free acid removed. The concentration of the free acid in the plating solution Q for use in the plating process is controlled in the preferable range of, e.g., 60 to 250 g/L.

[0038] In operation, while the pump 24 is driven and the plating solution Q in the plating bath 10 circulates through the plating solution circulation line 32, the substrate W held by the substrate holder 16 is disposed at a predetermined position in the plating bath 10, and the insoluble anode 12 is connected to the positive electrode of the plating power source 18 and a surface conductive layer, such as a seed layer, of the substrate W is connected to the negative electrode of the plating power source 18 to thereby initiate plating of the substrate W. At this time, the plating solution flow control valve 52 and the water flow control valve 58 are in a closed state.

[0039] As the plating solution Q in the plating bath 10 circulates through the plating solution circulation line 32 in this manner, a part of the plating solution Q is extracted through the plating solution extraction pipe 66 and fed to the free acid concentration analyzer 62, where the concentration of the free acid in the plating solution Q is analyzed several times a day, for example. The results of analysis (the analytical values of the concentration of the free acid) are inputted into the controller 70.

[0040] Based on the results of analysis (analytical values of the concentration of the free acid) by the free acid concentration analyzer 62, the controller 70 sends signals respectively to the plating solution flow control valve 52 and to the water flow control valve 58 in order to adjust the opening degree of the plating solution flow control valve 52 and the opening degree of the water flow control valve 58 so that the concentration of the free acid in the plating solution Q for use in the plating process lies in the range of, e.g., 60 to 250 g/L. In this manner, the concentration of the free acid in the plating solution Q is controlled, e.g., in the range of 60 to 250 g/L, by controlling the flow rate of the plating solution which is fed through the plating solution dialysis line 48 to the dialysis cell 42 that removes the free acid (methanesulfonic acid) from the plating solution, and also controlling the flow rate of water for use in the removal of the free acid (methanesulfonic acid). The opening degree of the plating solution flow control valve 52 and the opening degree of the water flow control valve 58 are adjusted every time the concentration of the free acid in the plating solution Q is analyzed by the free acid concentration analyzer 62.

[0041] By thus controlling the flow rate of the plating solution flowing through the plating solution dialysis line 48, which has the dialysis cell 42 for removing the free acid from the plating solution, based on the concentration of the free acid measured by the free acid concentration analyzer 62, plating can be performed with the controlled concentration of the free acid in the plating solution, e.g., in the preferable range of 60 to 250 g/L.

[0042] According to this embodiment, the free acid can be removed from the plating solution under the condition of the controlled flow rate of the plating solution flowing through the plating solution dialysis line 48, while the plating solution is circulating through the plating solution circulation line 32.

[0043] It is preferable to adjust the opening degree of the plating solution flow control valve 52 such that a coefficient *a* (= A/v) [A (m^2) represents the effective area of the anion exchange membrane 40 of the dialysis cell 42, and v (L/h) represents the flow rate of the plating solution supplied through the plating solution dialysis line 48 to the dialysis cell 42] lies in the range of 0.3 to 0.7 (*a* = 0.3 to 0.7). Further, it is preferable to adjust the opening degree of the water flow control valve 58 such that a ratio V/v [V (L/h) represents the flow rate of water supplied through the water supply line 54 into the dialysis cell 42, and v (L/h) represents the flow rate of the plating solution supplied through the plating solution dialysis line 48 to the dialysis cell 42] lies in the range of 0.3 to 1 (V/v = 0.3 to 1, i.e., V is 30% to 100% of v).

[0044] In this embodiment the controller 70 calculates an integrated value of a quantity of electricity applied to the plating solution Q in the plating bath 10. The "quantity of electricity applied to the plating solution Q" herein refers to the product of an electric current, which flows from the positive electrode to the negative electrode of the plating power source 18 via the insoluble anode 12, the plating solution Q, and the surface conductive layer of the substrate W, and a period of time of the application of the electric current. The "integrated value" herein refers to the total quantity of electricity applied to the plating solution Q during a period of time from supply of a fresh plating solution Q into the plating bath 10 to withdrawal of that plating solution Q from the plating bath 10. The free acid in the plating solution Q is produced, as the metal ions in the plating solution Q are consumed by plating. Thus, the integrated value of the quantity of electricity applied to the plating solution Q can give an indication of an increase in the concentration of the free acid. Therefore, based on the integrated value of the quantity of electricity applied to the plating solution Q, the controller 70 sends signals respectively to the plating solution flow control valve 52 and to the water flow control valve 58 in order to adjust the opening degree of the plating solution flow control valve 52 and the opening degree of the water flow control valve 58 such that the concentration of the free acid in the plating solution Q lies in the range of, e.g., 60 to 250 g/L. For example, plating may be carried out in the following manner. Plating of substrates is performed successively using a predetermined amount of the plating solution Q while replenishing it with metal ions. When the integrated value of the quantity of electricity applied to the plating solution has reached a predetermined value, the plating solution flow control valve 52 and the water flow control valve 58 are each opened to a certain degree to carry out dialysis of the plating solution, so that the free acid is removed.

[0045] Also by thus controlling the flow rate of the plating solution Q flowing through the plating solution dialysis line 48, which has the dialysis cell 42 for removing the free acid from the plating solution, based on the integrated value of the quantity of electricity applied to the plating solution Q in the plating bath 10, plating can be performed while controlling the concentration of the free acid in the plating solution in the preferable range of, e.g., 60 to 250 g/L.

[0046] In this embodiment, based on at least one of the concentration of the free acid, measured by the free acid concentration analyzer 62, and the integrated value of the quantity of electricity applied to the plating solution Q, the controller 70 sends signals respectively to the plating solution flow control valve 52 and to the water flow control valve 58 in order to adjust the opening degree of the plating solution flow control valve 52 and the opening degree of the water flow control valve 58 so that the concentration of the free acid in the plating solution Q lies in the range of, e.g., 60 to 250 g/L. The plating solution flow control valve 52 and the water flow control valve 58 may be controlled based on only one of the concentration of the free acid, measured by the free acid concentration analyzer 62, and the integrated value of the quantity of electricity applied to the plating solution Q.

[0047] Instead of the plating solution flow control valve 52 and the water flow control valve 58, it is possible to use on-off valves which are each on-off controllable by means of a timer and which respectively constitute the plating solution flow control mechanism and the water flow control mechanism. Thus, the flow rate of the plating solution Q flowing through the plating solution dialysis line 48 into the dialysis cell 42 and the flow rate of water flowing through the water supply line 54 into the dialysis cell 42 may be controlled by the use of the plating solution flow control mechanism and the water flow control mechanism, including the on-off valves.

[0048] FIG. 6 is a schematic view of a plating apparatus according to another embodiment of the present invention. This embodiment differs from the embodiment shown in FIG. 1 in that the plating solution dialysis line 48 is provided with an on-off valve 80 and a first tube pump 82, both constituting the plating solution flow control mechanism, instead of the plating solution flow control valve 52, and that the water supply line 54 is provided with an on-off valve 84 and a second tube pump 86, both constituting the water flow control mechanism, instead of the water flow control valve 58. The controller 70 controls the plating solution flow control mechanism, i.e., the on-off valve 80 and the first tube pump 82, and the water flow control mechanism, i.e., the on-off valve 84 and the second tube pump 86.

[0049] According to this embodiment, the controller 70 can regulate the flow rate of the plating solution flowing through the plating solution dialysis line 48 by controlling the first tube pump 82 with the on-off valve 80 opened. The controller 70 can further regulate the flow rate of the water flowing through the water supply line 54 by controlling the second tube pump 86 with the on-off valve 84 opened.

[0050] FIG. 7 is a schematic view of the plating apparatus according to yet another embodiment of the present invention. This embodiment differs from the embodiment shown in FIG. 6 in that, instead of coupling the plating solution supply pipe 44 of the plating solution dialysis line 48 to the plating solution return pipe 34 of the plating solution circulation line 32, the plating solution supply pipe 44 extends from the bottom of the overflow bath 22. According to this embodiment, a part of the plating solution Q that has flown into and accumulated in the overflow bath 22 can be supplied through the plating solution dialysis line 48 to the dialysis cell 42 and, after the free acid is removed by the dialysis cell 42, can be returned to the overflow bath 22.

[0051] In order to verify that the free acid (methanesulfonic acid) in the plating solution can be removed by the apparatus of the present invention, an experiment was conducted using a dialysis cell incorporating nine anion exchange membranes, each being a commercially-available DSV (an effective area is 0.0172 m^2) manufactured by AGC Engineering Co., Ltd. The plating solution was supplied to the dialysis cell at a flow rate of 2.9 ml/min, while pure water was supplied to the dialysis cell at a flow rate of 2.9 ml/min. Thus, the coefficient a (= A/v) [A (m^2) is the effective area of the anion exchange membrane of the dialysis cell, and v (L/h) is the flow rate of the plating solution supplied to the dialysis cell] is 0.9 (a = A/v = 0.9). Further, the ratio V/v [V (L/h) is the flow rate of water supplied to the dialysis cell, and v (L/h) is the flow rate of the plating solution supplied to the dialysis cell] is 1 (V/v = 1, i.e., V is 100% of v).

[0052] As a result of the experiment, the concentration of the free acid in the plating solution, which was 242 g/L before dialysis, decreased to 45 g/L after dialysis. This result showed the fact that the free acid can be removed from the plating solution. However, the plating solution after dialysis was so cloudy that it was not suitable for use in plating. As is appreciated from this fact, the plating solution containing the free acid with a concentration of less than 60 g/L is not suitable for use in plating, and the concentration of the free acid in the plating solution should preferably be not less than 60 g/L, more preferably not less than 80 g/L.

[0053] A further experiment for examining the removal of the free acid from the plating solution was conducted using a dialysis cell having a reduced total area of ion exchange membranes, more specifically using a dialysis cell incorporating five anion exchange membranes, each being a commercially-available DSV (an effective area is 0.0172 m^2) manufactured by AGC Engineering Co., Ltd. The plating solution was supplied to the dialysis cell at a flow rate of 2.9 ml/min, while pure water was supplied to the dialysis cell at a flow rate of 1.7 ml/min. Thus, the coefficient a (= A/v) [A (m^2) is the effective area of the anion exchange membrane of the dialysis cell, and v (L/h) is the flow rate of the plating solution supplied to the dialysis cell] is 0.45 (a = A/v = 0.45). Further, the ratio V/v [V (L/h) is the flow rate of the water supplied to the dialysis cell, and v (L/h) is the flow rate of the plating solution supplied to the dialysis cell] is 0.59 (V/v = 0.59, i.e., V is 59% of v).

[0054] As a result of the experiment, the concentration of the free acid in the plating solution, which was 256 g/L before dialysis, decreased to 115 g/L after dialysis.

[0055] A further experiment was conducted in the same manner as in the preceding experiment except that the flow rate of the pure water supplied to the above-described dialysis cell incorporating five anion exchange membranes was changed from 1.7 ml/min to 1.23 ml/min. The flow rate of the plating solution supplied to the dialysis cell was maintained at 2.9 ml/min. Thus, the coefficient a (= A/v) [A (m^2) is the effective area of the anion exchange membrane of the dialysis cell, and v (L/h) is the flow rate of the plating solution supplied to the dialysis cell] is 0.45 (a = A/v = 0.45). Further, the ratio V/v [V (L/h) is the flow rate of water supplied to the dialysis cell, and v (L/h) is the flow rate of the plating solution supplied to the dialysis cell] is 0.42 (V/v = 0.42, i.e., V is 42% of v).

[0056] As a result of the experiment, the concentration of the free acid in the plating solution, which was 256 g/L before dialysis, decreased to 150 g/L after dialysis. It can be seen from this result that the free acid removal effect is lowered by reducing the flow rate of the water supplied to the dialysis cell.

[0057] An experiment was conducted to examine the effect of the concentration of the free acid in the plating solution on formation of a plating film on a substrate surface. A plating film, which was for forming bumps, was formed on a substrate surface in a single plating bath (volume 28L). Plating of the substrate was carried out while applying electricity to the plating solution at 8.7 Ah/L per day and performing the dialysis (for removing the free acid) of the plating solution in the dialysis cell. For comparison, plating of a substrate was carried out without performing the dialysis of the plating solution. Measurements were made to determine a change in the concentration of the free acid in the plating solution and a change in the uniformity (in-plane uniformity) of the heights of bumps (thickness of the plating film) over the entire substrate surface with the change (the increase) in the integrated value of the quantity of electricity applied to the plating solution.

[0058] The dialysis was performed by using a dialysis cell incorporating 19 anion exchange membranes, each being a commercially-available DSV (the effective area is 0.0172 m^2) manufactured by AGC Engineering Co., Ltd. The flow rate of the plating solution and the flow rate of the water were controlled by tube pumps so that the plating solution was supplied to the dialysis cell at a flow rate of 9 to 10 ml/min and the pure water was supplied to the dialysis cell at a flow rate of 6 to 7 ml/min. Thus, the coefficient a (= A/v) [A (m^2) is the effective area of the anion exchange membrane of the dialysis cell, and v (L/h) is the flow rate of the plating solution supplied to the dialysis cell] is 0.5 to 0.6 (a = A/v = 0.5 to 0.6). Further, the ratio V/v [V (L/h) is the flow rate of the water supplied to the dialysis cell, and v (L/h) is the flow rate of the plating solution supplied to the dialysis cell] is 0.6 to 0.8 (V/v = 0.6 to 0.8, i.e., V is 60% to 80% of v).

[0059] The dialysis was started when the integrated value of the quantity of electricity applied to the plating solution had exceeded 20 Ah/L. The application of electricity to the plating solution was stopped when the integrated value of the quantity of electricity had reached 59 Ah/L because the concentration of the free acid in the plating solution almost reached 200 g/L. Then the dialysis of the plating solution was performed for 24 hours without the application of electricity to thereby lower the concentration of the free acid in the plating solution.

[0060] FIG. 8 shows a relationship between the integrated value (Ah/L) of the quantity of electricity applied to the plating solution and the concentration of the free acid in the plating solution (g/L), determined by the above experiment in which plating was carried out while performing the dialysis of the plating solution, and also shows the same relationship but determined by the comparative experiment in which plating was carried out without dialysis of the plating solution. FIG. 9 shows a relationship between the integrated value (Ah/L) of the quantity of electricity applied to the plating solution and the in-plane uniformity (%) of the heights of bumps (i.e., the thickness of the plating film), determined by the above experiment in which plating was carried out while performing the dialysis of the plating solution, and also shows the same relationship but determined by the comparative experiment in which plating was carried out without dialysis of the plating solution.

[0061] As can be seen in FIGS. 8 and 9, the concentration of the free acid in the plating solution can be controlled at a level of not more than 200 g/L and the in-plane uniformity of the heights of bumps can be controlled at a level of not more than 10% by performing the dialysis of the plating solution (i.e., the removing process of the free acid). In contrast, without the dialysis of the plating solution, the concentration of the free acid in the plating solution exceeds 250 g/L and the in-plane uniformity of the heights of the bumps exceeds 10% with the increase in the integrated value of the quantity of electricity applied to the plating solution.

[0062] The in-plane uniformity of the heights of bumps is generally required to be not more than 10%. As can be seen from the data in FIGS. 8 and 9, the in-plane uniformity can be controlled at a level of not more than 10% by controlling the concentration of the free acid in the plating solution at a level of not more than 250 g/L, preferably not more than 200 g/L, more preferably not more than 170 g/L. Therefore, in each of the above-described plating apparatuses, the concentration of the free acid in the plating solution may be controlled at a level of not more than 250 g/L, preferably not more than 200 g/L, more preferably not more than 170 g/L. On the other hand, as described above, the concentration of the free acid in the plating solution is preferably controlled at a level of not less than 60 g/L, more preferably not less than 80 g/L in order to prevent the plating solution from becoming too cloudy for use in plating.

[0063] FIGS. 10A through 10F each illustrates a change in a schematic cross-sectional shape of the bump (the plating film) with the increase in the integrated value of the quantity of electricity applied to the plating solution, as observed in the above experiment in which plating was carried out while performing the dialysis of the plating solution. More specifically, FIGS. 10A through 10F illustrate the cross-sectional shapes of the bumps (the plating films) formed on substrates when the integrated value of the quantity of electricity applied to the plating solution was 0 Ah/L (FIG. 10A), 20 Ah/L (FIG. 10B), 40 Ah/L (FIG. 10C), 59 Ah/L (FIG. 10D), 80 Ah/L (FIG. 10E), and 130 Ah/L (FIG. 10F), respectively.

[0064] As can be seen from FIGS. 10A through 10F, the bump (plating film) has a normal shape or appearance when the integrated value of the quantity of electricity applied to the plating solution is not more than 80 Ah/L. A poor appearance of the bump (plating film) shown in FIG. 10F is considered to be due to the fact that coarsening of crystal grains occurs when the integrated value of the quantity of electricity applied to the plating solution reaches 130 Ah/L, resulting in roughened surface of the bump.

[0065] FIGS. 11A through 11D each illustrates the change in the schematic cross-sectional shape of the bump (plating film) with the increase in the integrated value of the quantity of electricity applied to the plating solution, as observed in the above experiment (comparative test) in which plating was carried out without the dialysis of the plating solution. More specifically, FIGS. 11A through 11D illustrate the cross-sectional shapes of the bumps (plating films) formed on substrates when the integrated value of the quantity of electricity applied to the plating solution was 0 Ah/L (FIG. 11A), 19 Ah/L (FIG. 11B), 59 Ah/L (FIG. 11C), and 100 Ah/L (FIG. 11D), respectively.

[0066] As can be seen from FIGS. 11A through 11D, a roughened surface of the bump (plating film) was observed when the integrated value of the quantity of electricity applied to the plating solution reached 59 Ah/L. A more roughened surface of the bump (plating film) was observed when the integrated value reached 100 Ah/L. Such a roughened surface of the bump (plating film) is considered to be due to a decrease in Ag in the bump (plating film) with the increase in the concentration of the free acid in the plating solution.

[0067] FIG. 12 is a graph showing a relationship between the coefficient *a* (= A/v) [A (m^2) is the effective area of the anion exchange membrane, and v (L/h) is the flow rate of the plating solution supplied to the dialysis cell] and a removal rate (%)of the free acid, determined by the above experiment in which plating was carried out while performing the dialysis of the plating solution (i.e., the removing process of the free acid) in the dialysis cell incorporating the 19 anion exchange membranes. The flow rate of the water supplied to the dialysis cell was 6.3 ml/min.

[0068] As can be seen from FIG. 12, the removal rate of the free acid can be controlled in an appropriate range of about 30% to 65% by controlling the coefficient *a* (= A/v) in the range of 0.3 to 0.7. The same holds true for the above-described plating apparatuses. That is, the removal rate of the free acid can be controlled in the appropriate range of about 30% to 65% by regulating the opening degree of the plating solution flow control valve 52 so that the coefficient *a* (= A/v) [A (m^2) is the effective area of the anion exchange membrane 40 of the dialysis cell 42, and v (L/h) is the flow rate of the plating solution supplied through the plating solution dialysis line 48 to the dialysis cell 42] lies in the range of 0.3 to 0.7 (i.e., *a* = 0.3 to 0.7).

[0069] FIGS. 13 and 14 are graphs each showing a relationship between the ratio V/v [V (L/h) is the flow rate of the water supplied to the dialysis cell, and v (L/h) represents the flow rate of the plating solution supplied to the dialysis cell] and the removal rate of the free acid, determined by the above experiment in which plating was carried out while performing the dialysis of the plating solution in the dialysis cell incorporating the 19 anion exchange membranes. FIG. 13 shows the relationship observed when the flow rate of the plating solution supplied to the dialysis cell was changed while keeping the flow rate of the water supplied to the dialysis cell constant at 6.3 ml/min. FIG. 14 shows the relationship observed when the flow rate of the water supplied to the dialysis cell was changed while keeping the flow rate of the plating solution supplied to the dialysis cell constant at 10.3 ml/min.

[0070] As can be seen from FIGS. 13 and 14, the removal rate of the free acid can be controlled in the appropriate range of about 30% to 65% by controlling the ratio V/v in the range of 0.3 to 1. The same holds true for the above-described plating apparatuses. That is, the removal rate of the free acid can be controlled in the appropriate range of about 30% to 65% by regulating the opening degree of the water flow control valve 58 so that the ratio V/v [V (L/h) is the flow rate of the water supplied through the water supply line 54 into the dialysis cell 42, and v (L/h) is the flow rate of the plating solution supplied through the plating solution dialysis line 48 into the dialysis cell 42] lies in the range of 0.3 to 1 (i.e., V/v = 0.3 to 1, i.e., V is 30% to 100% of v).

[0071] While the present invention has been described with reference to preferred embodiments, it is understood that the present invention is not limited to the embodiments described above, but is capable of various changes and modifications within the scope of the inventive concept as expressed herein.

Claims

1. A plating apparatus for plating a substrate with Sn alloy to form an Sn alloy film on a surface of the substrate, comprising:

    a plating bath for retaining a plating solution therein and having an insoluble anode disposed in the plating solution, the substrate being immersed in the plating solution in a position opposite to the insoluble anode;
    a plating solution dialysis line for extracting the plating solution from the plating bath and returning the plating solution to the plating bath;
    a dialysis cell provided in the plating solution dialysis line and configured to remove a free acid from the plating solution by dialysis using an anion exchange membrane;
    a free acid concentration analyzer configured to measure a concentration of the free acid in the plating solution; and
    a controller for controlling a flow rate of the plating solution flowing through the plating solution dialysis line, based on the concentration of the free acid measured by the free acid concentration analyzer.

2. The plating apparatus according to claim 1, further comprising:

    a plating solution circulation line for extracting the plating solution from the plating bath and returning the plating solution to the plating bath during plating of the substrate, the plating solution dialysis line being coupled to the plating solution circulation line.

3. The plating apparatus according to claim 1, wherein the controller is configured to control the flow rate of the plating solution flowing through the plating solution dialysis line such that the concentration of the free acid in the plating solution lies in a range of 60 to 250 g/L.

4. The plating apparatus according to claim 1, wherein the plating solution dialysis line is provided with a plating solution flow control mechanism located between the plating bath and the dialysis cell, and the controller is configured to control the plating solution flow control mechanism such that a coefficient lies in a range of 0.3 to 0.7, the coefficient being determined by dividing an effective area (m^2) of the anion exchange membrane by the flow rate (L/h) of the plating solution.

5. The plating apparatus according to claim 4, further comprising:

a water supply line coupled to the dialysis cell and provided with a water flow control mechanism,
wherein the controller is configured to control the water flow control mechanism such that a flow rate of water, supplied through the water supply line into the dialysis cell, is 30% to 100% of the flow rate of the plating solution supplied through the plating solution dialysis line into the dialysis cell.

6. A plating apparatus for plating a substrate with Sn alloy to form an Sn alloy film on a surface of the substrate, comprising:

a plating bath for retaining a plating solution therein and having an insoluble anode disposed in the plating solution, the substrate being immersed in the plating solution in a position opposite to the insoluble anode;
a plating solution dialysis line for extracting the plating solution from the plating bath and returning the plating solution to the plating bath;
a dialysis cell provided in the plating solution dialysis line and configured to remove a free acid from the plating solution by dialysis using an anion exchange membrane; and
a controller for controlling a flow rate of the plating solution flowing through the plating solution dialysis line, based on an integrated value of a quantity of electricity applied to the plating solution in the plating bath.

7. The plating apparatus according to claim 6, further comprising:

a plating solution circulation line for extracting the plating solution from the plating bath and returning the plating solution to the plating bath during plating of the substrate, the plating solution dialysis line being coupled to the plating solution circulation line.

8. The plating apparatus according to claim 6, wherein the controller is configured to control the flow rate of the plating solution flowing through the plating solution dialysis line such that a concentration of the free acid in the plating solution lies in a range of 60 to 250 g/L.

9. The plating apparatus according to claim 6, wherein the plating solution dialysis line is provided with a plating solution flow control mechanism located between the plating bath and the dialysis cell, and the controller is configured to control the plating solution flow control mechanism such that a coefficient lies in a range of 0.3 to 0.7, the coefficient being determined by dividing an effective area (m^2) of the anion exchange membrane by the flow rate (L/h) of the plating solution.

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

a water supply line coupled to the dialysis cell and provided with a water flow control mechanism,
wherein the controller is configured to control the water flow control mechanism such that a flow rate of water, supplied through the water supply line into the dialysis cell, is 30% to 100% of the flow rate of the plating solution supplied through the plating solution dialysis line into the dialysis cell.

11. A plating solution management method comprising:

forming an Sn alloy film on a surface of a substrate by applying a voltage between an insoluble anode and the substrate disposed opposite to each other in a plating solution retained in a plating bath;
measuring a concentration of a free acid in the plating solution by a free acid concentration analyzer;
extracting the plating solution from the plating bath through a plating solution dialysis line and then returning the plating solution to the plating bath; and
removing the free acid from the plating solution flowing through the plating solution dialysis line by a dialysis cell having an anion exchange membrane, while controlling a flow rate of the plating solution flowing through the plating solution dialysis line based on the concentration of the free acid measured by the free acid concentration analyzer.

12. The plating solution management method according to claim 11, wherein the flow rate of the plating solution flowing through the plating solution dialysis line is controlled such that the concentration of the free acid in the plating solution lies in a range of 60 to 250 g/L.

13. The plating solution management method according to claim 11, wherein the plating solution dialysis line is provided with a plating solution flow control mechanism located between the plating bath and the dialysis cell, and the plating solution flow control mechanism is controlled such that a coefficient lies in a range of 0.3 to 0.7, the coefficient being determined by dividing an effective area (m^2) of the anion exchange membrane by the flow rate (L/h) of the plating solution.

14. The plating solution management method according to claim 13, wherein a water supply line provided with a water flow control mechanism is coupled to the dialysis cell, and the water flow control mechanism is controlled such that a flow rate of water, supplied through the water supply line into the dialysis cell, is 30% to 100% of the flow rate of the plating solution supplied through the plating solution dialysis line into the dialysis cell.

15. A plating solution management method comprising:

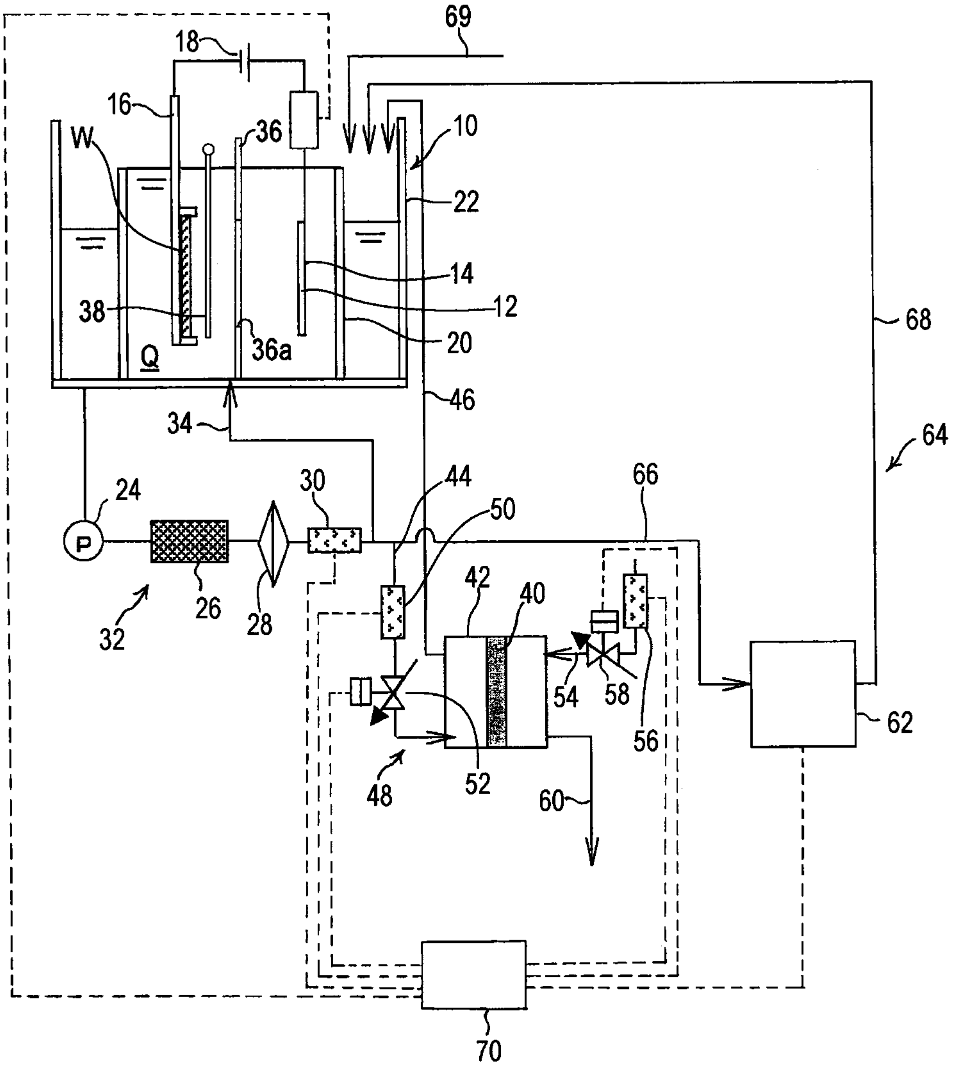
forming an Sn alloy film on a surface of a substrate by applying a voltage between an insoluble anode and the substrate disposed opposite to each other in a plating solution retained in a plating bath;
extracting the plating solution from the plating bath through a plating solution dialysis line and then returning the plating solution to the plating bath; and
removing a free acid from the plating solution flowing through the plating solution dialysis line by a dialysis cell having an anion exchange membrane, while controlling a flow rate of the plating solution flowing through the plating solution dialysis line based on an integrated value of a quantity of electricity applied to the plating solution in the plating bath.

16. The plating solution management method according to claim 15, wherein the flow rate of the plating solution flowing through the plating solution dialysis line is controlled such that a concentration of the free acid in the plating solution lies in a range of 60 to 250 g/L.

17. The plating solution management method according to claim 15, wherein the plating solution dialysis line is provided with a plating solution flow control mechanism located between the plating bath and the dialysis cell, and the plating solution flow control mechanism is controlled such that a coefficient lies in a range of 0.3 to 0.7, the coefficient being determined by dividing an effective area (m^2) of the anion exchange membrane by the flow rate (L/h) of the plating solution.

18. The plating solution management method according to claim 17, wherein a water supply line provided with a water flow control mechanism is coupled to the dialysis cell, and the water flow control mechanism is controlled such that a flow rate of water, supplied through the water supply line into the dialysis cell, is 30% to 100% of the flow rate of the plating solution supplied through the plating solution dialysis line into the dialysis cell.

FIG. 1


69
18
16
W
36
10
22
14
12
38
Q
36a
20
46
68
34
64
24
P
30
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66
42
40
32
26
28
54
58
56
62
48
52
60
70

FIG. 2

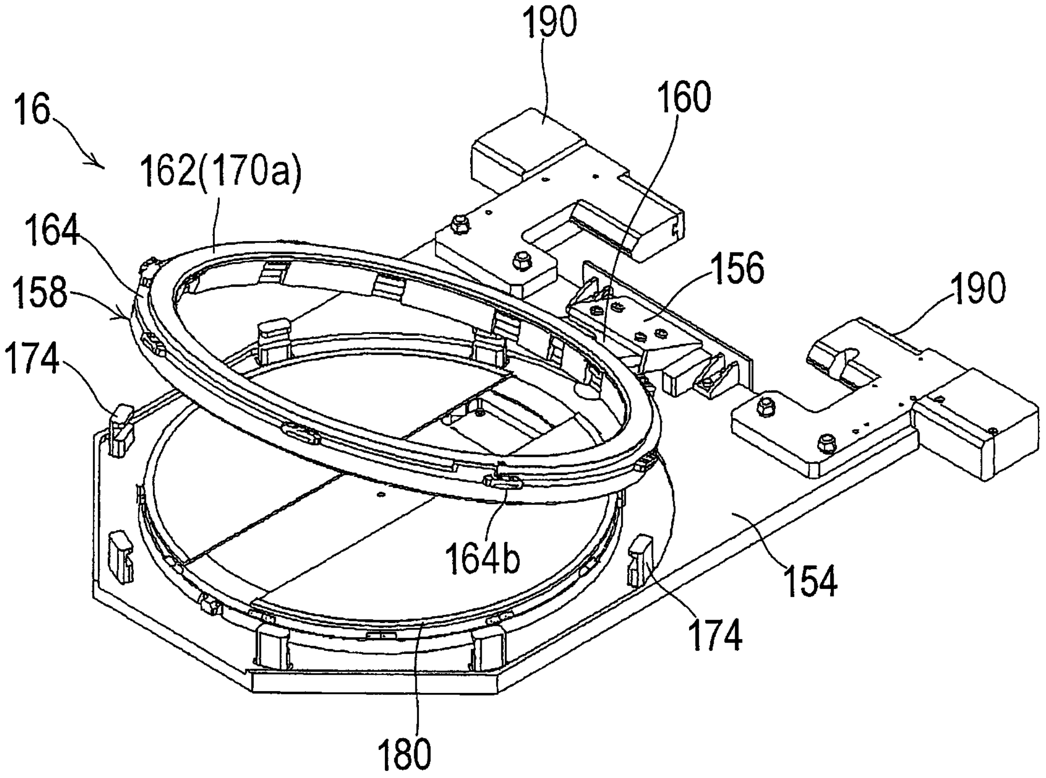


FIG. 3

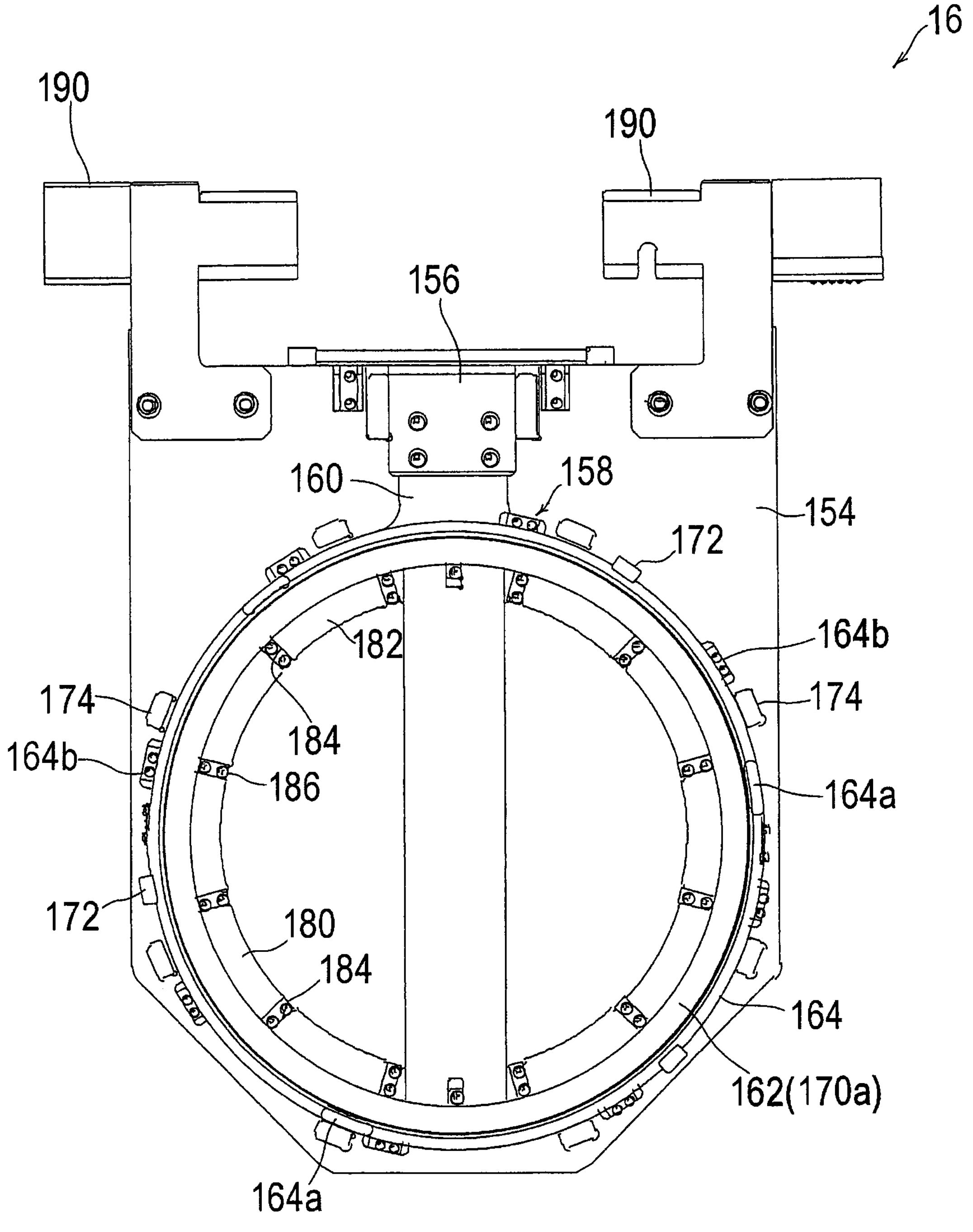

16
190
190
156
160
158
154
172
182
164b
174
174
184
164b
186
164a
172
180
184
164
162(170a)
164a

FIG. 4

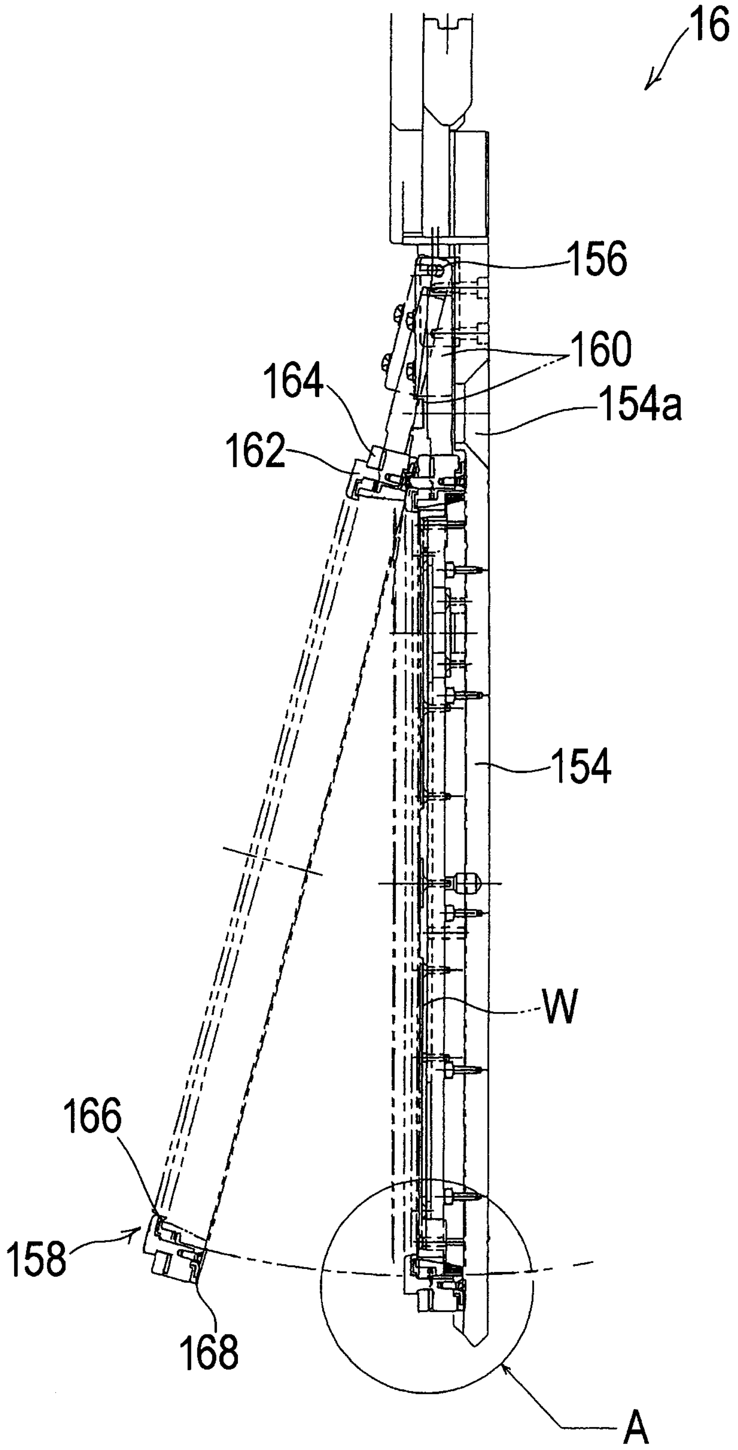


FIG. 5

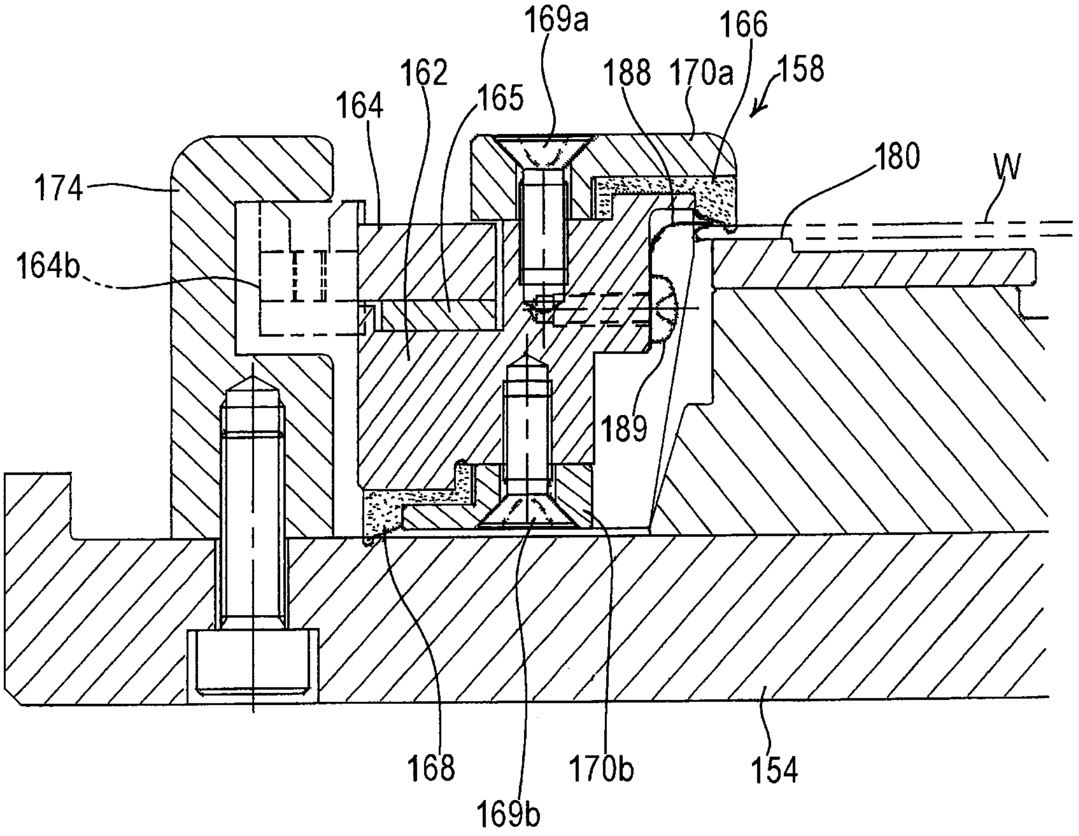

169a
166
162
188
170a
158
164
165
180
W
174
164b
189
168
169b
170b
154

FIG. 6

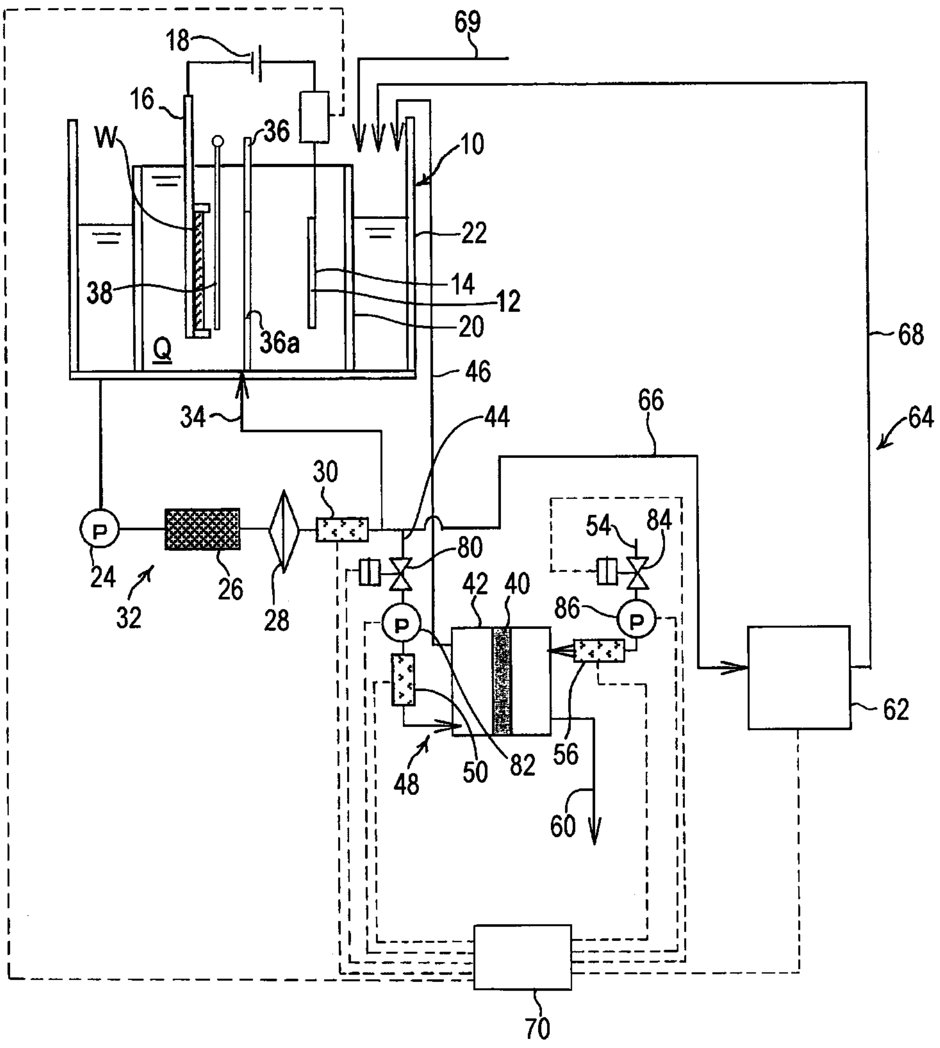

69
18
16
W
36
10
22
14
12
38
36a
20
Q
46
34
44
66
68
64
30
P
24
32
26
28
80
54
84
42
40
86
P
P
62
48
50
82
56
60
70

FIG. 7

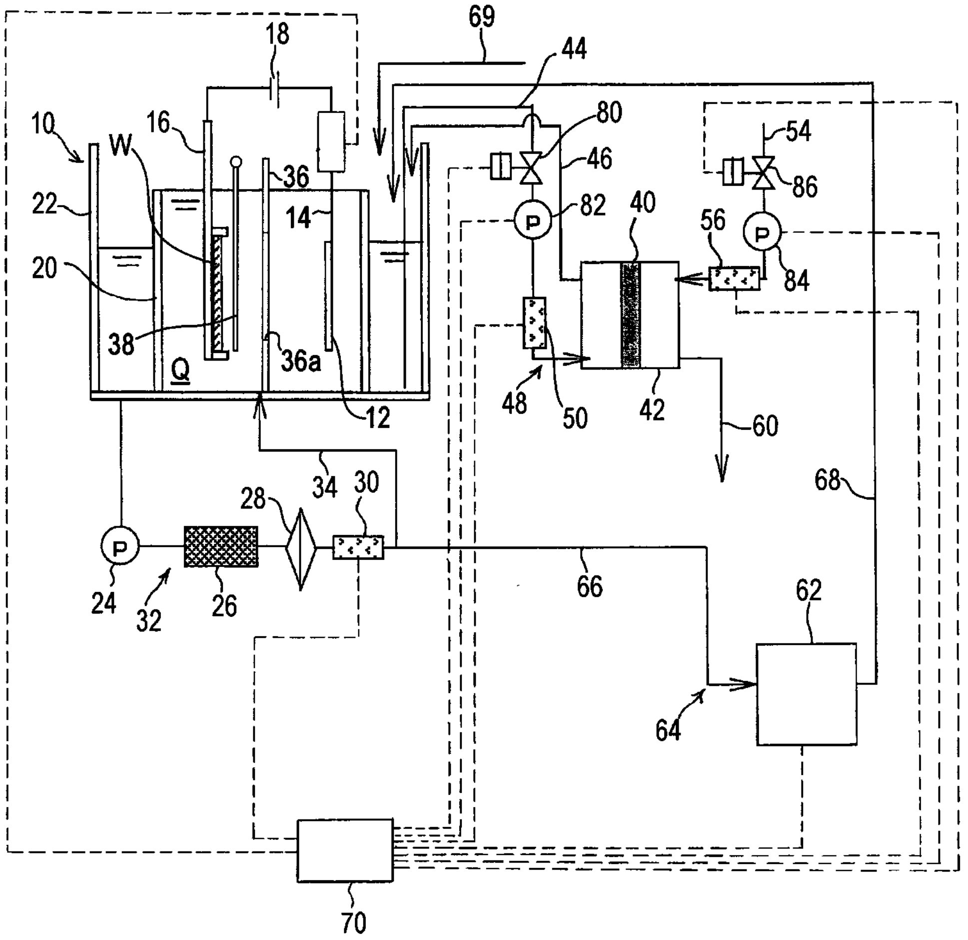

69
18
44
80
10
16
W
54
36
46
86
22
14
82
40
56
84
20
38
36a
Q
12
48
50
42
60
28
34
30
68
24
32
26
66
62
64
70
P
P
P
P

FIG. 8

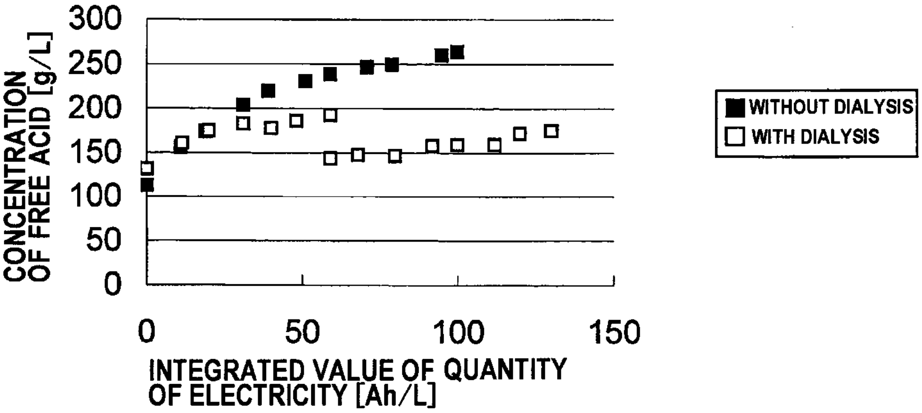

CONCENTRATION OF FREE ACID [g/L]
300
250
200
150
100
50
0
0
50
100
150
INTEGRATED VALUE OF QUANTITY OF ELECTRICITY [Ah/L]
■ WITHOUT DIALYSIS
□ WITH DIALYSIS

FIG. 9

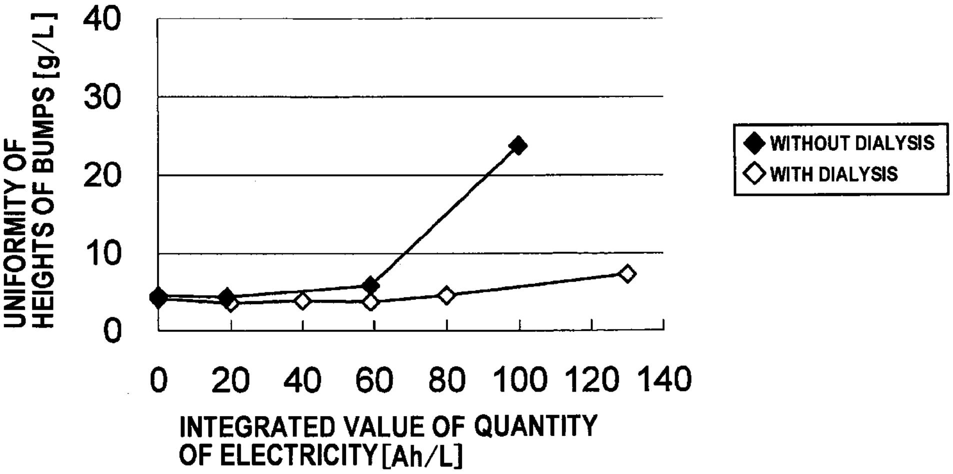

UNIFORMITY OF HEIGHTS OF BUMPS [g/L]
40
30
20
10
0
0
20
40
60
80
100
120
140
INTEGRATED VALUE OF QUANTITY OF ELECTRICITY[Ah/L]
◆ WITHOUT DIALYSIS
◇ WITH DIALYSIS

FIG. 10A

FIG. 10B

FIG. 10C

FIG. 10D

FIG. 10E

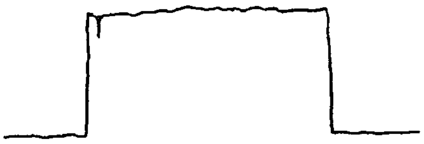


FIG. 10F

FIG. 11A

FIG. 11B

FIG. 11C

FIG. 11D

FIG. 12

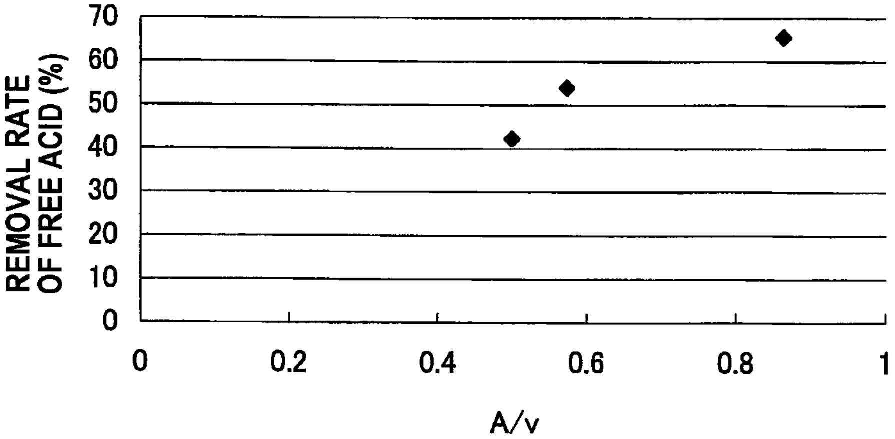

REMOVAL RATE
OF FREE ACID (%)
70
60
50
40
30
20
10
0
0
0.2
0.4
0.6
0.8
1
A/v

FIG. 13

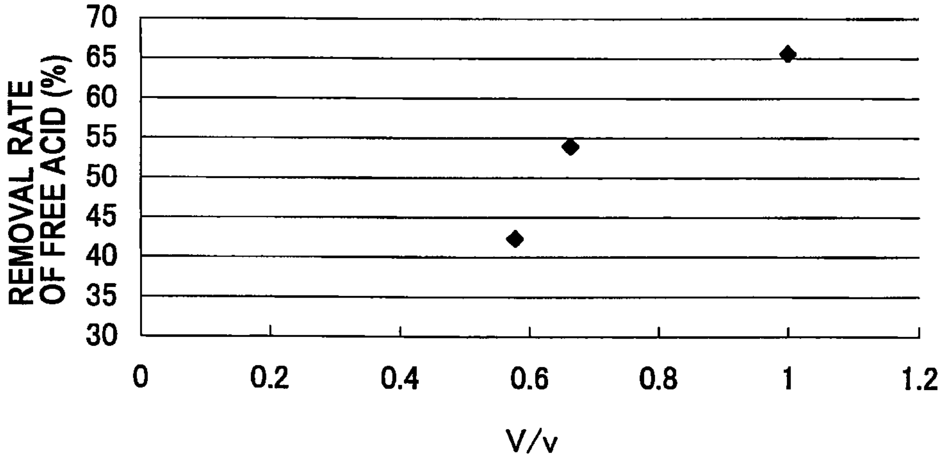
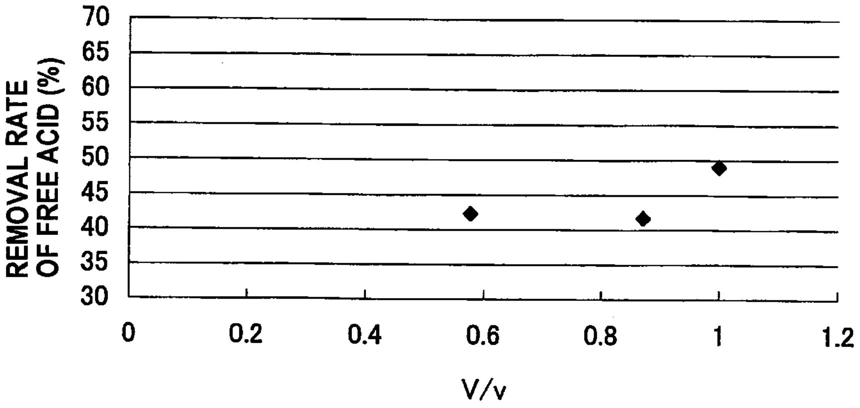

REMOVAL RATE
OF FREE ACID (%)
70
65
60
55
50
45
40
35
30
0
0.2
0.4
0.6
0.8
1
1.2
V/v

FIG. 14


REMOVAL RATE
OF FREE ACID (%)
70
65
60
55
50
45
40
35
30
0
0.2
0.4
0.6
0.8
1
1.2
V/v

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 4698904 B **[0003]**
- JP H1312099 B **[0004]**
- JP S5729600 B **[0005] [0006]**
- JP S5928584 B **[0005]**
- JP H975681 B **[0005]**