An Sn alloy plating apparatus includes: a plating bath having a cathode chamber for holding therein an Sn alloy plating solution in which the substrate is to be immersed and an anode chamber for holding therein an anolyte containing Sn ions and an acid; an Sn anode located in the anode chamber; and an electrolytic solution supply line configured to supply an electrolytic solution containing the acid into the anode chamber such that a Sn ion concentration of the anolyte in the anode chamber is kept not less than a predetermined value and a concentration of the acid in the anolyte is kept not less than a predetermined acceptable value. The electrolytic solution supply line supplies the electrolytic solution into the anode chamber to increase an amount of the anolyte in the anode chamber and supply the anolyte into the Sn alloy plating solution by the increased amount.
FIG. 10
SN ALLOY PLATING APPARATUS AND METHOD

CROSS-REFERENCE TO RELATED APPLICATION


BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention relates to an Sn alloy plating apparatus and method useful for forming a metal film of an alloy of Sn and a metal which is nobler than Sn (e.g., a lead-free Sn—Ag alloy having good soldering properties) on a substrate surface.

[0004] 2. Description of the Related Art

[0005] As is known in the art, a plating film of an alloy of Sn (tin) and a metal which is nobler than Sn (e.g., an Sn—Ag alloy which is an alloy of Sn and silver), formed by electroplating on a substrate surface, can be used for lead-free solder bumps. Sn—Ag alloy plating is typically carried out by applying a voltage between an anode and a substrate surface, which are disposed opposite to each other and immersed in an Sn—Ag alloy plating solution containing Sn ions and Ag ions, thereby forming an Sn—Ag alloy film on the substrate surface. Other than the Sn—Ag alloy, an Sn—Cu alloy which is an alloy of Sn and Cu (copper), an Sn—Bi alloy which is an alloy of Sn and Bi (bismuth), and the like can be used as an alloy of Sn and a metal which is nobler than Sn.

[0006] An insoluble anode is often used in plating of such an alloy of Sn and a metal which is nobler than Sn. This is because, if a soluble anode made of Sn (i.e., Sn anode) is used, displacement deposition of the nobler metal on the surface of the Sn anode will occur, leading to unstable concentration of metal component and contamination of the plating solution.

[0007] Various Sn alloy plating apparatuses and methods using a soluble anode made of Sn (Sn anode) have been proposed. For example, a plating method has been proposed which involves separating an anode chamber, in which an Sn anode is disposed, from a plating bath by using an anion exchange membrane, and putting an Sn plating solution and an acid or a salt thereof into the anode chamber and putting an Sn alloy plating solution into the plating bath (see Japanese Patent No. 4441725). The Sn ion-containing solution in the anode chamber can be supplied through a supply line to the Sn alloy plating solution in the plating bath. A plating method has been proposed which comprises carrying out plating of a plating object in a plating bath by using an Sn anode which is isolated by an anode bag or box formed of a cation exchange membrane (see Japanese Patent No. 3568860).

[0008] Further, an Sn—Ag alloy plating method has been proposed which involves providing a plating bath with an auxiliary cell, having a cathode chamber and an anode chamber which are separated by a diaphragm so that a substance that can cause deterioration of a plating solution will not diffuse into the cathode chamber, and supplying Sn ions to the plating solution (anolyte) in the anode chamber in the auxiliary bath (see Japanese Patent Laid-Open Publication No. H11-21692).

[0009] The abovementioned Japanese Patent No. 4441725 describes the method including the steps of separating an anode chamber and a cathode chamber by an anion exchange membrane, putting an Sn anode into an electrolytic solution (anolyte) containing Sn ions and an acid or a salt thereof, held in the anode chamber, to allow dissolution of Sn ions from the Sn anode into the anolyte, and supplying the Sn ion in the anode chamber to the cathode chamber. In this method, it has been found by the present inventors that it is important to control the acid concentration of the anolyte in the anode chamber in order to achieve stable dissolution of Sn ions into the anolyte in the anode chamber. The method described in this Japanese Patent No. 4441725 necessitates a supply line and a supply device, such as a pump, to supply the Sn ion to the cathode chamber, leading to a complicated construction of the apparatus.

SUMMARY OF THE INVENTION

[0010] The present invention has been made in view of the above situation. It is therefore an object of the present invention to provide an Sn alloy plating apparatus and method which appropriately control a concentration of Sn ions and a concentration of an acid that forms a complex with a divalent Sn ion in an anolyte to be supplied to an Sn alloy plating solution, to thereby enable relatively easy control of the Sn alloy plating solution and simplified construction of the apparatus.

[0011] An Sn alloy plating apparatus for electrodepositing an Sn alloy plating apparatus for electrodepositing an alloy of Sn and a metal which is nobler than Sn on a surface of a substrate is provided. The apparatus comprises: a plating bath whose interior is separated by an anion exchange membrane into a cathode chamber for holding therein an Sn alloy plating solution in which the substrate, serving as a cathode, is to be immersed and an anode chamber for holding therein an anolyte containing Sn ions and an acid that forms a complex with a divalent Sn ion; an Sn anode located in the anode chamber; and an electrolytic solution supply line configured to supply an electrolytic solution containing the acid into the anode chamber such that an Sn ion concentration of the anolyte in the anode chamber is kept not less than a predetermined value and a concentration of the acid in the anolyte is kept not less than a predetermined acceptable value, the electrolytic solution supply line being configured to supply the electrolytic solution into the anode chamber to increase an amount of the anolyte in the anode chamber and supply the anolyte into the Sn alloy plating solution by the increased amount.

[0012] According to the apparatus as described above, the Sn ion concentration of the anolyte and the concentration of the acid that forms a complex with a divalent Sn ion are controlled appropriately, the anolyte, having a high Sn ion concentration and in which divalent Sn ions exist stably, is supplied to the Sn alloy plating solution. Therefore, it is possible to supply Sn ions to the Sn alloy plating solution stably.

[0013] In an embodiment, the electrolytic solution supply line is configured to supply the electrolytic solution into the anode chamber to increase an amount of the anolyte in the anode chamber to thereby cause the anolyte to overflow the anode chamber into the Sn alloy plating solution.

[0014] According to this embodiment, the anolyte, having a high Sn ion concentration and in which divalent Sn ions exist stably, can be supplied to the Sn alloy plating solution without use of any power.

[0015] In an embodiment, the Sn alloy plating apparatus further includes: an overflow bath configured to store the Sn alloy plating solution that has overflowed the cathode cham-
and a plating solution circulation line configured to return the Sn alloy plating solution in the overflow bath to the cathode chamber to thereby circulate the Sn alloy plating solution.

According to this embodiment, the Sn alloy plating solution in the cathode chamber circulates through the plating solution circulation line, so that the plating solution can be agitated.

In an embodiment, the Sn alloy plating apparatus further includes a pure water supply line configured to supply pure water into the anode chamber.

By adjusting the amount of pure water to be supplied through the pure water supply line into the anode chamber or the amount of the electrolytic solution to be supplied through the electrolytic solution supply line into the anode chamber, the concentration of the acid in the anolyte can be controlled in a preferable range.

In an embodiment, the Sn alloy plating apparatus further comprises an acid concentration measuring device for measuring the concentration of the acid in the anolyte in the anode chamber.

In an embodiment, the Sn alloy plating apparatus further comprises a dialysis cell configured to draw out a part of the Sn alloy plating solution from the cathode chamber, remove at least a part of the acid from the Sn alloy plating solution, and then return the Sn alloy plating solution to the cathode chamber.

When the concentration of the acid in the Sn alloy plating solution is too high, at least a part of the acid can be removed from the Sn alloy plating solution by the dialysis cell so as to adjust the acid concentration to a preferable range.

In an embodiment, the Sn alloy plating apparatus further comprises an N₂ gas supply line configured to supply nitrogen gas into the anolyte in the anode chamber to form nitrogen gas bubbles in the anolyte.

According to this embodiment, the anolyte in the anode chamber can be sufficiently agitated with the bubbles of the nitrogen gas, so that Sn ions and the acid can be uniformly distributed in the anolyte. In addition, the bubbles of the nitrogen gas can prevent oxidation of the Sn ions in the anolyte.

In an embodiment, the Sn alloy plating apparatus further comprises an auxiliary electrolytic cell configured to supply an anolyte having an increased concentration of Sn ions to the Sn alloy plating solution. The auxiliary electrolytic cell includes an auxiliary anode chamber for holding an anolyte therein, an auxiliary cathode chamber for holding a catholyte therein, an anion exchange membrane separating the auxiliary anode chamber and the auxiliary cathode chamber from each other, an auxiliary Sn anode located in the auxiliary anode chamber, an auxiliary cathode located in the auxiliary cathode chamber, and an auxiliary power source configured to apply a voltage between the auxiliary Sn anode and the auxiliary cathode when the auxiliary Sn anode is immersed in the anolyte and the auxiliary cathode is immersed in the catholyte to produce the anolyte having the increased concentration of Sn ions.

In the event of a shortage of Sn ions in the entire system, the shortage can be compensated for by the supply of the anolyte, having a high Sn ion concentration, from the auxiliary anode chamber.

An Sn alloy plating method of electrodepositing an alloy of Sn and a metal which is nobler than Sn on a surface of a substrate, the method comprising: providing a plating bath whose interior is separated by an anion exchange membrane into a cathode chamber and an anode chamber; supplying an Sn alloy plating solution into the cathode chamber; immersing the substrate in the Sn alloy plating solution; supplying an anolyte, containing Sn ions and an acid that forms a complex with a divalent Sn ion, into the anode chamber to immerse an Sn anode in the anolyte; supplying an electrolytic solution containing the acid into the anode chamber such that a Sn ion concentration of the anolyte in the anode chamber is kept not less than a predetermined value and a concentration of the acid in the anolyte is kept not less than a predetermined acceptable value; and applying a voltage between the Sn anode and the substrate serving as a cathode to plate the surface of the substrate, while supplying the electrolytic solution into the anode chamber to increase an amount of the anolyte in the anode chamber and supplying the anolyte into the Sn alloy plating solution by the increased amount.

In an embodiment, the supplying the electrolytic solution into the anode chamber to increase an amount of the anolyte in the anode chamber and the supplying the anolyte into the Sn alloy plating solution by the increased amount comprises supplying the electrolytic solution into the anode chamber to increase an amount of the anolyte in the anode chamber to thereby cause the anolyte to overflow the anode chamber into the Sn alloy plating solution.

In an embodiment, the Sn alloy plating method further includes circulating the Sn alloy plating solution in the cathode chamber.

In an embodiment, the Sn alloy plating method further includes controlling an amount of the electrolytic solution or pure water to be supplied into the anode chamber based on the concentration of the acid in the anolyte held in the anode chamber.

In an embodiment, the Sn alloy plating method further includes determining the concentration of the acid in the anolyte from an initial acid concentration of the anolyte, a quantity of electricity and a current efficiency at the Sn anode, an amount of the electrolytic solution supplied, and a permeability of the anion exchange membrane with respect to methanesulfonic acid that passes through the anion exchange membrane and migrates from the cathode chamber into the anode chamber.

In an embodiment, the Sn alloy plating method further includes drawing out a part of the Sn alloy plating solution from the cathode chamber; removing at least a part of the acid from the Sn alloy plating solution that has been drawn out; and then returning the Sn alloy plating solution to the cathode chamber.

In an embodiment, the Sn alloy plating method further includes supplying nitrogen gas into the anolyte in the anode chamber to form nitrogen gas bubbles in the anolyte.

In an embodiment, the Sn alloy plating method further includes immersing an auxiliary Sn anode in an anolyte held in an auxiliary anode chamber; immersing an auxiliary cathode in a catholyte held in an auxiliary cathode chamber that is separated from the auxiliary anode chamber by an anion exchange membrane; applying a voltage between the auxiliary Sn anode and the auxiliary cathode to produce the anolyte having an increased concentration of Sn ions; and supplying the anolyte having the increased concentration of Sn ions into the Sn alloy plating solution.

According to the present invention, the electrolytic solution containing the acid that forms a complex with a divalent Sn ion is supplied into the anode chamber so that the
Sn ion concentration of the anolyte in the anode chamber is kept not less than a predetermined value and the concentration of the acid does not become lower than an acceptable value. The concentration of Sn ions and the concentration of the acid in the anolyte can thus be appropriately controlled. Further, the anolyte, whose amount has been increased by the supply of the electrolytic solution, in the anode chamber is supplied to the Sn alloy plating solution. Thus, the anolyte, having a high Sn ion concentration and in which divalent Sn ions exist stably, is supplied to the Sn alloy plating solution. This makes it possible to stably replenish the Sn alloy plating solution with Sn ions.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic view of an Sn alloy plating apparatus according to an embodiment; FIG. 2 is a perspective view of an exemplary anode bath configured to cause an anolyte to overflow the bath; FIG. 3 is a cross-sectional view of a main portion of another exemplary anode bath configured to cause an anolyte to overflow the bath; FIG. 4 is a perspective view of a main portion of yet another exemplary anode bath configured to cause an anolyte to overflow the bath; FIG. 5 is a schematic perspective view of a substrate holder shown in FIG. 1; FIG. 6 is a plan view of the substrate holder shown in FIG. 1; FIG. 7 is a right side view of the substrate holder shown in FIG. 1; FIG. 8 is an enlarged view of the portion A of FIG. 7; FIG. 9 is a diagram illustrating a main portion of the Sn alloy plating apparatus when performing the plating process; FIG. 10 is a graph showing a theoretical Sn ion concentration of an anolyte in an anode chamber, calculated from a quantity of electricity, in comparison with actually measured Sn ion concentration of the anolyte; FIG. 11 is a schematic view of another example of a plating bath; FIG. 12 is a schematic view of an Sn alloy plating apparatus according to another embodiment; FIG. 13 is a schematic view of an Sn alloy plating apparatus according to yet another embodiment; FIG. 14 is a schematic view of an Sn alloy plating apparatus according to yet another embodiment; and FIG. 15 is a schematic view of an Sn alloy plating apparatus according to yet another embodiment.

DETAILED DESCRIPTION

Embodiments will now be described in detail with reference to the drawings. The same reference numerals are used in the figures and descriptions to refer to the same or like members, components, etc., and duplicate descriptions thereof are omitted.

The following embodiment illustrates an exemplary case where Ag (silver) is used as a metal which is nobler than Sn (tin) and a film of an Sn—Ag alloy is formed on a substrate surface. Methanesulfonic acid is used as an acid that forms a complex with a divalent Sn ion. Thus, an Sn—Ag alloy plating solution is used which contains tin methanesulfonate as a source of Sn ions (Sn²⁺) and silver methanesulfonate as a source of Ag ions (Ag⁺). It is also possible to use silver alkylsulfonate as a source of Ag ions (Ag⁺).

FIG. 1 is a schematic view of an Sn alloy plating apparatus according to an embodiment. As shown in FIG. 1, the Sn alloy plating apparatus includes a plating bath 16 in which a box-shaped anode bath 10 is disposed. The interior of the plating bath 16 is divided by the anode bath 10 into a cathode chamber 12 and an anode chamber 14 which is defined in the anode bath 10.

The cathode chamber 12 is coupled via an overflow bath 36, which will be described later, to a plating solution supply line 20 extending from a plating solution supply source 18. The cathode chamber 12 is configured to hold an Sn—Ag alloy plating solution (hereinafter referred to simply as a plating solution) Q therein. A substrate W, which is detachably held by a substrate holder 22 and serves as a cathode during plating thereof, is put at a predetermined position in the cathode chamber 12 and immersed in the plating solution Q when plating of the substrate W is performed.

An anolyte supply line 23, an electrolytic solution supply line 24, a pure water supply line 26, and a liquid discharge line 28 are coupled to the anode chamber 14. The anode chamber 14 is configured to hold an anolyte E therein. A soluble Sn anode 32, which is made of Sn and held by an anode holder 30, is disposed at a predetermined position in the anode chamber 14 and immersed in the anolyte E. Further, an N₂ gas supply line 33 for supplying nitrogen gas into the anolyte E to form nitrogen gas bubbles in the anolyte E is provided at a bottom of the anode chamber 14.

In this embodiment, a solution, containing Sn ions and methanesulfonic acid that forms a complex with a divalent Sn ion and not containing Ag ions, is used as the anolyte E. A part of methanesulfonate ions in the anolyte E surrounds the divalent Sn ion to form the complex with the Sn ion, while the other part of methanesulfonate ions exists as a free acid in the anolyte E. The methanesulfonic acid concentration herein refers to the concentration of the free acid unless otherwise stated. Because of the absence of Ag ions in the anolyte E, there is no possibility of a reaction between Ag ions and the Sn anode 32, and a consequent displacement deposition of Ag on the surface of the Sn anode 32 does not occur when the Sn anode 32 is immersed in the anolyte E. An aqueous solution containing methanesulfonic acid (i.e., an aqueous methanesulfonic acid solution) is used as the electrolytic solution which is supplied into the anode chamber 14 through the electrolytic solution supply line 24.

When carrying out plating of the substrate W, the Sn anode 32 is electrically connected to a positive pole of a plating power source 34, and a conductive layer (not shown), such as a seed layer, formed on the surface of the substrate W is electrically connected to a negative pole of the plating power source 34. As a result, a metal film of an Sn—Ag alloy is formed on the surface of the conductive layer. This metal film may be used for lead-free solder bump.

The plating bath 16 is provided with the overflow bath 36 which is located adjacent to the cathode chamber 12. The plating solution Q is allowed to overflow the top of the cathode chamber 12 into the overflow bath 36. One end of a plating solution circulation line 46 is coupled to the bottom of the overflow bath 36, and the other end of the plating solution circulation line 46 is coupled to the bottom of the cathode chamber 12. The plating solution circulation line 46 is provided with a pump 38, a heat exchanger (temperature regula-
tor) 40, a filter 42, and a flow meter 44. The plating solution supply line 20 extending from the plating solution supply source 18 is coupled to the top of the overflow bath 36.

[0058] A regulation plate 50 for regulating a distribution of electric potential in the cathode chamber 12 is disposed in the cathode chamber 12. This regulation plate 50 is located between the substrate holder 22, disposed in the cathode chamber 12, and the Sn anode 32. In this embodiment, the regulation plate 50 is made of vinyl chloride, which is a dielectric material, and has a central hole 50a having such a size as to sufficiently restrict spreading of an electric field. A lower end of the regulation plate 50 reaches the bottom plate of the cathode chamber 12.

[0059] A vertically-extending agitating paddle 52 serving as an agitating tool is disposed in the cathode chamber 12 at a position between the substrate holder 22, disposed in the cathode chamber 12, and the regulation plate 50. This agitating paddle 52 is configured to make a reciprocating movement parallel to the substrate W so as to agitate the plating solution Q that exists between the substrate holder 22 and the regulation plate 50. By agitating the plating solution Q with the agitating paddle (agitating tool) 52 during plating, a sufficient amount of metal ions can be supplied uniformly to the surface of the substrate W.

[0060] An anion exchange membrane 54 is incorporated in a cathode-chamber-side wall 10a of the anode bath 10 which divides the interior of the plating bath 16 into the cathode chamber 12 and the anode chamber 14. The cathode chamber 12 and the anode chamber 14 are isolated by the anion exchange membrane 54. A commercially-available product AAV manufactured by AGC Engineering Co., Ltd., for example, can be used as the anion exchange membrane 54. The number of anion exchange membranes 54 and their arrangement may be arbitrarily adjusted depending on the necessary membrane area and an amount of permeation of water molecules, which will be described later. The anion exchange membrane 54 is incorporated into the wall 10a in a liquid-tight manner, e.g., by use of an O-ring so that the plating solution Q in the cathode chamber 12 will not enter the anode chamber 14.

[0061] The wall 10a and the anion exchange membranes 54 are arranged between the Sn anode 32 and the substrate W. The wall 10a functions as an overflow weir which stems the anolyte E in the anode chamber 14 and allows the anolyte E to overflow the top of the wall 10a into the cathode chamber 12. Specifically, the anolyte E is stemmed by the wall (overflow weir) 10a and stored in the anode chamber 14 at a predetermined liquid level H (see FIG. 9). After the liquid level H is reached, the anolyte E overflows the top of the wall 10a into the anode chamber 14.

[0062] A plating solution supply pipe 64 for supplying the plating solution Q to a dialysis cell 62, which has an anion exchange membrane 60 therein, is coupled to the plating solution circulation line 46. This plating solution supply pipe 64 is located downstream of the flow meter 44. A plating solution discharge pipe 66, extending from the dialysis cell 62, is coupled to a top of the overflow bath 36. The plating solution supply pipe 64 and the plating solution discharge pipe 66 constitute a plating solution dialysis line 68 that is coupled to the plating solution circulation line 46 and takes in a part of the plating solution Q from the plating solution circulation line 46 to cause the plating solution Q to circulate therethrough. A pure water supply line 70 for supplying pure water into the dialysis cell 62 and a pure water drainage line 72 for discharging the pure water from the dialysis cell 62 are coupled to the dialysis cell 62.

[0063] The plating solution Q, flowing through the plating solution dialysis line 68, is supplied into the dialysis cell 62, where at least a part of the methanesulfonic acid as a free acid is removed by dialysis using the anion exchange membrane 60. The plating solution Q after dialysis is returned to the overflow bath 36. The methanesulfonic acid that has been removed from the plating solution Q by the dialysis diffuses into the pure water supplied into the dialysis cell 62 through the pure water supply line 70, and is discharged to the exterior of the dialysis cell 62 through the pure water drainage line 72.

[0064] The anion exchange membrane 60 used in this embodiment is DSV manufactured by AGC Engineering Co., Ltd. An arbitrary number of anion exchange membranes 60 may be incorporated in the dialysis cell 62 depending on the amount of the plating solution to be dialyzed (i.e., the amount of the methanesulfonic acid to be removed).

[0065] In this embodiment, at least a part of the methanesulfonic acid as a free acid in the plating solution Q is removed by using the dialysis cell 62 that employs the diffusion dialysis. It is also possible to remove at least a part of the methanesulfonic acid from the plating solution Q by using a free-acid removal cell that employs electrodialysis or an ion-exchange resin method.

[0066] The plating solution circulation line 46 is provided with an Sn ion concentration measuring device 74 for measuring the Sn ion concentration of the plating solution Q flowing through the plating solution circulation line 46. The plating solution circulation line 46 is further provided with a methanesulfonic acid concentration measuring device 76 for measuring the methanesulfonic acid concentration of the plating solution Q flowing through the plating solution circulation line 46. The output of the Sn ion concentration measuring device 74 and the output of the methanesulfonic acid concentration measuring device 76 (i.e., concentration measurement values) are inputted into the plating solution supply source 18 and a controller 80.

[0067] FIG. 2 is a perspective view of the anode bath 10. As shown in FIG. 2, in an off-centered position at the top of the wall 10a of the anode bath 10 that functions as the overflow weir, there is provided a cutout portion 10b which serves as an outlet for allowing the anolyte E to overflow the anode chamber 14. The liquid level H (see FIG. 9) of the anolyte E held in the anode chamber 14 is determined by the position of a lower end of the cutout portion 10b.

[0068] The electrolytic solution supply line 24 extends downward along the side of the anode bath 10. The electrolytic solution supply line 24 has at its lower end an electrolytic solution supply outlet 24a for supplying the electrolytic solution (aqueous methanesulfonic acid solution) into the anode chamber 14. This electrolytic solution supply outlet 24a reaches the bottom of the anode bath 10 and opens in a horizontal direction. Similarly, the pure water supply line 26 extends downward along the side of the anode bath 10. The pure water supply line 26 has at its lower end a pure water supply outlet 26a for supplying pure water into the anode chamber 14. This pure water supply outlet 26a reaches the bottom of the anode bath 10 and opens in a horizontal direction. The electrolytic solution supply outlet 24a and the pure water supply outlet 26a may open in a downward direction.

[0069] When the anode bath 10 is projected onto a horizontal plane, the electrolytic solution supply outlet 24a and the pure water supply outlet 26a are diagonally opposite to the
cutout portion 10b of the wall 10a so that when the pure water or the electrolytic solution is supplied into the anode chamber 14 through the pure water supply line 26 or the electrolytic solution supply line 24, the anolyte E containing Sn ions is agitated sufficiently by the supplied pure water or electrolytic solution and then overflows the cutout portion 10b into the cathode chamber 12.

[0070] The N₂ gas supply line 33 extends downward along the side of the anode bath 10 to reach the bottom of the anode bath 10, and further extends horizontally over approximately the entire length of the anode bath 10 in its longitudinal direction. Nitrogen gas is released or ejected upward through jet orifices 33a, which are provided in the N₂ gas supply line 33, to cause the anolyte E to bubble, thereby sufficiently agitating the anolyte E in the anode chamber 14. The bubbles of the nitrogen gas can promote uniform distribution of the Sn ions and the methanesulfonic acid throughout the anolyte E in the anode chamber 14 and, in addition, can prevent oxidation of the Sn ions in the anolyte E. In view of this, the nitrogen gas is preferably supplied into the anolyte E at the bottom of the anode chamber 14 to cause the bubbling of the anolyte E from the bottom of the anode chamber 14.

[0071] It is preferred to stop the supply of the nitrogen gas immediately before the pure water or the electrolytic solution is supplied into the anode chamber 14 so as not to carry out the bubbling of the anolyte E with the nitrogen gas during the supply of the pure water or the electrolytic solution. This enables the anolyte E containing Sn ions in a sufficiently dispersed state, to overflow the wall 10a into the cathode chamber 12 while preventing the anolyte E from being excessively diluted with the pure water or the electrolytic solution supplied.

[0072] In order to detect a decrease in the amount of the anolyte E in the anode chamber 14 due to its evaporation, a liquid level detection sensor 82 for detecting the liquid level of the anolyte E in the anode chamber 14 is provided above the anode chamber 14. Upon detection of the decrease in the amount of the anolyte E due to its evaporation, the pure water may be supplied into the anolyte E in the anode chamber 14 through the pure water supply line 26. This makes it possible to keep the anolyte E in the anode chamber 14 at a constant liquid level. Further, it is possible to control the amount of Sn ions to be supplied to the cathode chamber 12 with the amount of the anolyte E to be supplied into the anode chamber 14.

[0073] A mechanical structure may be used to cause the anolyte E in the anode chamber 14 to overflow into the cathode chamber 12. For example, as shown in FIG. 3, a float 84 may be put on the anolyte E in the anode chamber 14 and may be submerged into the anolyte E so as to cause the anolyte E to overflow into the cathode chamber 12 with an amount corresponding to a volume of the float 84. This structure involves no supply of pure water or the electrolytic solution, and thus no introduction of water into the anolyte E. Therefore, the anolyte E can be supplied into the cathode chamber 12 without dilution of the anolyte E.

[0074] As shown in FIG. 4, a vertically movable weir 86 may be provided in a rectangular cutout portion 10c that is formed in the top of the wall 10a that serves as the overflow weir. In this example shown in FIG. 4, the anolyte E can be supplied into the cathode chamber 12 by lowering the movable weir 86. This structure also has the advantage of no dilution of the anolyte E when supplied into the cathode chamber 12.

[0075] In the event of a shortage of Sn ions in the entire system, it is necessary to replenish the plating solution Q with Sn ions. A conceivable Sn ion replenishing method is to supply an Sn replenishing solution having a high Sn ion concentration to the plating solution Q. However, such a high-concentration Sn replenishing solution is generally expensive, and therefore incurs high costs. Thus, in this embodiment, an auxiliary electrolytic cell 100 for replenishment of the Sn ions is provided separately from the plating bath 16.

[0076] A box-shaped cathode bath 102 is disposed in the auxiliary electrolytic cell 100, whereby the interior of the auxiliary electrolytic cell 100 is divided into an anode chamber (i.e., auxiliary anode chamber) 104 and a cathode chamber (i.e., auxiliary cathode chamber) 106 defined in the cathode bath 102. An anion exchange membrane 108 is incorporated in an anode-chamber-side wall 102a of the cathode bath 102 which divides the interior of the auxiliary electrolytic cell 100 into the anode chamber 104 and the cathode chamber 106. The anode chamber 104 and the cathode chamber 106 are isolated by the anion exchange membrane 108.

[0077] An anolyte supply line 110 for supplying an anolyte A containing Sn ions and methanesulfonic acid and not containing Ag ions, and an electrolytic solution supply line 112 for supplying an electrolytic solution comprising an aqueous solution containing methanesulfonic acid (i.e., aqueous methanesulfonic acid solution) are coupled to the anode chamber 104. An Sn anode (i.e., auxiliary Sn anode) 118 which is held by an anode holder 116, is disposed in the anode chamber 104 and immersed in the anolyte A. One end of the Sn ion replenishing line 114 is coupled to the anode chamber 104, and the other end of the Sn ion replenishing line 114 is coupled to the top of the overflow bath 36 of the plating bath 16. The Sn ion replenishing line 114 is provided with a pump 120.

[0078] A catholyte supply line 122 for supplying a catholyte B comprising an aqueous solution containing methanesulfonic acid (i.e., aqueous methanesulfonic acid solution), and a liquid discharge line 124 for discharging the catholyte B are coupled to the cathode chamber 106. A cathode (i.e., an auxiliary cathode) 128, which is made of, e.g. SUS and held by a cathode holder 126, is disposed in the cathode chamber 106 and immersed in the catholyte B. The above-described wall 102a and the anion exchange membrane 108 are located between the Sn anode 118 and the cathode 128.

[0079] In operation of the auxiliary electrolytic cell 100, the anolyte A, containing Sn ions at a high concentration (e.g., 220 g/L to 350 g/L) and methanesulfonic acid and not containing Ag ions, is supplied into the anode chamber 104 through the anolyte supply line 110, thereby immersing the Sn anode 118 in the anolyte A. The catholyte B containing an aqueous methanesulfonic acid solution is supplied into the cathode chamber 106 through the catholyte supply line 122, thereby immersing the cathode 128 in the catholyte B.

[0080] In this state, a positive pole and a negative pole of an auxiliary power source 130 are electrically connected to the Sn anode 118 and the cathode 128, respectively, to start electrolysis. Once the electrolysis is started, the Sn ion concentration of the anolyte A increases as a result of the dissolution of Sn ions from the Sn anode 118. Because the anode chamber 104 and the cathode chamber 106 are isolated by the anion exchange membrane 108, the Sn ions do not migrate into the cathode chamber 106 and therefore the cathode 128 is not plated. Because the anolyte A does not contain Ag ions,
displacement deposition of Ag on the surface of the Sn anode 118 does not occur. The Sn ions in the anolyte A are supplied through the anolyte supply line 110 before the start of electrolysis, while the Sn ions are supplied by the dissolution from the Sn anode 118 after the start of electrolysis.

[0081] After a predetermined Sn ion concentration is reached in the anolyte A, the pump 120 is driven to supply the anolyte A into the overflow bath 36 of the plating bath 16 through the Sn ion replenishing line 114. The amount of the anolyte A in the anode chamber 104 decreases as a result of the supply of the anolyte A to the overflow bath 36. Thus, the electrolytic solution, in an amount that compensates for the decrease in the amount of the anolyte A, is supplied into the anode chamber 104 through the electrolytic solution supply line 112. The Sn ion concentration of the anolyte A is preferably as high as possible from the viewpoint of decreasing the amount of waste liquid discharged from the entire system.

[0082] Methanesulphonate ions contained in the catholyte B in the cathode chamber 106 pass through the anion exchange membrane 108 and migrate into the anode chamber 104. Accordingly, the conductivity of the catholyte B in the cathode chamber 106 decreases with time. Therefore, a fresh catholyte B is supplied into the cathode chamber 106 through the catholyte supply line 122, while discharging the catholyte B from the cathode chamber 106 to the exterior through the liquid discharge line 124 so that the catholyte B does not overflow.

[0083] As shown in FIGS. 5 through 8, the substrate holder 22 includes a first holding member 154 having a rectangular plate shape and made of e.g., vinyl chloride, and a second 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.

[0084] 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. An annular substrate-side sealing member 166 (see FIGS. 7 and 8) 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 22. An annular holder-side sealing member 168 (see FIGS. 7 and 8) 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.

[0085] As shown in FIG. 8, 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.

[0086] 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 through a spacer 165. The retaining ring 164 is inescapably held by an outwardly projecting retaining plates 172 (see FIG. 6) 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.

[0087] Inverted L-shaped clamps 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 164a arranged along the circumferential direction of the retaining ring 164 at positions corresponding to positions of the dampers 174. A lower surface of the inwardly projecting portion of each damper 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 164a from a lateral direction by means of a rotating pin (not shown).

[0088] 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 164a of the retaining ring 164 slides into the inwardly projecting portion of each damper 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 dampers 174. The lock of the second holding member 158 can be released by rotating the retaining ring 164 counterclockwise and to disengage the projecting portions 164a of the retaining ring 164 from the inverted L-shaped dampers 174.

[0089] When the second holding member 158 is locked in the above-described manner, the 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. The substrate-side sealing member 166 is placed in pressure contact with the periphery of the surface of the substrate W and the second holding member 158. Similarly, when the second holding member 158 is locked, the downwardly-protruding portion of the holder-side sealing member 168 is placed in pressure contact with the surface of the first holding member 154. The sealing holder-side sealing member 168 is uniformly pressed against the first holding member 154 to thereby seal the gap between the first holding member 154 and the second holding member 158.

[0090] A pair of T-shaped holder hangers 190 are provided on end portions of the first holding member 154. These holder hangers 190 serve as a support when the substrate holder 22 is transported and when the substrate holder 22 is held in a
suspended state. A protruding portion 182 is formed on the upper surface 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 an annular 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.

[0091] As shown in FIG. 6, a plurality of electrical conductors (electrical contacts) 186 (e.g., 12 conductors as illustrated), coupled respectively to wires extending from external contacts (not shown) provided in the holder hanger 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, end portions of the electrical conductors 186 resiliently contact the lower portions of the electrical contacts 188 shown in FIG. 8.

[0092] The electrical contacts 188, which are 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 support of the substrate W supported on the support surface 180 of the first holding member 154.

[0093] 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 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.

[0094] Next, operations of the plating apparatus according to the embodiment will be described. The pump 38 is set in motion to circulate the plating solution Q in the cathode chamber 12 through the plating solution circulation line 46 to thereby agitate the plating solution Q. In this state, the substrate W, held by the substrate holder 22, is put at the predetermined position in the cathode chamber 12 and immersed in the plating solution Q. The anode chamber 14 is filled with the initial anolyte E so that the Sn anode 32 is immersed in the anolyte E.

[0095] In this state, the Sn anode 32 is electrically connected to the positive pole of the plating power source 34, and a conductive layer, such as a seed layer, formed on the surface of the substrate W is electrically connected to the negative pole of the plating power source 34 to start plating of the surface of the substrate W. During the plating, the agitating paddle (agitating tool) 52 reciprocates or oscillates parallel to the substrate W, as necessary, to agitate the plating solution Q in the cathode chamber 12. At the same time, the nitrogen gas is supplied into the anolyte E through the N2 gas supply line 33 to form the bubbles of the nitrogen gas in the anolyte E in the anode chamber 14.

[0096] During the plating, Sn ions dissolve from the Sn anode 32 into the anolyte E in the anode chamber 14 as shown in FIG. 9. The dissolution of the Sn ions occurs every time a plating of a substrate is performed, and therefore the Sn ion concentration of the anolyte E in the anode chamber 14 increases. Further, the volume of the anolyte E in the anode chamber 14 increases when the electrolytic solution or the pure water is supplied into the anode chamber 14 from the electrolytic solution supply line 24 or the pure water supply line 26. When the liquid level of the anolyte E in the anode chamber 14 rises over the predetermined liquid level H by ΔH, the anolyte E overflows the cutout portion 106 (see FIG. 2) formed in the wall 10a of the anode chamber 14 and flows into the cathode chamber 12 by an amount corresponding to the increase ΔH in the liquid level. Therefore, some of the Sn ions in the anode chamber 14 are supplied into the cathode chamber 12, and can compensate for the shortage of the Sn ions that have been consumed in plating of the substrate W. In view of the increase in the amount of the plating solution Q when the anolyte E is supplied to the plating solution Q, the plating solution Q is discharged in advance by an amount corresponding to the amount of the anolyte E supplied into the cathode chamber 12.

[0097] When an electric field is formed between the Sn anode 32 and the substrate W as a cathode, the methanesulfonic acid in the cathode chamber 12, together with water molecules, passes through the anion exchange membrane 54 into the anode chamber 14. This migration also increases the amount of the anolyte E in the anode chamber 14, and as a result the anolyte E overflows the wall 10a into the cathode chamber 12 by an amount exceeding the predetermined liquid level H. In this manner, the Sn ions in the anode chamber 14 can be supplied into the cathode chamber 12.

[0098] The present inventors have verified through experiments the fact that the concentration of methanesulfonic acid as a free acid in the anolyte E in the anode chamber 14 is important for stabilizing the Sn ions that have dissolved from the Sn anode. In particular, an experiment was conducted in which an anolyte of an aqueous methanesulfonic acid solution, initially having a methanesulfonic acid concentration of 100 g/L, was supplied in an anode chamber at the start of electrolysis. In this case, the anolyte in the anode chamber was found to become cloudy as the electrolysis was continued. This indicates that Sn ions cannot exist stably as divalent ions in the anolyte, and precipitate as metal Sn or tetravalent Sn ions are generated.

[0099] In contrast, in an experiment in which the electrolysis was started with an initial methanesulfonic acid concentration of 140 g/L, the anolyte in the anode chamber did not become cloudy during the electrolysis. Moreover, the Sn ion concentration of the anolyte agreed with a calculation value that was determined on condition that Sn has dissolved as divalent Sn ions. This indicates that because of the presence of a sufficient amount of methanesulfonate ions in the anolyte, divalent Sn ions exist stably in the form of a complex surrounded by methanesulfonate ions. As will be appreciated from the foregoing, the methanesulfonic acid concentration of the anolyte should preferably be controlled in such a range as to allow the divalent Sn ions to exist stably in the anolyte.

[0100] As described above, by supplying the pure water into the anode chamber 14 through the pure water supply line 26, the anolyte E in the anode chamber 14 can overflow into the cathode chamber 12 to supply Sn ions to the cathode chamber 12. The plating apparatus of this embodiment is also
provides the electrolytic solution supply line 24 for supplying the electrolytic solution (the aqueous methanesulfonic acid solution) into the anode chamber 14. This is because of the following reasons.

[0101] When the pure water is supplied into the anode chamber 14 through the pure water supply line 26 to cause the anolyte E in the anode chamber 14 to overflow into the cathode chamber 12, the methanesulfonic acid in the anolyte 14 flows into the cathode chamber 12, and therefore the methanesulfonic acid concentration of the anolyte E in the anode chamber 14 decreases. The methanesulfonic acid in the cathode chamber 12 passes through the anion exchange membrane 54 and migrates into the anode chamber 14 by forming an electric field between the Sn anode 32 and the substrate W as a cathode. The transference number of methanesulfonic acid is not 100%, but can be 50% to 90% due to a loss, although it depends on conditions. Thus, a ratio of the mol concentration of the methanesulfonic acid that passes through the anion exchange membrane 54 into the anode chamber 14 to the mol concentration of Sn ions that dissolve from the Sn anode 32 into the anolyte E in the anode chamber 14 will deviate from 1:2. Consequently, the methanesulfonic acid concentration of the anolyte E in the anode chamber 14 will decrease, whereby Sn ions in the anode chamber 14 may become unstable as described above.

[0102] It is therefore necessary to supply the electrolytic solution containing the methanesulfonic acid into the anode chamber 14 through the electrolytic solution supply line 24 so that the methanesulfonic acid concentration of the anolyte E in the anode chamber 14 is not lowered below an acceptable value.

[0103] In order to operate the plating apparatus efficiently, it is desirable to supply the anolyte E into the cathode chamber 12 by causing the anolyte E to overflow the anode chamber 14 while keeping the Sn ion concentration of the anolyte E in the anode chamber 14 as high as possible. If the anolyte E with a low Sn ion concentration is supplied into the cathode chamber 12, a larger amount (overflow amount) of the anolyte E needs to be supplied from the anode chamber 14 in order to supply a certain amount of Sn ions into the cathode chamber 12. As a result, a larger amount of the plating solution Q should be discharged from the circulation system including the cathode chamber 12, making the plating process uneconomical.

[0104] Specifically, the Sn ion concentration of the anolyte E in the anode chamber 14 is controlled typically in the range of 80 g/L to 500 g/L, preferably in the range of 200 g/L to 400 g/L, more preferably in the range of 220 g/L to 350 g/L. The Sn ion concentration of the anolyte E can be determined from the Sn ion concentration of a fresh anolyte E which has been put into the anode chamber 14 before the start of plating and the Sn ion concentration converted from the quantity of electricity at the Sn anode 32 after the start of plating. The Sn ion concentration of the anolyte E is of significant importance for controlling the concentration of Sn ions in the entire plating bath. The Sn ion concentration of the Sn—Ag plating solution Q is usually 50 g/L to 80 g/L. When the decrease in the Sn ion concentration of the plating solution Q in the cathode chamber 12 is to be compensated by the supply of the anolyte E containing the Sn ion in the anode chamber 14, the use of the anolyte E with a higher Sn ion concentration can reduce its volume to be supplied into the cathode chamber 12. The amount of the plating solution Q in the cathode chamber 12 usually decreases due to evaporation of the solution, etc.

When the anolyte E in the anode chamber 14 is supplied to the plating solution Q in the cathode chamber 12 in an amount more than the decrease in the amount of the plating solution Q, the excess amount of the plating solution Q needs to be finally discharged from the cathode chamber 12. However, the Sn ion concentration of the anolyte E cannot be increased to a value more than a saturation concentration of tin methanesulfonate. Further, the Sn ion concentration of the anolyte E should be kept less than the saturation concentration in order for the Sn ions to exist stably.

[0105] The pure water supply line 26 is used not only for supplying the pure water into the anode chamber 14 when replenishing the anode chamber 14 with water by an amount corresponding to the amount of evaporated water, but also for causing the anolyte E in the anode chamber 14 to overflow the wall 10a so as to supply the Sn ions to the cathode chamber 12 when the methanesulfonic acid concentration of the anolyte E in the anode chamber 14 is sufficiently high. Further, the pure water supply line 26 is used for supplying the pure water into the anode chamber 14 so as to adjust the concentration of a component of the anolyte E in the anode chamber 14.

[0106] An exemplary operation of the Sn alloy plating apparatus shown in FIG. 1 will now be described.

[0107] Before starting the operation of the Sn alloy plating apparatus, the anolyte E, containing Sn ions at a high concentration (e.g., 220 g/L to 350 g/L) and methanesulfonic acid, is supplied into the anode chamber 14 to fill the anode chamber 14 with the anolyte E. As described above, it is preferable to supply the anolyte E at a high Sn ion concentration in the anode chamber 14 into the cathode chamber 12 because the amount of the plating solution Q to be discharged as waste can be reduced. If the operation of the apparatus is started with the anolyte E at a low Sn concentration, it is necessary to wait to supply the anolyte E into the cathode chamber 12 until a high Sn ion concentration of the anolyte E is reached.

[0108] The pump 38 is actuated to circulate the plating solution Q in the cathode chamber 12 through the plating solution circulation line 46, thereby agitating the plating solution Q in the cathode chamber 12. In this state, a substrate W, which is held by the substrate holder 22, is put at a predetermined position in the cathode chamber 12 and immersed in the plating solution Q.

[0109] The Sn anode 32 is electrically connected to the positive pole of the plating power source 34, and a conductive layer, such as a seed layer, formed on the surface of the substrate W is electrically connected to the negative pole of the plating power source 34 to start plating of the surface of the substrate W. During the plating, the agitating paddle (agitating tool) 52 is caused to make a reciprocating movement parallel to the substrate W, as necessary, so as to agitate the plating solution Q in the cathode chamber 12. At the same time, the nitrogen gas is supplied into the anolyte E in the anode chamber 14 through the N2 gas supply line 33 to form nitrogen gas bubbles in the anolyte E.

[0110] While the plating of the substrate W is performed in this manner, the Sn ion concentration of the plating solution Q is measured by the Sn ion concentration measuring device 74, and a signal of the measurement results (i.e., a measurement value) is sent to the controller 80. In this embodiment, the controller 80 estimates the methanesulfonic acid concentration of the anolyte E in the anode chamber 14 and, based on the estimated value, determines whether to supply the electrolytic solution into the anode chamber 14 through the electrolytic solution supply line 24 or to supply the pure water into
the anode chamber 14 through the pure water supply line 26, or to supply both the electrolytic solution and the pure water. Specifically, when the concentration of methanesulfonic acid as a free acid in the anolyte E has been reduced below a predetermined value, the electrolytic solution, containing the methanesulfonic acid, is supplied into the anode chamber 14 through the electrolytic solution supply line 24 so that the methanesulfonic acid concentration of the anolyte E does not become lower than a lower limit value. When replenishing the plating solution Q in the cathode chamber 12 with Sn ions through the supply of the anolyte E having a sufficiently high methanesulfonic acid concentration, the pure water is supplied into the anode chamber 14 through the pure water supply line 26. The supply of the pure water into the anode chamber 14 causes the anolyte E to overflow into the cathode chamber 12, thereby supplying Sn ions to the plating solution Q in the cathode chamber 12.

[0111] The concentration of methanesulfonic acid as a free acid contained in the anolyte E in the anode chamber 14 is controlled to be not less than 30 g/L, so that the Sn ions at a high concentration, e.g., 220 g/L to 350 g/L, can exist stably as divalent ions. When the methanesulfonic acid concentration of the anolyte E is high, the supply of the anolyte E to the plating solution Q can appreciably increase the methanesulfonic acid concentration of the plating solution Q in the cathode chamber 12, which may result in poor film-thickness uniformity in the plating process as will be described later. Therefore, the methanesulfonic acid concentration of the plating solution Q is controlled so as not to exceed a particular value which is determined by taking the actual operating conditions of the apparatus into consideration.

[0112] The concentration of methanesulfonic acid as a free acid in the plating solution Q in the cathode chamber 12 varies with the quantity of electricity and the current efficiency at the Sn anode 32, the amount of the anolyte E that has overflowed into the plating solution Q, the amount of waste liquid (drain-out) discharged from the plating solution circulation line 46, and the permeability of the anion exchange membrane 54 with respect to the methanesulfonic acid. The film-thickness uniformity in plating of the substrate tends to be poor when the methanesulfonic acid concentration of the plating solution Q in the cathode chamber 12 exceeds about 250 g/L. Therefore, when the methanesulfonic acid concentration measuring device 76 detects that the methanesulfonic acid concentration of the plating solution Q in the cathode chamber 12 exceeds an upper limit value, the plating solution Q is forced to flow into the plating solution dialysis line 68 having the dialysis cell 62, which removes the methanesulfonic acid from the plating solution Q. The plating solution Q, from which the methanesulfonic acid has been removed, is returned to the overflow bath 36. The dialysis of the plating solution Q in the dialysis cell 62 can adjust the methanesulfonic acid concentration of the plating solution Q preferably in the range of 60 g/L to 250 g/L, more preferably in the range of 90 g/L to 150 g/L.

[0113] The concentration of the methanesulfonic acid as a free acid in the anolyte E during operation of the Sn alloy plating apparatus may be controlled based on an estimated value of the methanesulfonic acid concentration of the anolyte E in the anode chamber 14. This estimated value of the methanesulfonic acid concentration can be determined theoretically or experimentally from an initial methanesulfonic acid concentration of the anolyte E, the quantity of electricity and the current efficiency at the Sn anode 32, the amount of the electrolytic solution supplied through the electrolytic solution supply line 24, the amount of pure water supplied through the pure water supply line 26, and the permeability of the anion exchange membrane 54 with respect to the methanesulfonic acid that passes through the anion exchange membrane 54 and migrates from the cathode chamber 12 into the anode chamber 14. The Sn ion concentration and the methanesulfonic acid concentration of the anolyte E in the anode chamber 14 can be estimated from a curve of the amount of dissolved Sn ions associated with the quantity of electricity during plating and from the permeability of the anion exchange membrane with respect to the acid.

[0114] As described above, before starting the operation of the Sn alloy plating apparatus, the anolyte E, containing Sn ions at a high concentration (e.g., 220 g/L to 350 g/L) and methanesulfonic acid, is supplied into the anode chamber 14. When the Sn ion concentration of the anolyte E in the anode chamber 14, as estimated e.g., from the quantity of electricity at the Sn anode and the efficiency of electrolysis, reaches a predetermined threshold value (e.g., 300 g/L) during operation of the Sn alloy plating apparatus, the electrolytic solution is supplied into the anode chamber 14 through the electrolytic solution supply line 24 to cause the anolyte E to overflow the wall 10a, thereby replenishing the plating solution Q in the cathode chamber 12 with Sn ions.

[0115] Although the Sn ion concentration of the anolyte E in the anode chamber 14 decreases as a result of the supply of the electrolytic solution, the Sn ion concentration increases gradually during plating and eventually reaches the threshold value. During this plating process, Sn ions in the plating solution Q are consumed in plating of the substrate W. Assuming that the efficiency of electrolysis at the substrate W is equal to the efficiency of electrolysis at the Sn anode 32 and that no Sn ions are discharged out of the system, Sn ions will dissolve from the Sn anode 32 in an amount equal to the amount of Sn ions consumed in plating of the substrate W. Thus, the amount of Sn ions in the entire system is kept constant. In fact, however, the efficiency of electrolysis decreases with the increase in the Sn ion concentration of the anolyte E in the anode chamber 14. Accordingly, the amount of Sn ions that are supplied to the anolyte E by the dissolution from the Sn anode 32 becomes smaller than the amount of Sn ions consumed in plating, resulting in a shortage of Sn ions in the entire system.

[0116] FIG. 10 is a graph showing the theoretical Sn ion concentration of the anolyte E in the anode chamber 14, calculated from the quantity of electricity, in comparison with the actually measured Sn ion concentration of the anolyte E. As can be seen in FIG. 10, while the efficiency of electrolysis is approximately 100% when the Sn ion concentration of the anolyte E in the anode chamber 14 is not more than about 130 g/L, the electrolysis efficiency decreases when the Sn ion concentration is more than about 150 g/L, and the electrolysis efficiency decreases to about 80% at an Sn ion concentration of 300 g/L. The data shown in FIG. 10 thus indicates that when it is intended to control the Sn ion concentration of the anolyte E at a high level as 220 g/L to 350 g/L, 10% to 20% of Sn ions will be in short supply in the entire system. It is also noted that since the anolyte E in the anode chamber 14 overflows into the cathode chamber 12, the plating solution Q containing the Sn ions in the cathode chamber 12 or the overflow bath 36 is discharged in advance, resulting in the shortage of the amount of Sn ions in the entire system.
Thus, the Sn alloy plating apparatus of this embodiment includes the auxiliary electrolytic cell 100 for compensating for the shortage of the Sn ions in the entire system. The electrolysis operation of the auxiliary electrolytic cell 100 is started simultaneously with the start of operation of the Sn alloy plating apparatus or at an appropriate time. The pump 120 is driven based on the concentration of Sn ions measured by the Sn ion concentration measuring device 74 to thereby supply the anolyte A having a high Sn ion concentration in the anode chamber 104 to the overflow bath 36 of the plating bath 16. The supply of Sn ions from the auxiliary electrolytic cell 100 can compensate for the shortage of Sn ions caused by the difference between the electrolytic efficiency of plating on the substrate W and the efficiency of electrolysis at the Sn anode 32 in the anode chamber 14 and by the discharge of the plating solution Q from the plating bath 16.

When the Sn alloy plating apparatus is operated over a long period of time, the Sn ion concentration and the methanesulfonic acid concentration of the anolyte E in the anode chamber 14 may deviate from the estimated concentrations. Therefore, the Sn concentration and the methanesulfonic acid concentration of the plating solution Q are measured by the Sn ion concentration measuring device 74 and the methanesulfonic acid concentration measuring device 76, and their changes are recorded. If the Sn ion concentration tends to become higher or lower than a concentration as estimated from the operating conditions, then the efficiency of Sn ion dissolution, which is used for the estimation of the concentration, will be changed. If the methanesulfonic acid concentration tends to become higher or lower than an estimated concentration, then the permeability of the anion exchange membrane with respect to the acid will be changed. After changing such a factor(s), control of the Sn concentration and the methanesulfonic acid concentration is continued.

The supply of the anolyte E, containing a high concentration of Sn ions, from the anode chamber 14 to the cathode chamber 12 is preferably performed by forcing the anolyte E to overflow the anode chamber 14, rather than by passing the anolyte E through a pipe using a dedicated pump. This is because of the following reasons.

If the anolyte E containing Sn ions with a high concentration resides in a pipe for a long time, deposition of a metal (which is abnormal deposition) on an interior surface of the pipe will occur even when the surface of the pipe is made of an insulating material. Once the metal begins to deposit on the interior surface of the pipe, the metal tends to grow continuously on the surface. If the supply of the anolyte E from the anode chamber 14 to the cathode chamber 12 is continued in order to pass the anolyte E continuously through the pipe, then the total amount of the liquid in the cathode chamber increases. As a result, it is necessary to continuously discharge the plating solution Q from the cathode chamber by the same amount as the amount of the anolyte E supplied.

The above-described metal deposition in the pipe can be avoided by using the overflow method to supply the anolyte E. The anolyte E in the anode chamber 14 is constantly agitated by bubbling thereof with the supply of the nitrogen gas. This can prevent deposition of a metal on the inner surface of the anode chamber 14. In the embodiment, the anolyte E overflows the anode chamber 14 as a result of the migration of methanesulfonic acid and water molecules caused by the electrolysis. The amount or volume of the anolyte E overflowing into the cathode chamber 12 is exactly equal to the amount or volume of the methanesulfonic acid and the water that have passed through the anion exchange membrane 54. Thus, there is no change in the volume of the plating solution Q in the cathode chamber 12, and therefore there is no need to discharge the plating solution Q.

FIG. 11 schematically shows a plating bath 16a which is another example. An anode holder 30, holding a disk-shaped Sn anode 32, is disposed in the anode chamber 14 of the plating bath 16a. An anodic anode mask 200 for restricting a contact area of the Sn anode 32 with anolyte E is mounted to a front surface of the anode holder 30 in a manner such that the anodic anode mask 200 hermetically contacts a peripheral area of the Sn anode 32. An opening 10a is formed in the cathode-chamber-side wall 10a of the anode bath 10. Anion exchange membrane 54 is mounted to the wall 10a along the edge of the opening 10a, with its peripheral portion held between a mask member 202 and the wall 10a. The mask member 202 is provided for restricting a contact area of the anion exchange membrane 54 with the plating solution Q. Since the wall 10a and the mask member 202 hold the anion exchange membrane 54 therewithin to seal a gap along the peripheral portion of the anion exchange membrane 54, a liquid leakage between the cathode chamber 12 and the anode chamber 14 can be prevented.

The anion exchange membrane 54 and the opening 10d may have a rectangular shape, and the mask member 202 may be a rectangular ring. The opening sizes of the opening 10d and the mask member 202 may be equal to or larger than the inner diameter of the anode mask 200. In order to reduce an overall resistance between the anode and the cathode, the anion exchange membrane 54 may preferably contact the anolyte E or the plating solution Q at an area larger than an area at which the Sn anode 32 contacts the anolyte E.

An electric field shield 204, having approximately the same external shape as that of the mask member 202 and having an opening 204a of a circular shape similar to the shape of the substrate W, is mounted to the front surface of the mask member 202. The diameter of the opening 204a is smaller than the opening size of the mask member 202. The electric field shield 204, which is provided in the cathode chamber 12 at a position near the Sn anode 32, can reduce a thickness of a seed layer formed on the substrate, making it possible to make the distribution of the film thickness uniform even in a case where the film thickness would otherwise be relatively large in a peripheral area of the substrate. The electric field shield 204 may have a mechanism to change its opening area in order to control the film-thickness distribution. The diameter of the opening 204a of the electric field shield 204 is set equal to or smaller than the diameter of the central hole 50a of the regulation plate 50 which is located between the substrate W and the Sn anode 32. In this embodiment, the regulation plate 50 includes a plate 206 and a cylindrical member 208 mounted to the plate 206.

When the anolyte E in the anode chamber 14 overflows the wall 10a and is supplied into the cathode chamber 12, not only the Sn ions but unnecessary water is supplied as well, resulting in a considerable increase in the amount of the plating solution Q in the cathode chamber 12 and the overflow bath 36. When the amount of the plating solution Q exceeds a predetermined value, the excess solution must be discharged, leading to increased costs. In order to avoid such an issue, the Sn alloy plating apparatus of this embodiment has a gas supply unit 210, which is disposed above the plating bath 16a, for promoting evaporation of water. The gas supply unit 210 can evaporate water in the cathode chamber 12 with the same
amount as the amount of the anolyte E supplied from the anode chamber 14. This makes it possible to stably keep the concentrations of the components of the plating solution Q in the cathode chamber 12, thereby eliminating the need of discharging the plating solution Q or reducing the amount of the plating solution Q to be discharged.

In order to further reduce the amount of the plating solution to be discharged, the plating solution circulation line 46 may be provided with a deaerating device, which can remove only water, so that the plating solution Q passes through the deaerating device.

FIG. 12 is a schematic view of the Sn alloy plating apparatus according to another embodiment. This embodiment differs from the embodiment illustrated in FIG. 1 in that the plating bath 16b of this embodiment includes an inner bath 220 which is integral with the anode bath 10, and overflow bath 36 provided around the inner bath 220, and that a wall 10e, which is adjacent to the overflow bath 36, of the anode bath 10 functions as an overflow weir which stems the anolyte E in the anode chamber 14 and allows the anolyte E to overflow its top into the overflow bath 36. Thus, the anolyte E is stemmed by the wall (overflow weir) 10e and held in the anode chamber 14 at a predetermined liquid level H (see FIG. 9). After the liquid level H is reached, the anolyte E overflows the top of the wall 10e and flows into the overflow bath 36 surrounding the plating bath 16b. Sn ions, which have been thus led into the overflow bath 36, are supplied into the cathode chamber 12 via the plating solution circulation line 46.

FIG. 13 is a schematic view of the Sn alloy plating apparatus according to yet another embodiment. This embodiment differs from the embodiment illustrated in FIG. 1 in that the anode bath 10 of this embodiment is provided with an anolyte circulation line 230 for drawing out a part of the anolyte in the anode chamber 14 from the bottom of the anode bath 10 and returning the anolyte to the top of the anode bath 10. The anolyte circulation line 230 is provided with a pump 232 and a methanesulfonic acid concentration measuring device 234.

According to this embodiment, the pump 232 is driven to circulate the anolyte E in the anode chamber 14 through the anolyte circulation line 230, while the methanesulfonic acid concentration measuring device 234 can measure the methanesulfonic acid concentration of the anolyte E continuously or periodically.

FIG. 14 is a schematic view of the Sn alloy plating apparatus according to yet another embodiment. This embodiment differs from the embodiment illustrated in FIG. 1 in that the liquid discharge line 28 of the plating bath 16 and the electrolytic solution supply line 112 of the auxiliary electrolytic cell 100, shown in FIG. 1, are coupled by a connection line 242 which is provided with a pump 240, and that the Sn ion replenishing line 114, extending from the anode chamber 104 of the auxiliary electrolytic cell 100, is coupled to the top of the anode chamber 14 of the plating bath 16.

According to this embodiment, the anolyte E in the anode chamber 14 of the plating bath 16 can be used as an electrolytic solution to be supplied to the anode chamber 104 of the auxiliary electrolytic cell 100, while the anolyte A having a high Sn ion concentration in the anode chamber 104 of the auxiliary electrolytic cell 100 can be returned to the anode chamber 14 of the plating bath 16. The circulating anolyte can compensate for the shortage of Sn ions in the plating system.

FIG. 15 is a schematic view of the Sn alloy plating apparatus having a plurality of plating baths, according to yet another embodiment. As shown in FIG. 15, the Sn alloy plating apparatus includes a plurality of plating baths 250, each having the same construction as the plating bath 16 shown in FIG. 1, and a single reservoir bath 252. The anode chambers of the respective plating baths 250 coupled to the reservoir bath 252 by an anolyte supply line 254 and an anolyte recovery line 256. The anolyte supply line 254 is provided with a pump 258a. The anolyte supply line 254 branches into branch lines extending to the plating baths 250, respectively. Branch points of the anolyte supply line 254 are located downstream of the pump 258a. Switching valves 260a are provided at the branch points of the anolyte supply line 254. The anolyte recovery line 256 is provided with a pump 258b. The anolyte recovery line 256 branches into branch lines extending to the plating baths 250, respectively. Branch points of the anolyte recovery line 256 are located upstream of the pump 258b. Switching valves 260b are provided at the branch points of the anolyte recovery line 256.

A heater 262 for heating the anolyte is installed in the reservoir bath 252 in order to raise the temperature of the anolyte so as to increase the efficiency of electrolysis. The temperature of the anolyte is controlled e.g., in the range of 26°C to 40°C.

According to this embodiment, the Sn ion concentration and the methanesulfonic acid concentration of the anolyte can be made equal in all the anode chambers of the plating baths 250 by circulating the anolyte between the anode chambers of the plating baths 250 and the reservoir bath 252. Thus, control of the Sn ion concentration and the methanesulfonic acid concentration of the anolyte can be performed in a considerably simple manner according to this embodiment as compared to the case of controlling these concentrations of the anolyte individually in each of the plating baths 250.

In this embodiment, the anolyte circulates between the reservoir bath 252 and one of the plating baths 250 by using the two pumps 258a, 258b and operating the switching valves 260a, 260b. This enables easy control of the anolyte in the anode chamber of each plating bath 250. Pumps may be provided for the plating baths 250, respectively, in order to circulate the anolyte between the anode chambers of the plating baths 250 and the reservoir bath 252. Thus, the circulation of the anolyte between one plating bath 250 and the reservoir bath 252 may be performed independently of the other baths 250.

In order to eliminate the shortage of Sn ions caused by the difference between the electrolytic efficiency of the substrate plating and the electrolytic efficiency at the Sn anode in each anode chamber and by the discharge of the plating solution from each plating bath, the reservoir bath 252 may be provided with an auxiliary electrolytic cell, having the same construction as the auxiliary electrolytic cell 100 shown in FIG. 1, so as to compensate for the shortage of the Sn ions.

Yet another embodiment, the Sn alloy plating apparatus may include one outer bath (overflow bath) and a plurality of cathode chambers. An anolyte is supplied from the outer bath into each cathode chamber from a bottom of each cathode chamber by means of a pump, and the liquid in the cathode chamber is returned by overflow to the outer bath. This configuration enables easy control of the liquid in the cathode chambers.
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.

What is claimed is:

1. An Sn alloy plating apparatus for electrodepositing an alloy of Sn and a metal which is nobler than Sn on a surface of a substrate, the apparatus comprising:
   a plating bath whose interior is separated by an anion exchange membrane into a cathode chamber for holding therein an Sn alloy plating solution in which the substrate, serving as a cathode, is to be immersed and an anode chamber for holding therein an anolyte containing Sn ions and an acid that forms a complex with a divalent Sn ion;
   an Sn anode located in the anode chamber; and
   an electrolytic solution supply line configured to supply an electrolytic solution containing the acid into the anode chamber such that a Sn ion concentration of the anolyte in the anode chamber is kept not less than a predetermined value and a concentration of the acid in the anolyte is kept not less than a predetermined acceptable value;
   the electrolytic solution supply line being configured to supply the electrolytic solution into the anode chamber to increase an amount of the anolyte in the anode chamber and supply the anolyte into the Sn alloy plating solution by the increased amount.

2. The Sn alloy plating apparatus according to claim 1, wherein the electrolytic solution supply line is configured to supply the electrolytic solution into the anode chamber to increase an amount of the anolyte in the anode chamber thereby cause the anolyte to overflow the anode chamber into the Sn alloy plating solution.

3. The Sn alloy plating apparatus according to claim 1, further comprising:
   an overflow bath configured to store the Sn alloy plating solution that has overflowed the cathode chamber; and
   a plating solution circulation line configured to return the Sn alloy plating solution in the overflow bath to the cathode chamber to thereby circulate the Sn alloy plating solution.

4. The Sn alloy plating apparatus according to claim 1, further comprising:
   a pure water supply line configured to supply pure water into the anode chamber.

5. The Sn alloy plating apparatus according to claim 1, further comprising:
   an acid concentration measuring device configured to measure the concentration of the acid in the anolyte in the anode chamber.

6. The Sn alloy plating apparatus according to claim 1, further comprising:
   a dialysis cell configured to draw out a part of the Sn alloy plating solution from the cathode chamber, remove at least a part of the acid from the Sn alloy plating solution, and then return the Sn alloy plating solution to the cathode chamber.

7. The Sn alloy plating apparatus according to claim 1, further comprising:
   an N₂ gas supply line configured to supply nitrogen gas into the anolyte in the anode chamber to form nitrogen gas bubbles in the anolyte.

8. The Sn alloy plating apparatus according to claim 1, further comprising:
   an auxiliary electrolytic cell configured to supply an anolyte having an increased concentration of Sn ions to the Sn alloy plating solution,
   the auxiliary electrolytic cell including
   an auxiliary anode chamber for holding an anolyte therein,
   an auxiliary cathode chamber for holding a catholyte therein,
   an anion exchange membrane separating the auxiliary anode chamber and the auxiliary cathode chamber from each other,
   an auxiliary Sn anode located in the auxiliary anode chamber,
   an auxiliary cathode located in the auxiliary cathode chamber, and
   an auxiliary power source configured to apply a voltage between the auxiliary Sn anode and the auxiliary cathode when the auxiliary Sn anode is immersed in the anolyte and the auxiliary cathode is immersed in the catholyte to produce the anolyte having the increased concentration of Sn ions.

9. An Sn alloy plating method of electrodepositing an alloy of Sn and a metal which is nobler than Sn on a surface of a substrate, the method comprising:
   providing a plating bath whose interior is separated by an anion exchange membrane into a cathode chamber and an anode chamber;
   supplying an Sn alloy plating solution into the cathode chamber;
   immersing the substrate in the Sn alloy plating solution;
   supplying an anolyte, containing Sn ions and an acid that forms a complex with a divalent Sn ion, into the anode chamber to immerse an Sn anode in the anolyte;
   supplying an electrolytic solution containing the acid into the anode chamber such that a Sn ion concentration of the anolyte in the anode chamber is kept not less than a predetermined value and a concentration of the acid in the anolyte is kept not less than a predetermined acceptable value; and
   applying a voltage between the Sn anode and the substrate serving as a cathode to plate the surface of the substrate, while supplying the electrolytic solution into the anode chamber to increase an amount of the anolyte in the anode chamber and supplying the anolyte into the Sn alloy plating solution by the increased amount.

10. The Sn alloy plating method according to claim 9, wherein the supplying the electrolytic solution into the anode chamber to increase an amount of the anolyte in the anode chamber and the supplying the anolyte into the Sn alloy plating solution by the increased amount comprises supplying the electrolytic solution into the anode chamber to increase an amount of the anolyte in the anode chamber thereby cause the anolyte to overflow the anode chamber into the Sn alloy plating solution.

11. The Sn alloy plating method according to claim 9, further comprising:
   circulating the Sn alloy plating solution in the cathode chamber.

12. The Sn alloy plating method according to claim 9, further comprising:
controlling an amount of the electrolytic solution or pure water to be supplied into the anode chamber based on the concentration of the acid in the anolyte held in the anode chamber;

13. The Sn alloy plating method according to claim 9, further comprising:

determining the concentration of the acid in the anolyte from an initial acid concentration of the anolyte, a quantity of electricity and a current efficiency at the Sn anode, an amount of the electrolytic solution supplied, and a permeability of the anion exchange membrane with respect to methanesulfonic acid that passes through the anion exchange membrane and migrates from the cathode chamber into the anode chamber;

14. The Sn alloy plating method according to claim 9, further comprising:

drawing out a part of the Sn alloy plating solution from the cathode chamber;

removing at least a part of the acid from the Sn alloy plating solution that has been drawn out; and then

returning the Sn alloy plating solution to the cathode chamber.

15. The Sn alloy plating method according to claim 9, further comprising:

supplying nitrogen gas into the anolyte in the anode chamber to form nitrogen gas bubbles in the anolyte.

16. The Sn alloy plating method according to claim 9, further comprising:

immersing an auxiliary Sn anode in an anolyte held in an auxiliary anode chamber;

immersing an auxiliary cathode in a catholyte held in an auxiliary cathode chamber that is separated from the auxiliary anode chamber by an anion exchange membrane;

applying a voltage between the auxiliary Sn anode and the auxiliary cathode to produce the anolyte having an increased concentration of Sn ions; and

supplying the anolyte having the increased concentration of Sn ions into the Sn alloy plating solution.

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