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(56) References cited:
US-A- 5 656 386
US-A- 5 883 762
US-A1- 2004 016 636
US-A1- 2004 016 647
US-A1- 2004 118 694

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Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] Embodiments of the present invention generally relate to a plating cell having isolated catholyte and anolyte regions, wherein the isolated regions are separated from each other by an ionic membrane.

Description of the Related Art

[0002] Metallization of sub-quarter micron sized features is a foundational technology for present and future generations of integrated circuit manufacturing processes. More particularly, in devices such as ultra large scale integration-type devices, *i.e.,* devices having integrated circuits with more than a million logic gates, the multilevel interconnects that lie at the heart of these devices are generally formed by filling high aspect ratio, *i.e.,* greater than about 4:1, interconnect features with a conductive material, such as copper or aluminum. Conventionally, deposition techniques such as chemical vapor deposition (CVD) and physical vapor deposition (PVD) have been used to fill these interconnect features. However, as the interconnect sizes decrease and aspect ratios increase, void-free interconnect feature fill via conventional metallization techniques becomes increasingly difficult. Therefore, plating techniques, *i.e.,* electrochemical plating (ECP) and electroless plating, have emerged as promising processes for void free filling of sub-quarter micron sized high aspect ratio interconnect features in integrated circuit manufacturing processes.

[0003] In an ECP process, for example, sub-quarter micron sized high aspect ratio features formed into the surface of a substrate (or a layer deposited thereon) may be efficiently filled with a conductive material, such as copper. ECP plating processes are generally two stage processes, wherein a seed layer is first formed over the surface features of the substrate, and then the surface features of the substrate are exposed to an electrolyte solution, while an electrical bias is applied between the seed layer and a copper anode positioned within the electrolyte solution. The electrolyte solution generally contains ions to be plated onto the surface of the substrate, and therefore, the application of the electrical bias causes these ions to be urged out of the electrolyte solution and to be plated onto the biased seed layer.

[0004] Conventional chemical plating cells generally utilize an overflow weir-type plater containing a plating solution, which is also generally termed a catholyte herein. The substrate is positioned at the top of the weir during plating and an electrical plating bias is applied between the substrate and an anode positioned on a lower portion of the plating solution. This bias causes metal ions in the plating solution to go through a reduction that causes the ions to be plated on the substrate. However, one challenge associated with conventional plating cells is that the plating solution contains additives that are configured to control the plating process, and these additives are known to react with the anode during plating processes. This reaction with the anode causes the additives to breakdown, which generally renders the additives ineffective. Further, when the additives breakdown and are no longer able to facilitate process control, then the additives essentially become contaminants in the plating solution.

[0005] Additionally, other conventional plating cells have implemented a porous membrane into the plating cell that operates to separate an anolyte solution (discussed herein) from the plating solution or catholyte. The intent of this configuration is to prevent additives in the plating solution from contacting the anode and depleting or degrading. Conventional applications of the porous membrane include microporous chemical transport barriers, which are supposed to limit chemical transport of most species, while allowing migration of anion and cation species, and hence passage of current. Examples of conventional membranes include porous glass, porous ceramics, silica aerogels, organic aerogels, porous polymeric materials, and filter membranes. Specific membranes include carbon filter layers, Kynar layers, or polypropylene membranes. However, in similar fashion to weir-type plating cells, conventional cells that use porous membranes to isolate the catholyte from the anolyte have also been shown to leak additives through the membrane, which allows for the additives to again contact the anode and deplete. Additionally, conventional membranes present challenges to maintaining plating metal ion concentrations in the catholyte solutions. More particularly, conventional membranes generally allow several different types of ions from the plating solution to pass therethrough, and as such, the plating metal ion transport is hindered, as these ions must compete with the other ions to pass through the membrane. As such, conventional plating cells that attempt to isolate the catholyte from the anolyte are generally ineffective in preventing plating solution additives from reaching the anode, and further, generate plating metal ion diffusion challenges, as the membranes are resistant to a constant metal ion transfer rate as a result of crowding at the membrane pores.

[0006] Therefore, there is a need for a plating cell configured to minimize additive breakdown at the anode, while allowing for adequate metal ion permeability.

[0007] US 5883762 describes an electroplating apparatus and method that reduces oxidation of thermodynamically unstable and oxidizable ionic species in an electroplating solution to deposit complex magnetic alloys onto substrates.

SUMMARY OF INVENTION

[0008] The present invention provides an electrochemical plating cell, comprising:

an anolyte compartment positioned in a lower portion of a fluid basin;
a catholyte compartment positioned in an upper portion of the fluid basin; and a poly tetrafluoroethylene based ionomer cationic membrane having a fluorized polymer matrix positioned to separate the anolyte compartment from the catholyte compartment; and a diffusion member positioned above the cationic membrane in the catholyte compartment, wherein preferably the diffusion member is a porous disk having a uniform thickness.

[0009] The present invention further provides a method for plating metal onto a substrate using this electrochemical plating cell, comprising:

positioning the substrate in a catholyte solution contained in a catholyte chamber of a plating cell, the catholyte solution comprising:

an acid source at a concentration of between 5 g/L and 15 g/L;
a copper source at a concentration of between 0.8M and 0.9M; and
chlorine ions at a concentration of between 25 ppm and 75 ppm; and

applying a plating bias between the substrate and an anode positioned in an anolyte chamber of the plating cell, the anolyte chamber being separated from the catholyte chamber by an ionic membrane and being supplied with an anolyte solution comprising a copper source having a concentration of greater than 51 g/L.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] So that the manner in which the above recited features of the present invention can be understood in detail, a more particular description of the invention, briefly summarized above, may be had by reference to embodiments, some of which are illustrated in the appended drawings. It is to be noted, however, that the appended drawings illustrate only typical embodiments of this invention and are therefore not to be considered limiting of its scope, for the invention may admit to other equally effective embodiments.

[0011] Figure 1 illustrates a partial sectional perspective view of an exemplary electrochemical, plating slim cell of the invention.

[0012] Figure 2 illustrates a perspective view of an anode base plate of the invention.

[0013] Figure 3 illustrates a perspective view of an exemplary anode base plate of the invention having an anode positioned therein.

[0014] Figure 4 illustrates an exploded perspective view of an exemplary membrane support member of the invention.

[0015] Figure 5 illustrates a partial sectional view of an edge of the plating cell of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0016] The present invention generally provides an electrochemical plating cell configured to plate metal onto semiconductor substrates using a small volume cell, *i.e.,* a cell weir volume that houses less than about 4 liters of electrolyte in the cell itself, preferably between about 1 and 3 liters, and potentially between about 2 and about 8 liters of electrolyte solution in an adjacent fluidly connected supply tank. These small volumes of fluid required to operate the cell of the invention allow the electroplating cell to be used for a predetermined range of substrates, *i.e.,* 100 - 200, and then the solution may be discarded and replaced with new solution. The electrochemical plating cell is generally configured to fluidly isolate an anode of the plating cell from a cathode or plating electrode of the plating cell via a cation membrane positioned between the substrate being plated and the anode of the plating cell. Additionally, the plating cell of the invention is generally configured to provide a first fluid solution to an anode compartment, *i.e.,* the volume between the upper surface of the anode and the lower surface of the membrane, and a second fluid solution (a plating solution) to the cathode compartment, *i.e.,* the volume of fluid positioned above the upper membrane surface. The anode of the plating cell generally includes a plurality of slots formed therein, the plurality of slots being positioned parallel to each other and are configured to remove a concentrated hydrodynamic Newtonian fluid layer from the anode chamber surface during plating processes. A membrane support having a plurality of slots or channels formed in a first side of the assembly, along with a plurality of bores formed into a second side of the membrane support, wherein the plurality of bores are in fluid communication with the slots on the opposing side of the membrane support

[0017] Figure 1 illustrates a perspective and partial sectional view of an exemplary electrochemical plating cell 100 of

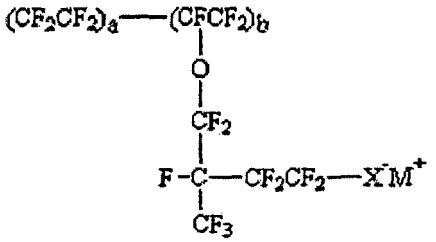
the invention. Plating cell 100 generally includes an outer basin 101 and an inner basin 102 positioned within outer basin 101. Inner basin 102 is generally configured to contain a plating solution that is used to plate a metal, e.g., copper, onto a substrate during an electrochemical plating process. During the plating process, the plating solution is generally continuously supplied to inner basin 102 (at about 3.8 Liters 1 gallon) per minute for a 10 liter plating cell, for example), and therefore, the plating solution continually overflows the uppermost point of inner basin 102 and runs into outer basin 101. The overflow plating solution is then collected by outer basin 101 and drained therefrom for recirculation into inner basin 102. As illustrated in Figure 1, plating cell 100 is generally positioned at a tilt angle, *i.e.,* the frame portion 103 of plating cell 100 is generally elevated on one side such that the components of plating cell 100 are tilted between about 3° and about 30°. Therefore, in order to contain an adequate depth of plating solution within inner basin 102 during plating operations, the uppermost portion of inner basin 102 may be extended upward on one side of plating cell 100, such that the uppermost point of inner basin 102 is generally horizontal and allows for contiguous overflow of the plating solution supplied thereto around the perimeter of inner basin 102.

[0018] The frame member 103 of plating cell 100 generally includes an annular base member 104 secured to frame member 103. Since frame member 103 is elevated on one side, the upper surface of base member 104 is generally tilted from the horizontal at an angle that corresponds to the angle of frame member 103 relative to a horizontal position. Base member 104 includes an annular or disk shaped recess formed therein, the annular recess being configured to receive a disk shaped anode member 105. Base member 104 further includes a plurality of fluid inlets/drains 109 positioned on a lower surface thereof. Each of the fluid inlets/drains 109 are generally configured to individually supply or drain a fluid to or from either the anode compartment or the cathode compartment of plating cell 100. Anode member 105 generally includes a plurality of slots 107 formed therethrough, wherein the slots 107 are generally positioned in parallel orientation with each other across the surface of the anode 105. The parallel orientation allows for dense fluids generated at the anode surface to flow downwardly across the anode surface and into one of the slots 107. Plating cell 100 further includes a membrane support assembly 106 configured to support the membrane 112. Membrane support assembly 106 is generally secured at an outer periphery thereof to base member 104, and includes an interior region 108 configured to allow fluids to pass therethrough via a sequence of oppositely positioned slots and bores. The membrane support assembly may include an o-ring type seal positioned near a perimeter of the membrane, wherein the seal is configured to prevent fluids from traveling from one side of the membrane secured on the membrane support 106 to the other side of the membrane.

[0019] The membrane 112, which is polytetrafluoroethylene based, generally operates to fluidly isolate the anode chamber from the cathode chamber of the plating cell. Membrane 112 is generally an ionic membrane. The ion exchange membrane generally includes fixed negatively charged groups, such as SO_3^-, COO^-, HPO_2^-. SeO_3^-, PO_3^{2-}, or other negatively charged groups amenable to plating processes. Membrane 112 allows a particular type of ions to travel through the membrane, while preventing another type of ion from traveling or passing through the membrane. More particularly, membrane 112 may be a cationic membrane that is configured to allow positively charged copper ions (Cu^{2+}) to pass therethrough, *i.e.,* to allow copper ions to travel from the anode in the anolyte solution through the membrane 112 into the catholyte solution, where the copper ions may then be plated onto the substrate. Further, the cationic membrane may be configured to prevent passage of negatively charged ions and electrically neutral species in the solution, such as the ions that make up the plating solution and catholyte additives. It is desirable to prevent these catholyte additives from traveling through the membrane 112 and contacting the anode, as the additives are known to break down upon contacting the anode. More particularly, membranes with negatively charged ion groups like SO_3^- etc. not only to facilitate Cu ions transport from the anolyte to the catolyte, but also to prevent penetration of accelerators to anode. The accelerator is generally negatively charged organic ion: SO_3^--C_3H_6-S-S-C_3H_6-SO_3^-, so it can't penetrate into or through the cation membrane. This is important, as consumption of accelerators on copper anodes on conventional plating apparatuses without the ionic membrane is very high.

[0020] Membrane 112 may be a Nafion®-type membrane manufactured by Dupont Corporation. Nafion® is an example of a poly (tetrafluoroethylene) based ionomer. Nafion® has several desirable characteristics for electrochemical plating applications, such as its thermal and chemical resistance, ion-exchange properties, selectivity, mechanical strength, and insolubility in water. Nafion® is also a cationic membrane based on a fluorized polymer matrix. Because of fluorized matrix, Nafion® exhibits excellent chemical stability, even in concentrated basic solutions. More particularly, Nafion® is a perfluorinated polymer that contains small proportions of sulfonic or carboxylic ionic functional groups, and has shown to be effective in transmitting metal ions (copper ions in the present embodiment) therethrough, even at low plating current densities. Specifically, Nation® membranes have shown to be effective at transmitting between about 94% and about 98% of copper ions therethrough at plating current densities of between about 5 mA/cm^2 and about 20 mA/cm^2. Additionally, at current densities of between about 20 mA/cm^2 and about 60 mA/cm^2, Nafion® transmits between about 97% and about 93% of copper ions therethrough. The above noted transmission percentages were observed using a copper sulfate solution having a ph of about 3.4. Nafion's® general chemical structure (illustrated below), illustrates where X is either a sulfonic or carboxylic functional group and M is either a metal cation in the neutralized form or an H+ in the acid form. As a result of electrostatic interactions, the ionic groups that form Nafion® tend to aggregate to form

tightly packed regions referred to as clusters. The presence of these electrostatic interactions between the ions and the ion pairs enhance the intermolecular forces and thereby exert a significant effect on the properties of the parent polymer, which makes Nafion®, or other membranes having similar physical and/or operational characteristics, a desirable ionic membrane for use in electrochemical plating cells having separated anolyte and catholyte chambers.



[0021] As a result of electrostatic interactions, the ionic groups that form Nafion® tend to aggregate to form tightly packed regions referred to as clusters. The presence of these electrostatic interactions between the ions and the ion pairs enhance the intermolecular forces and thereby exert a significant effect on the properties of the parent polymer, which makes Nafion®, or other membranes having similar physical and/or operational characteristics, a desirable ionic membrane for use in electrochemical plating cells having separated anolyte and catholyte chambers.

[0022] With regard to other properties of the above noted membranes (Ionics, and Nafion®), each exhibit relatively high conductivity, *i.e.,* about 41.2, 35.3, and 24.2 ohm cm^2 at IOmA/cm^2 for Ionics, Neosepta and Nafion®, respectively. Additionally, water moves through the membranes from the anolyte into the catholyte compartment. This effect essentially dilutes the catolyte and is undesirable. For example, between about 0.5 and about 3 liters of water penetrates into the catholyte per 24 hours (or per 200 wafers) depending on the membrane type and electrolysis conditions. For example, CMX not in accordance with the present invention shows the minimal water transport at about 1.5 ml/wafer, the Ionics membrane shows about 5 ml/wafer, nd Nafion® shows about 6.5 ml/wafer. The transport properties of the CMX not in accordance with the present invention and Nafion® membranes result in the $CuSO_4/H_2SO_4$ concentration ratio remaining relatively constant, even after about 200 substrates are plated. This indicates that copper acid concentration changes will be lower than 2%, if the penetrated water will be removed, e.g., by enforced evaporation. As such, the use of Nafion® requires only a small device to accelerate the water evaporation to 4-6 liters/day. However, Ionics membranes require an additional device that extracts the excess of H2SO4 coming from the anolyte. Table 1 illustrates the respective properties of the above noted membranes.

Table 1

[0023] Vicor membranes may also be used to advantage in the plating cell of the invention. Other examples of membranes include Neosepta® membranes (ionic and non-ionic) manufactured by Tokuyama, Aciplex® membranes, Selemlon® membranes, and Flemion membranes (all of which are available as ionic and non-ionic) from Asahi Corporation, Raipare™ membranes from Pall Gellman Sciences Corporation, and C-class membranes from Solvay Corporation.

Membrane	Cu^{2+} transfer %	Water transfer ml/Amphr	Resistance ohm cm2	Cu/Acid Ratio Deviation %
Ionics	90-95	8-11.5	53	4%
Nafion	95- 98	4- 7.5	36	2%
CMX	97-98	5.0 -3.1	47	1%

[0024] The implementation of the membrane between the anode and the substrate being plated generates substantially different behaviors in the plating cell as compared to conventional plating cells, both without membranes and those with the membranes discussed in the background of this application. Specifically, the behavior of a copper anode in an acid-free $CuSO_4$ solution is different from conventional anode behavior. First, the sludge formation rate is lower at current densities of up to about 60 mA/cm_2 than that in $CuSOdH_2SO_4$ electrolyte, especially at concentrations of less than about 0.5M. In more concentrated $CuSO_4$ solutions both the amount of sludge and the probability of anode passiviation

increases, especially at low flow rates through the anode compartment. Further, although Cu+ generally forms on the anode in both conventional tools and the tool of the invention, in the configuration of the present invention it accumulates only into the anolyte, mainly at current densities of greater than about 30 mA/cm_2, when the oxygen dissolved in electrolyte has no time to convert Cu+ into Cu^{2+} again. Further still, the stability of the anolyte and catolyte compositions decrease dramatically because of the small volumes of tanks.

[0025] Figure 2 illustrates a perspective view of base member 104. The upper surface of base member 104 generally includes an annular recess 201 configured to receive a disk shaped anode 105 in the recessed portion 201. Further, the surface of annular recessed portion 201 generally includes a plurality of channels 202 formed therein. Each of channels 202 are generally positioned in parallel orientation with each other and terminate at the periphery of recessed region 201. Additionally, the periphery of recessed region 201 also includes an annular drain channel 203 that extends around the perimeter of recessed region 201. Each of the plurality of parallel positioned channels 202 terminate at opposing ends into annular drain channel 203. Therefore, channels 202 may receive dense fluids from anode channels 302 and transmit the dense fluids to a drain channel 203 via base channels 202. The vertical wall that defines recessed region 201 generally includes a plurality of slots 204 formed into the wall. The slots 204 are generally positioned in parallel orientation with each other, and further, are generally positioned in parallel orientation with the plurality of channels 202 formed into the lower surface of recessed region 201. Base member 104 also includes at least one fluid supply conduit 205 configured to dispense a fluid into the anode region of plating cell 100, along with at least one plating solution supply conduit 206 that is configured to dispense a plating solution into the cathode compartment of plating cell 100. The respective supply conduits 205 and 206 are generally in fluid communication with at least one fluid supply line 109 positioned on a lower surface of base member 104, as illustrated in Figure 1. Base member 104 generally includes a plurality of conduits formed therethrough (not shown), wherein the conduits are configured to direct fluids received by individual fluid supply lines 109 to the respective cathode and anode chambers of plating cell 100.

[0026] Figure 3 illustrates a perspective view of base member 104 having the disk shaped anode 105 positioned therein. Anode 105, which is generally a disk shaped copper member, *i.e.,* a soluble-type copper anode generally used to support copper electrochemical plating operations, generally includes a plurality of slots 302 formed therein. The slots 302 generally extend through the interior of anode 302 and are in fluid communication with both the upper surface and lower surface of anode 105. As such, slots 302 allow fluids to travel through the interior of anode 105 from the upper surface to the lower surface. Slots 302 are positioned in parallel orientation with each other. However, when anode 105 is positioned within annular recess 201 of base member 104, the parallel slots 302 of anode 105 are generally positioned orthogonal to both slots 204 and channels 202 of base member 104, as illustrated cooperatively by Figures 2 and 3. Additionally, slots 302 generally do not continuously extend across the upper surface of anode 105. Rather, slots 302 are broken into a longer segment 303 and a shorter segment 304, with a space 305 between the two segments, which operates to generate a longer current path through anode 105 from one side to the other. Further, adjacently positioned slots 302 have the space 305 positioned on opposite sides of the anode upper surface. The current path from the lower side of anode to the upper side of anode generally includes a back and forth type path between the respective channels 302 through the spaces 305. Further, the positioning of spaces 305 and channels 302 provides for improved concentrated Newtonian fluid removal from the surface of the anode 105, as the positioning of channels 302 provides a shortest possible distance of travel for the dense fluids to be received in channels 302. This feature is important, as dense fluids generally travel slowly, and therefore, it is desirable.

[0027] Figure 4 illustrates an exploded perspective view of an exemplary membrane support assembly 106 of the invention. Membrane support assembly 106 generally includes an upper ring shaped support member 401, an intermediate membrane support member 400, and a lower support member 402. Upper and lower support member's 401 and 402 are generally configured to provide structural support to intermediate membrane support member 400, *i.e.,* upper support member 401 operates to secure intermediate membrane support member 400 to lower support member 402, while lower support member 402 receives intermediate membrane support member 400. Intermediate membrane support member 400 generally includes a substantially planar upper surface having a plurality of bores partially formed therethrough. A lower surface of intermediate membrane support member 400 generally includes a tapered outer portion 403 and a substantially planar inner membrane engaging surface 404. An upper surface of lower support member 402 may include a corresponding tapered portion configured to receive the tapered section 403 of intermediate membrane support member 400 thereon. The membrane engaging surface 404 generally includes a plurality of parallel positioned/orientated channels (not shown). Each of the channels formed into the lower surface of intermediate membrane support member 400 are in fluid communication with at least one of the plurality of bores partially formed through the planar upper surface. The channels operate to allow a membrane positioned in the membrane support assembly to deform slightly upward in the region of the channels, which provides a flow path for air bubbles and less dense fluids in the cathode chamber to travel to the perimeter of the membrane and be evacuated from the anode chamber.

[0028] In operation, the plating cell 100 of the invention provides a small volume (electrolyte volume) processing cell that may be used for copper electrochemical plating processes, for example. Plating cell 100 may be horizontally positioned or positioned in a tilted orientation, *i.e.,* where one side of the cell is elevated vertically higher than the opposing

side of the cell, as illustrated in Figure 1. If plating cell 100 is implemented in a tilted configuration, then a tilted head assembly and substrate support member may be utilized to immerse the substrate at a constant immersion angle, *i.e.,* immerse the substrate such that the angle between the substrate and the upper surface of the electrolyte does not change during the immersion process. Further, the immersion process may include a varying immersion velocity, *i.e.,* an increasing velocity as the substrate becomes immersed in the electrolyte solution. The combination of the constant immersion angle and the varying immersion velocity operates to eliminate air bubbles on the substrate surface.

[0029] Assuming a tilted implementation is utilized, a substrate is first immersed into a plating solution contained within inner basin 102. Once the substrate is immersed in the plating solution, which generally contains copper sulfate, chlorine, and one or more of a plurality of organic plating additives (levelers, suppressors, accelerators, etc.) configured to control plating parameters, an electrical plating bias is applied between a seed layer on the substrate and the anode 105 positioned in a lower portion of plating cell 100. The electrical plating bias generally operates to cause metal ions in the plating solution to deposit on the cathodic substrate surface. The plating solution supplied to inner basin 102 is continually circulated through inner basin 102 via fluid inlet/outiets 109. More particularly, the plating solution may be introduced in plating cell 100 via a fluid inlet 109. The solution may travel across the lower surface of base member 104 and upward through one of fluid apertures 206. The plating solution may then be introduced into the cathode chamber via a channel formed into plating cell 100 that communicates with the cathode chamber at a point above membrane support 106. Similarly, the plating solution may be removed from the cathode chamber via a fluid drain positioned above membrane support 106, where the fluid drain is in fluid communication with one of fluid drains 109 positioned on the lower surface of base member 104. For example, base member 104 may include first and second fluid apertures 206 positioned on opposite sides of base member 404. The oppositely positioned fluid apertures 206 may operate to individually introduce and drain the plating solution from the cathode chamber in a predetermined direction, which also allows for flow direction control. The flow control direction provides control over removal of light fluids at the lower membrane surface, removal of bubbles from the anode chamber, and assists in the removal of dense or heavy fluids from the anode surface via the channels 202 formed into base 104.

[0030] Once the plating solution is introduced into the cathode chamber, the plating solution travels upward through diffusion plate 110. Diffusion plate 110, which is generally a ceramic or other porous disk shaped member, generally operates as a fluid flow restrictor to even out the flow pattern across the surface of the substrate. Further, the diffusion plate 110 operates to resistively damp electrical variations in the electrochemically active area the anode or cation membrane surface, which is known to reduce plating uniformities. Additionally, embodiments of the invention contemplate that the ceramic diffusion plate 110 may be replaced by a hydrophilic plastic member, *i.e.,* a treated PE member, a PVDF member, a PP member, or other material that is known to be porous and provide the electrically resistive damping characteristics provided by ceramics. However, the plating solution introduced into the cathode chamber, which is generally a plating catholyte solution, *i.e.,* a plating solution with additives, is not permitted to travel downward through the membrane (not shown) positioned on the lower surface 404 of membrane support assembly 106 into the anode chamber, as the anode chamber is fluidly isolated from the cathode chamber by the membrane. The anode chamber includes separate individual fluid supply and drain sources configured to supply an anolyte solution to the anode chamber. The solution supplied to the anode chamber, which may generally be copper sulfate in a copper electrochemical plating system, circulates exclusively through the anode chamber and does not diffuse or otherwise travel into the cathode chamber, as the membrane positioned on membrane support assembly 106 is not fluid permeable in either direction.

[0031] Additionally, the flow of the fluid solution (anolyte, *i.e.*, a plating solution without additives, which may be referred to as a virgin solution) into the anode chamber is directionally controlled in order to maximize plating parameters. For example, anolyte may be communicated to the anode chamber via an individual fluid inlet 109. Fluid inlet 109 is in fluid communication with a fluid channel formed into a lower portion of base member 104 and the fluid channel communicates the anolyte to one of apertures 205. A seal positioned radially outward of apertures 205, in conjunction with the surrounding structure, directs the anolyte flowing out of apertures 205 upward and into slots 204. Thereafter, the anolyte generally travels across the upper surface of the anode 105 towards the opposing side of base member 104, which in a tilted configuration, is generally the higher side of plating cell 100. The anolyte travels across the surface of the anode below the membrane positioned immediately above. Once the anolyte reaches the opposing side of anode 105, it is received into a corresponding fluid channel and drained from plating cell 100 for recirculation.

[0032] During plating operations, the application of the electrical plating bias between the anode and the cathode generally causes a breakdown of the anolyte solution contained within the anode chamber. More particularly, the application of the plating bias operates to generate multiple hydrodynamic or Newtonian layers of the copper sulfate solution within the anode chamber. The hydrodynamic layers generally include a layer of concentrated copper sulfate positioned proximate the anode, an intermediate layer of normal copper sulfate, and a top layer of lighter and depleted copper sulfate proximate the membrane. The depleted layer is generally a less dense and lighter layer of copper sulfate than the copper sulfate originally supplied to the anode compartment, while the concentrated layer is generally a heavier and denser layer of copper sulfate having a very viscous consistency. The dense consistency of the concentrated layer proximate the anode causes electrical conductivity problems (known as anode passivation) in anodes formed without

slots 302. However, slots 302, in conjunction with the tilted orientation of plating cell 100, operate to receive the concentrated viscous layer of copper sulfate and remove the layer from the surface of the anode, which eliminates conductivity variances. Further, plating cell 100 generally includes one side that is tilted upward or vertically positioned above the other side, and therefore, the surface of anode 105 is generally a plane that is also tilted. The tilt causes the layer of concentrated copper sulfate generated at the surface of the anode to generally flow downhill as a result of the gravitational force acting thereon. As the concentrated copper sulfate layer flows downhill, it is received within one of channels 302 and removed from the surface of the anode. As discussed above, channels 302 are generally parallel to each other and are orthogonal to channels 204. Therefore, channels 302 are also orthogonal to channels 202 and formed into the lower surface of base member 104. As such, each of slots 302 or finally intersect several of channels 202. This configuration allows the concentrated copper sulfate received within slots 302 to be communicated to one or more of channels 202. Thereafter, the concentrated copper sulfate may be communicated via channels 202 to the annular drain channel 203 positioned within recessed region 201. The drain 203 in communication with channels 202 may generally be communicated through base plate 104 and back to a central anolyte supply tank, where the concentrated copper sulfate removed from the anode surface may be recombined with a volume of stored copper sulfate used for the anolyte solution.

[0033] Similarly, the upper portion of anode chamber generates a diluted layer of copper sulfate proximate the membrane. The diluted layer of copper sulfate may be removed from the anode chamber via an air vent 501, as illustrated in Figure 5. Air vent 501, which may include multiple ports, is generally positioned on the upper side of electrochemical plating cell 100, and therefore, is positioned to receive both bubbles trapped within anode chamber, as well as the diluted copper sulfate generated at the membrane surface. Air vents 501 are generally in fluid communication with the anolyte tank discussed above, and therefore, communicates the diluted copper sulfate received therein back to the anolyte tank, where the diluted copper sulfate may combine with the concentrated copper sulfate removed via slots 302 to form the desired concentration of copper sulfate within the anolyte tank. Any bubbles trapped by air vent 501 may also be removed from the cathode chamber vented to atmosphere or simply maintained within the anolyte tank and not recirculated into the cathode chamber.

[0034] The catholyte solution (the solution used to contact and plate metal/copper onto the substrate) generally includes several constituents. The constituents generally include a virgin makeup plating solution (a plating solution that does not contain and plating additives, such as levelers, suppressors, or accelerators, such as that provided by Shipley Ronal of Marlborough, MA or Enthone, a division of Cookson Electronics PWB Materials & Chemistry of London), water (generally included as part of the VMS, but is may also be added), and a plurality of plating solution additives configured to provide control over various parameters of the plating process. The catholyte is generally a low acid-type of plating solution, *i.e.,* the catholyte generally has between about 5g/l of acid and about 50 g/l of acid, or more particularly, between about 5g/l and about 10 g/l. The acid may be sulfuric acid, sulfonic acid (including alkane sulfonic acids), pyrophosphoric acid, citric acid, and other acids known to support electrochemical plating processes. The desired copper concentration in the catholyte is generally between about 25g/l and about 70 g/l, preferably between about 30 g/l and about 50 g/l of copper. The copper is generally provided to the solution via copper sulfate, and/or through the electrolytic reaction of the plating process wherein copper ions are provided to the solution via the anolyte from a soluble copper anode positioned in the catholyte solution. More particularly, copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) may be diluted to obtain a copper concentration of about 40 g/l, for example. A common acid and copper source combination is sulfuric acid and copper sulfate, for example. The catholyte also has chlorine ions, which may be supplied by hydrochloric acid or copper chloride, for example, and the concentration of the chlorine may be between about 30 ppm and about 60 ppm.

[0035] As noted above, the plating solution (catholyte) generally contains one or more plating additives configured to provide a level of control over the plating process. The additives may include suppressors at a concentration of between about 1.5 ml/l and about 4 ml/l, preferably between about 2 ml/l and 3.0 ml/l. Exemplary suppressors include ethylene oxide and propylene oxide copolymers. Additives may also include accelerators at a concentration of between about 3 ml/l and about 10 ml/l, preferably within the range of between about 4.5 ml/l and 8.5 ml/l. Exemplary accelerators are based on sulfopropyl-disulfide or mercapto-propane-sulphonate and their derivatives.

[0036] Additionally, another additive that may optionally be added to the catholyte solution is a leveler at a concentration of between about 1 ml/l and about 12 ml/l, or more particularly, in the range of between about 1.5 ml/l and 4 ml/l

[0037] The anolyte solution, as noted above, is generally contained in the volume below the membrane and above the anode. The anolyte solution may be simply the catholyte solution without the plating additives, *i.e.,* levelers, suppressors, and/or accelerators. However, the inventors have found that specific anolyte solutions, other than just stripped catholyte solutions, provide a substantial improvement in plating parameters. Specifically, copper transfer through the membrane and prevention of copper sulfate and hydroxide precipitation, *i.e.,* when the Cu ions transport through membrane, copper sulfate accumulates in the anolyte and starts to precipitate on the anode provoking its passiviation are improved. When pH of the anolyte is maintained above about 4.5 to about 4.8, copper hydroxide starts to deposit from Cu salt solutions, *i.e.*, $Cu_2+ + 2H_2O = Cu(OH)_2$ (deposit) +2H+. More particularly, the inventors have found that if the anolyte can be configured to supply between about 90% and about 100% of the copper to the catholyte, then the membrane essentially operates as a clean copper anode, *i.e.,* the membrane provides copper to the catholyte without

the disadvantages associated with the electrochemical reaction that takes place at the surface of the anode (sludge formation, additive consumption, planarity variations due to erosion, etc.). The anolyte of the invention generally includes a soluble copper II salt (copper ions are not complexed with ligands like NH_3, or EDTA or phyrophoshoric acid anions, as Cu transports through the membrane together with this ligand, like $Cu(NH_3)4$ 2+ will transport together with NH_3, such as copper sulfate, copper sulfonate, copper chloride, copper bromide, copper nitrate, or a blend of any combination of these salts in an amount sufficient to provide a concentration of copper ions in the catholyte of between about 0.1M and about 2.5M, or more particularly, between about 0.25 M and about 2M.

[0038] Additionally, the pH of the anolyte solution will generally be between about 1.5 and about 6, or more particularly, between about 2 and 4.8, for example. The pH is maintained in this range, as increasing the pH above this range in conventional plating configurations has been shown cause copper hydroxide precipitation. Additionally, when the pH is below 2, and particularly if the pH is below 1.5, then the solution supports a substantial increase in the hydrogen ion (H^+) transport through the membrane from the anolyte to the catholyte. In this situation, the bulk of the plating current is carried by the H^+ ions and the copper ion transport is reduced. As such, the copper ion concentration in the catholyte decreases, potentially to a critical level that will not support plating, while simultaneously the sulfuric acid concentration in the catholyte increases. The anolyte can generally use any soluble Cu^{2+} salt, such as $CuSO_4$ (solubility 300 g/L), $CuBr_2$ (solubility more that 2 kg/L), $CuCl_2$ (solubility 700 g/L), CuF_2 (47 g/L), $Cu(NO_3)_2$ (1300 g/L) etc. The selection of anions depends on their impact to prevent or minimize Cu(I) formation and anode passiviation, on penetration through the membrane etc. For instance, the anolyte can be $CuSO_4$ (0.5 M) with small additions of $Cu(NO_3)$ to activate anode surface and minimize Cu(I) formation. To minimize Cu(I) formation, small additions of $Cu(ClO_3)_2$ (solubility 2 kg/L) or $Cu(IO_3)_2$ - solubility 1g/L may be used. In similar fashion to the catholyte, the source of copper in the anolyte (aside from the anode) may be copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) at between about 51 g/L and 70 g/L, or at between about 0.75 M and about 0.95 M. Alternatively, in a preferred embodiment, the copper source may be between about 51 g/L and about 60 g/L, preferably about 54 g/L, and at a molarity of between about 0.8 M and about 0.9 M, preferably about 0.85M.

Claims

1. An electrochemical plating cell (100), comprising:

an anolyte compartment positioned in a lower portion of a fluid basin;
a catholyte compartment positioned in an upper portion of the fluid basin;
a poly tetrafluoroethylene based ionomer cationic membrane (112) having a fluorized polymer matrix positioned to separate the anolyte compartment from the catholyte compartment; and
a diffusion member (110) positioned above the cationic membrane in the catholyte compartment.

2. The electrochemical plating cell of claim 1, wherein the diffusion member is a porous disk having a uniform thickness.

3. The electrochemical plating cell as in claim 1 or 2, wherein the cationic membrane is configured to transmit between 94% and 98% of metal ions therethrough at plating current densities of between 5 mA/cm^2 and 20 mA/cm^2 and between 93% and 97% of metal ions therethrough at plating current densities of between 20 mA/cm^2 and 60 mA/cm^2.

4. The electrochemical plating cell as in claim 1 or 2, wherein the cationic membrane has a conductivity of between 20 ohm cm^2 and 45 ohm cm^2 at a plating current density of 10 mA/cm^2 and between 20 ohm cm^2 and 30 ohm cm^2 at a plating current density of 10 mA/cm^2.

5. The electrochemical plating cell as in claim 1, wherein the cationic membrane has a water transfer of between 3 ml/Amphr and 7.5 ml/Amphr.

6. A method for plating metal onto a substrate using the electrochemical plating cell of claim 1, comprising:

positioning the substrate in a catholyte solution contained in a catholyte chamber of a plating cell, the catholyte solution comprising:

an acid source at a concentration of between 5 g/L and 15 g/L;
a copper source at a concentration of between 0.8M and 0.9M; and
chlorine ions at a concentration of between 25 ppm and 75 ppm; and

applying a plating bias between the substrate and an anode positioned in an anolyte chamber of the plating cell, the anolyte chamber being separated from the catholyte chamber by an ionic membrane and being supplied with an anolyte solution comprising a copper source having a concentration of greater than 51 g/L.

7. The method of claim 6, wherein the catholyte solution further comprises: a leveler at a concentration of between 2 mL/L and 3 mL/L; a suppressor at a concentration of between 2 mL/L and 3 mL/L; and an accelerator at a concentration of between 5.5 mUL and 8 mL/L.

8. The method of claim 6, wherein the anolyte has a pH of between 2 and 4.8.

9. The method of claim 8, wherein the anolyte comprises a copper 11 salt having a concentration of copper ions of between 0.1M and 2M.

10. The method of claim 9, wherein the copper 11 salt comprises at least one of copper sulfate, copper sulfonate, copper chloride, copper nitrate, and blends thereof.

11. The method of claim 9, wherein the anolyte provides a copper transport of copper ions through the ionic membrane of between 90% and 100%.

Patentansprüche

1. Elektrochemische Beschichtungszelle (100), umfassend:

- eine Anolytkammer, die in einem unteren Abschnitt eines Flüssigkeitsbeckens angeordnet ist,
- eine Katholytkammer, die in einem oberen Abschnitt des Flüssigkeitsbeckens angeordnet ist,
- eine Poly-Tetrafluorethylen-basierte Ionomer-Kationenmembran (112) mit einer fluorisierten Polymermatrix, die angeordnet ist, um die Anolytkammer von der Katholytkammer zu trennen, und
- ein Diffusionselement (110), das über der Kationenmembran in der Katholytkammer angeordnet ist.

2. Elektrochemische Beschichtungszelle nach Anspruch 1, wobei das Diffusionselement eine poröse Scheibe mit einer gleichmäßigen Dicke ist.

3. Elektrochemische Beschichtungszelle nach Anspruch 1 oder 2, wobei die Kationenmembran konfiguriert ist, zwischen 94% und 98% von Metallionen dort hindurch bei Beschichtungsstromdichten zwischen 5 mA/cm^2 und 20 mA/cm^2 und zwischen 93% und 97% von Metallionen dort hindurch bei Beschichtungsstromdichten zwischen 20 mA/cm^2 und 60 mA/cm^2 zu leiten.

4. Elektrochemische Beschichtungszelle nach Anspruch 1 oder 2, wobei die Kationenmembran eine Leitfähigkeit zwischen 20 ohm cm^2 und 45 ohm cm^2 bei einer Beschichtungsstromdichte von 10 mA/cm^2 und zwischen 20 ohm cm^2 und 30 ohm cm^2 bei einer Beschichtungsstromdichte von 10 mA/cm^2 aufweist.

5. Elektrochemische Beschichtungszelle nach Anspruch 1, wobei die Kationenmembran einen Wassertransfer zwischen 3 ml/Amphr und 7,5 ml/Amphr aufweist.

6. Verfahren zum Beschichten von Metall auf ein Substrat unter Verwendung der elektrochemischen Beschichtungszelle nach Anspruch 1, umfassend:

- Positionieren des Substrates in einer Katholytlösung, die in einer Katholytkammer einer Beschichtungszelle enthalten ist, wobei die Katholytlösung umfasst:

  - eine Säurequelle bei einer Konzentration zwischen 5 g/L und 15 g/L,
  - eine Kupferquelle bei einer Konzentration zwischen 0,8 M und 0,9 M und
  - Chlor-Ionen bei einer Konzentration zwischen 25 ppm und 75 ppm, und

- Anlegen einer Beschichtungsspannung zwischen dem Substrat und einer Anode, die in einer Anolytkammer der Beschichtungszelle positioniert ist, wobei die Anolytkammer von der Katholytkammer durch eine Ionen-Membran getrennt ist und mit einer Anolytlösung versorgt ist, welche eine Kupferquelle mit einer Konzentration

größer als 51 g/L umfasst.

7. Verfahren nach Anspruch 6, wobei die Katholytlösung ferner umfasst:

- einen Nivellierer bei einer Konzentration zwischen 2 mUL und 3 mUL,
- einen Unterdrücker bei einer Konzentration zwischen 2 mUL und 3 mL/L, und
- einen Beschleuniger bei einer Konzentration zwischen 5,5 mL/L und 8 mL/L.

8. Verfahren nach Anspruch 6, wobei das Anolyt einen pH-Wert zwischen 2 und 4,8 aufweist.

9. Verfahren nach Anspruch 8, wobei das Anolyt ein Kupfer-11-Salz mit einer Konzentration von Kupferionen zwischen 0,1 M und 2 M umfasst

10. Verfahren nach Anspruch 9, wobei das Kupfer-11-Salz wenigstens eines von Kupfersulfat, Kupfersulfonat, Kupferchlorid, Kupfernitrat und Mischungen davon umfasst.

11. Verfahren nach Anspruch 9, wobei das Anolyt einen Kupfertransport von Kupferionen durch die Ionenmembran zwischen 90 % und 100 % bereitstellt.

Revendications

1. Cellule de placage électrochimique (100), comprenant :

un compartiment anolytique positionné dans une partie inférieure d'un bassin de fluide ;
un compartiment catholytique positionné dans une partie supérieure du bassin de fluide ;
une membrane cationique d'ionomère à base de polytétrafluoroéthylène (112) ayant une matrice polymérique fluorée positionnée pour séparer le compartiment anolytique du compartiment catholytique ; et
un élément de diffusion (110) positionné au-dessus de la membrane cationique dans le compartiment catholytique.

2. Cellule de placage électrochimique de la revendication 1, dans laquelle l'élément de diffusion est un disque poreux ayant une épaisseur uniforme.

3. Cellule de placage électrochimique selon la revendication 1 ou 2, dans laquelle la membrane cationique est configurée pour faire passer à travers elle entre 94% et 98 d'ions métalliques à des densités de courant de placage entre 5 mA/cm^2 et 20 mA/cm^2 et entre 93% et 97% d'ions métalliques à des densités de courant de placage entre 30 mA/cm^2 et 60 mA/cm^2.

4. Cellule de placage électrochimique selon la revendication 1 ou 2, dans laquelle la membrane cationique a une conductivité entre 20 ohm cm^2 et 45 ohm cm^2 à une densité de courant de placage de 10 mA/cm^2 et entre 20 ohm cm^2 et 30 ohm cm^2 à une densité de courant de placage de 10 mA/cm^2.

5. Cellule de placage électrochimique selon la revendication 1, dans laquelle la membrane cationique a un transfert d'eau entre 3 ml/Amphr et 7,5 ml/Amphr.

6. Procédé de placage de métal sur un substrat utilisant la cellule de placage électrochimique de la revendication 1, comprenant le fait :

de positionner le substrat dans une solution catholytique contenue dans une chambre catholytique d'une cellule de placage, la solution catholytique comprenant :

une source d'acide à une concentration entre 5 g/L et 15 g/L ;
une source de cuivre à une concentration entre 0,8M et 0,9M ; et
des ions de chlore à une concentration entre 25 ppm et 75 ppm ; et
d'appliquer une polarisation de placage entre le substrat et une anode positionnée dans une chambre anolytique de la cellule de placage, la chambre anolytique étant séparée de la chambre catholytique par une membrane ionique et étant alimentée d'une solution anolytique comprenant une source de cuivre qui

a une concentration supérieure à 51 g/L.

7. Procédé de la revendication 6, dans lequel la solution catholytique comprend en plus : un niveleur à une concentration entre 2 mL/L et 3 mL/L ; un suppresseur à une concentration entre 2 mL/L et 3 mL/L ; et un accélérateur à une concentration entre 5,5 mL/L et 8 mL/L.

8. Procédé de la revendication 6, dans lequel l'anolyte a un pH entre 2 et 4,8.

9. Procédé de la revendication 8, dans lequel l'anolyte comprend un sel de cuivre 11 ayant une concentration d'ions de cuivre entre 0,1M et 2M.

10. Procédé de la revendication 9, dans lequel le sel de cuivre 11 comprend au moins l'un du sulfate de cuivre, du sulfonate de cuivre, du chlorure de cuivre, du nitrate de cuivre et leurs mélanges.

11. Procédé de la revendication 9, dans lequel l'anolyte fournit un transport de cuivre d'ions de cuivre à travers la membrane ionique entre 90% et 100%.

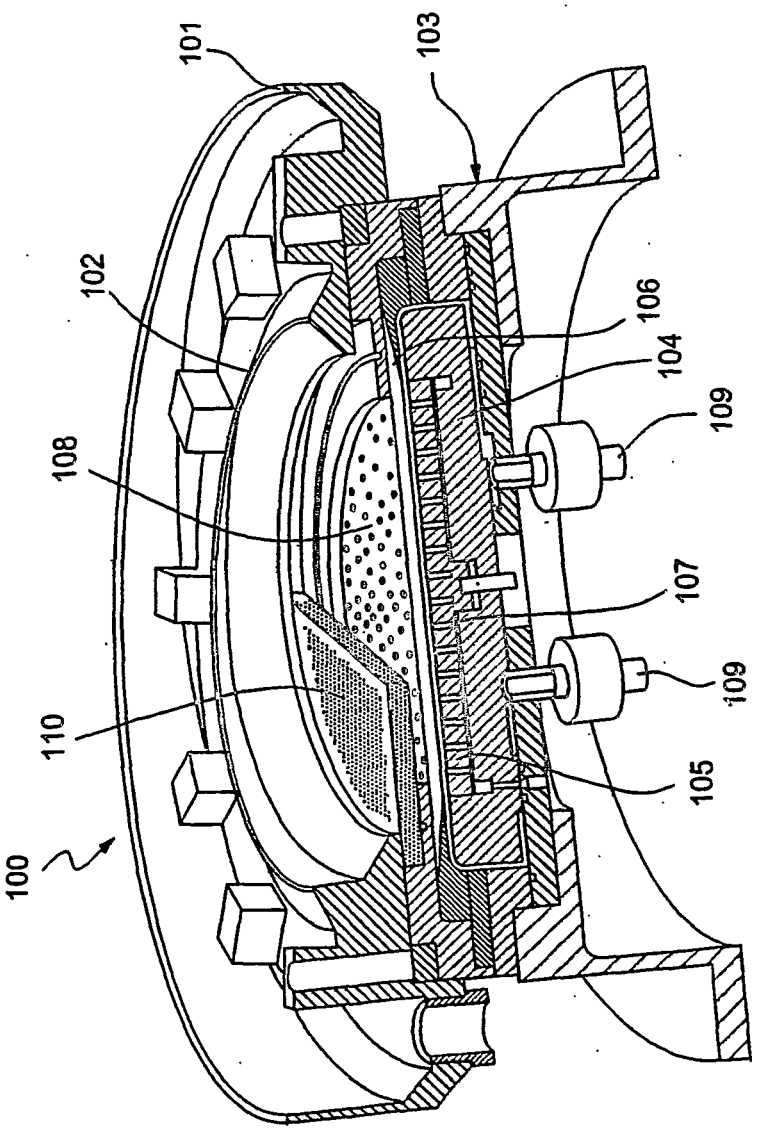


FIG. 1

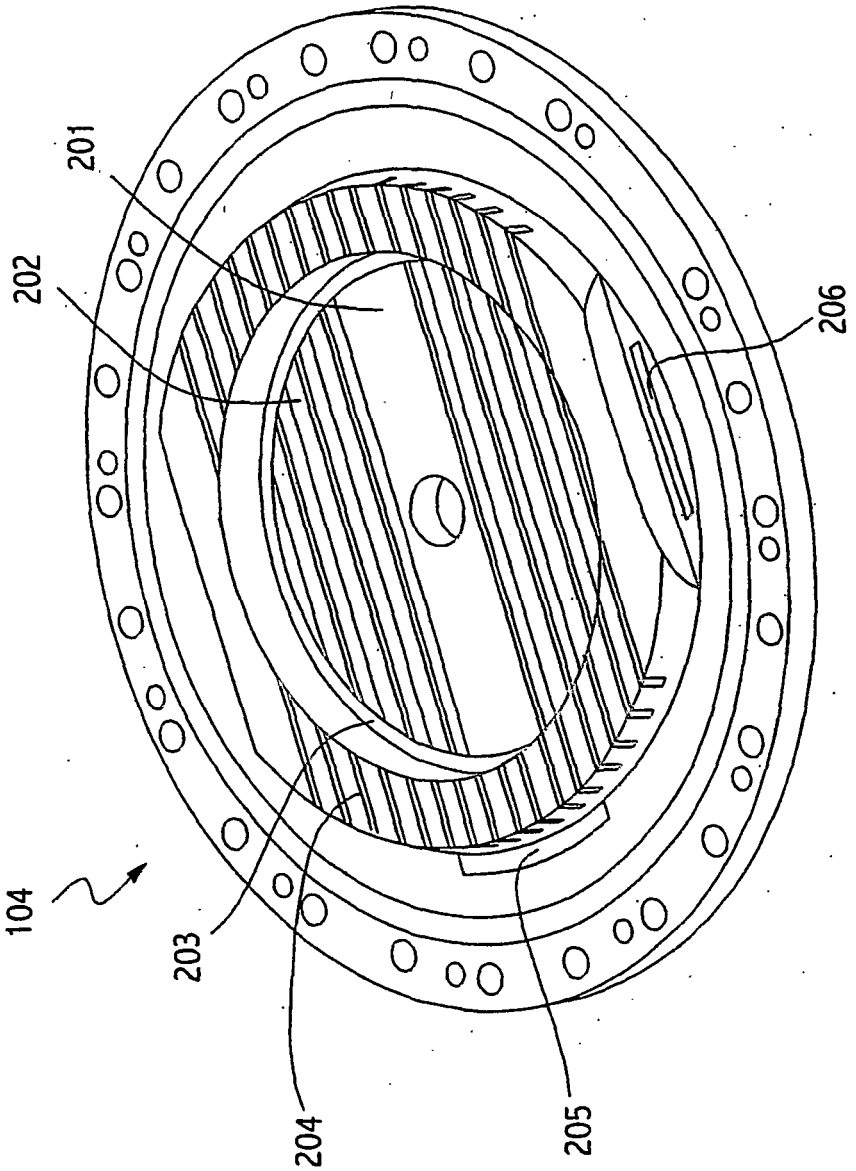


FIG. 2

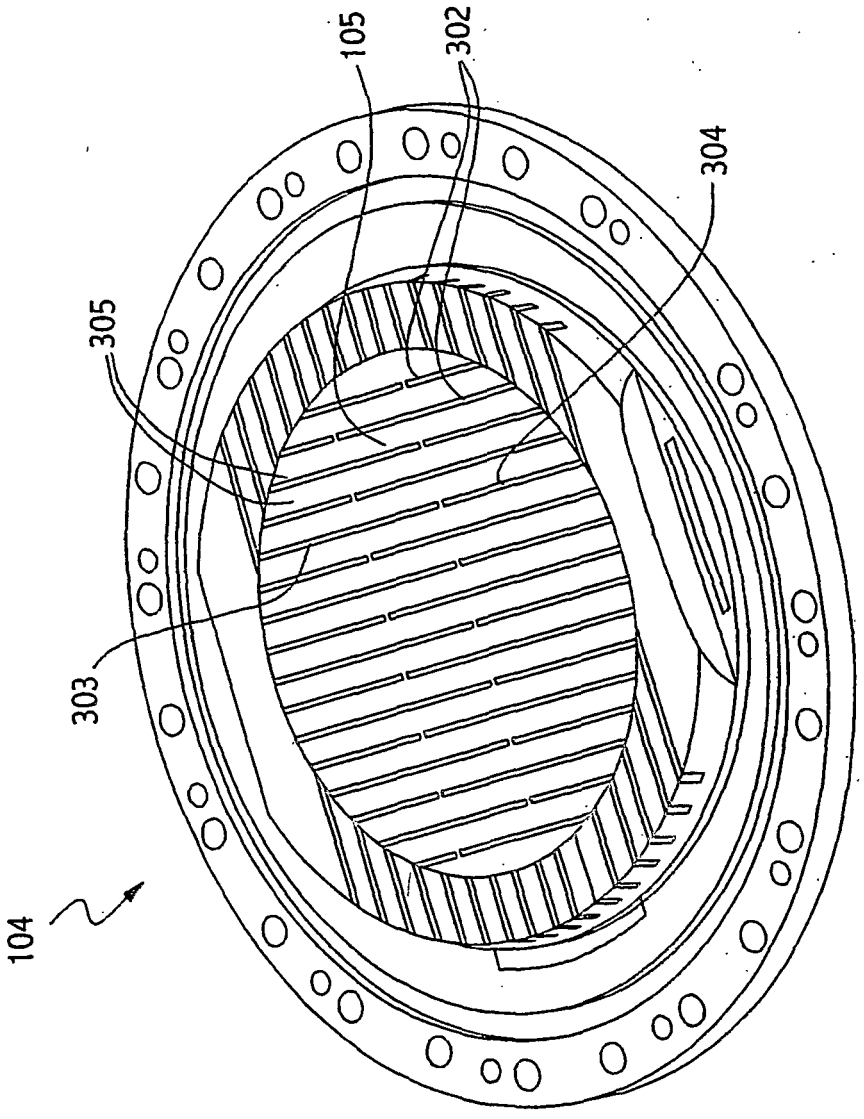


FIG. 3

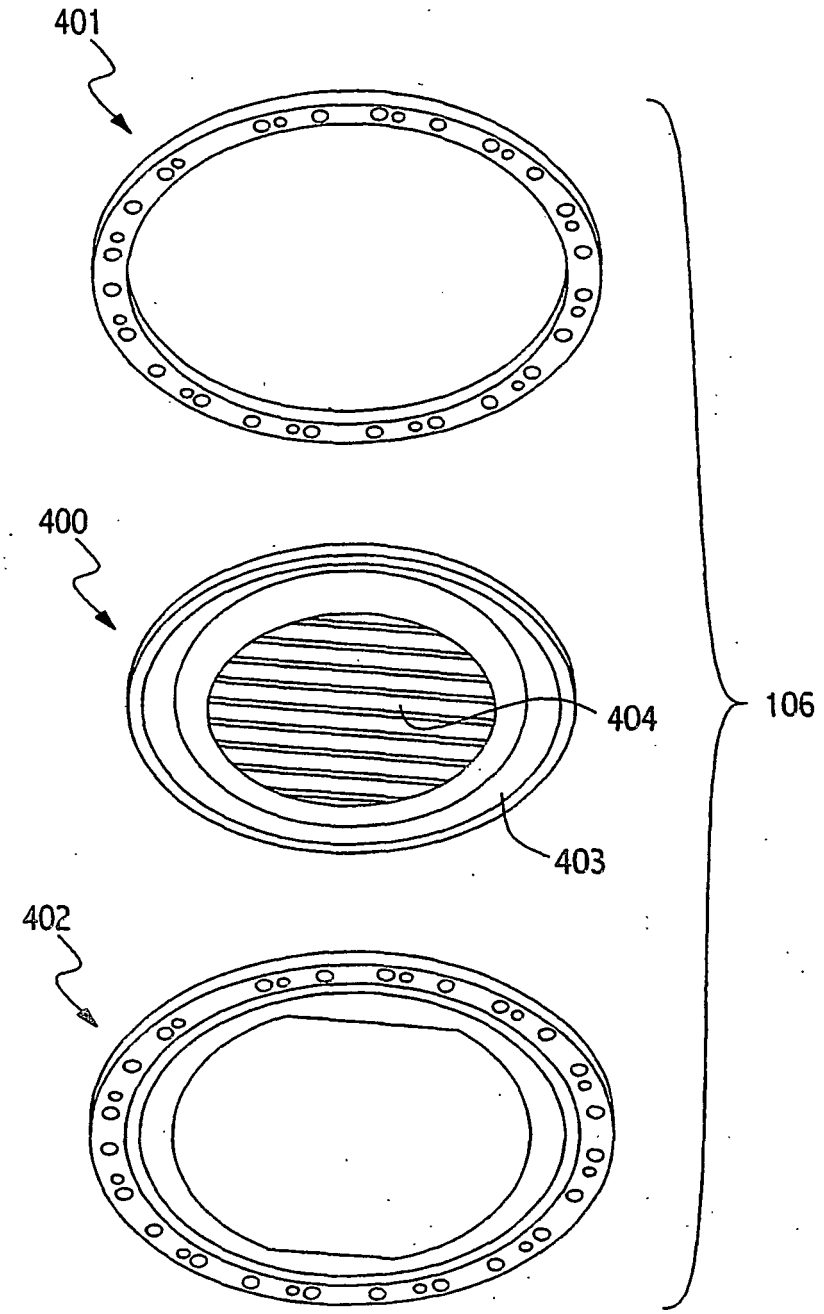


FIG. 4

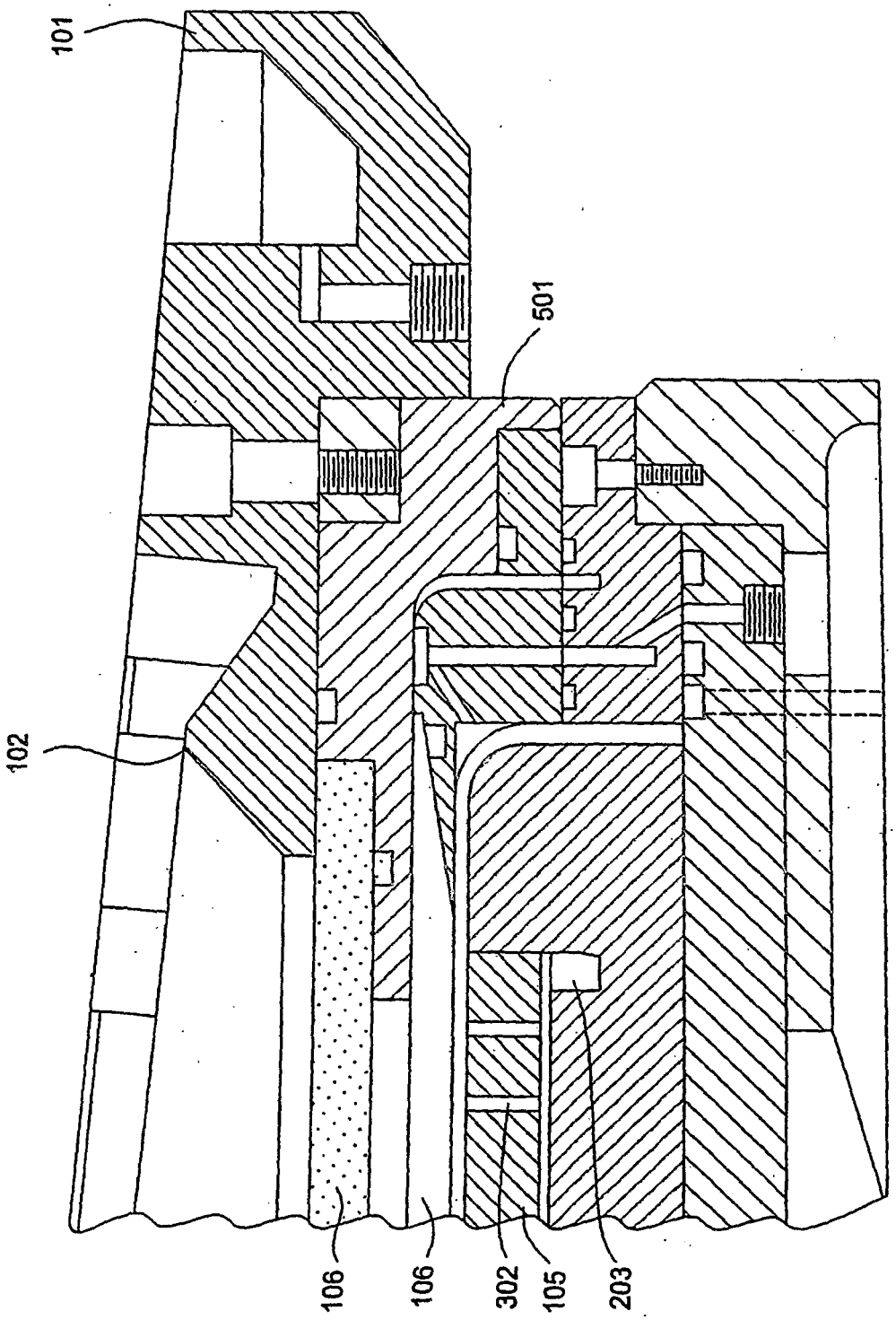


FIG. 5

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 5883762 A **[0007]**