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(54) **INSOLUBLE ANODE LOOP IN COPPER ELECTRODEPOSITION CELL FOR INTERCONNECT FORMATION**

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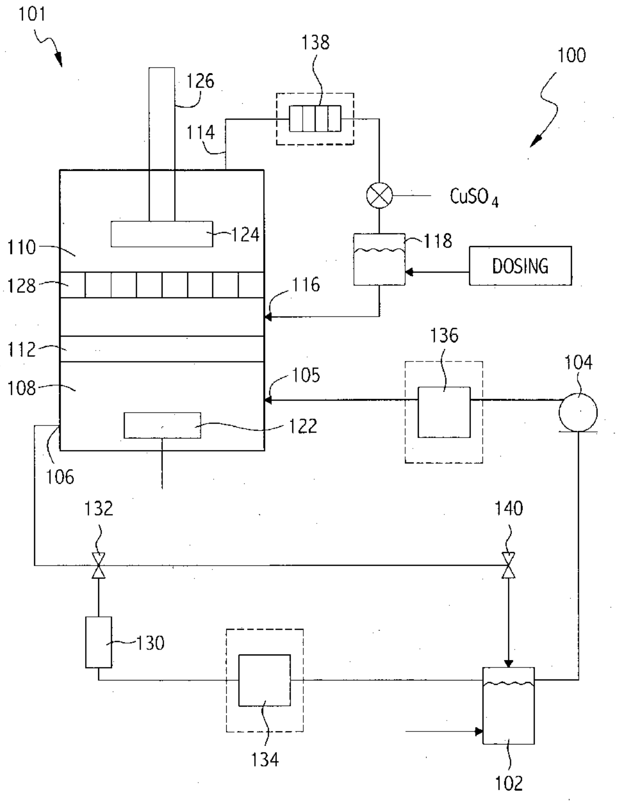
(57) **ABSTRACT**

Embodiments of the invention generally provide a method and apparatus for plating a metal on a substrate. The electrochemical plating system generally includes a plating cell having an anolyte compartment and a catholyte compartment, the anolyte compartment having an insoluble anode and an anolyte therein. The catholyte compartment generally includes a substrate support member and a catholyte therein. In addition, the plating cell generally includes an ion-exchange membrane disposed between the anolyte compartment and the catholyte compartment and a pump in fluid communication with the anolyte compartment, the pump configured to provide an anolyte to the anolyte compartment having a linear velocity of between about 0.5 cm/sec to about 50 cm/sec. The method generally includes supplying an anolyte solution to an anolyte compartment disposed in a plating cell having an anolyte compartment and a catholyte compartment. The anolyte solution generally passes through the anolyte compartment at a linear velocity of between about 0.5 cm/sec to about 50 cm/sec. The method further includes plating a metal onto the substrate with a catholyte solution disposed in a catholyte compartment of the plating cell, the catholyte compartment and the anolyte compartment separated by an ion-exchange membrane, removing used anolyte solution from the plating cell and passing at least a portion of the used anolyte solution through a correction device including at least one of copper oxide, copper hydroxide and combinations thereof.



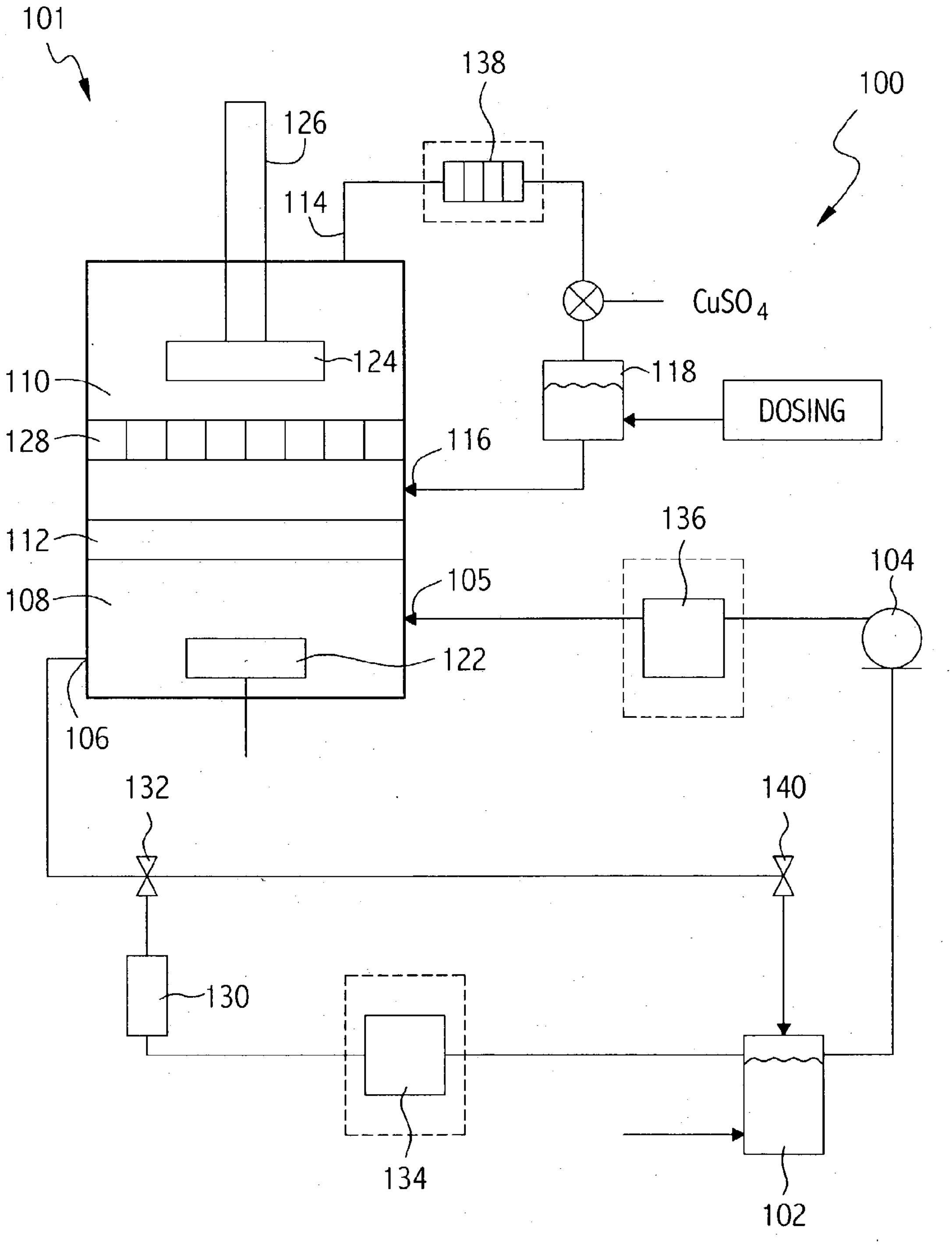

101
138
100
126
114
CuSO 4
124
118
110
DOSING
128
116
136
112
104
105
108
122
106
132
140
130
134
102

FIG. 1

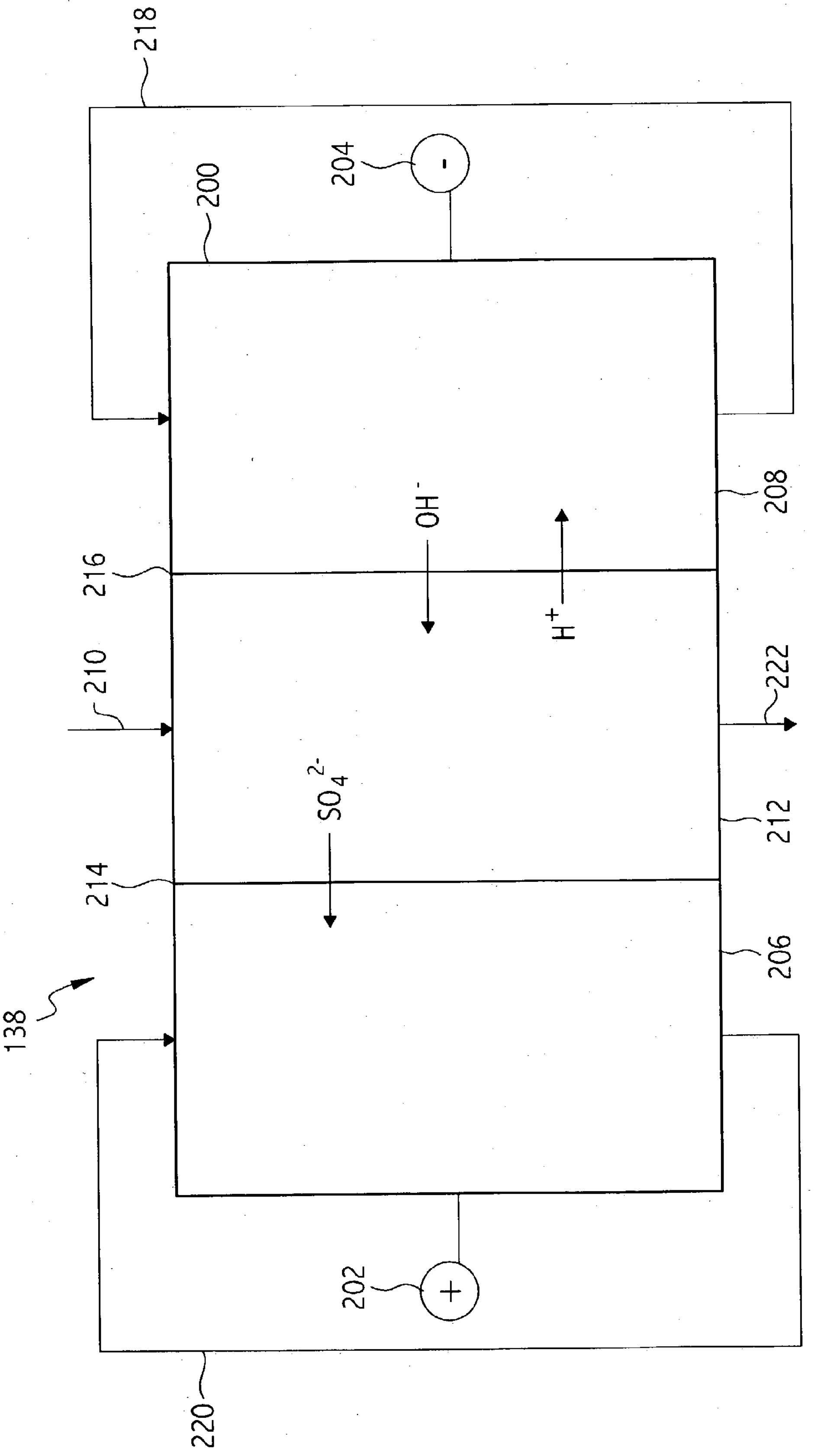


FIG. 2

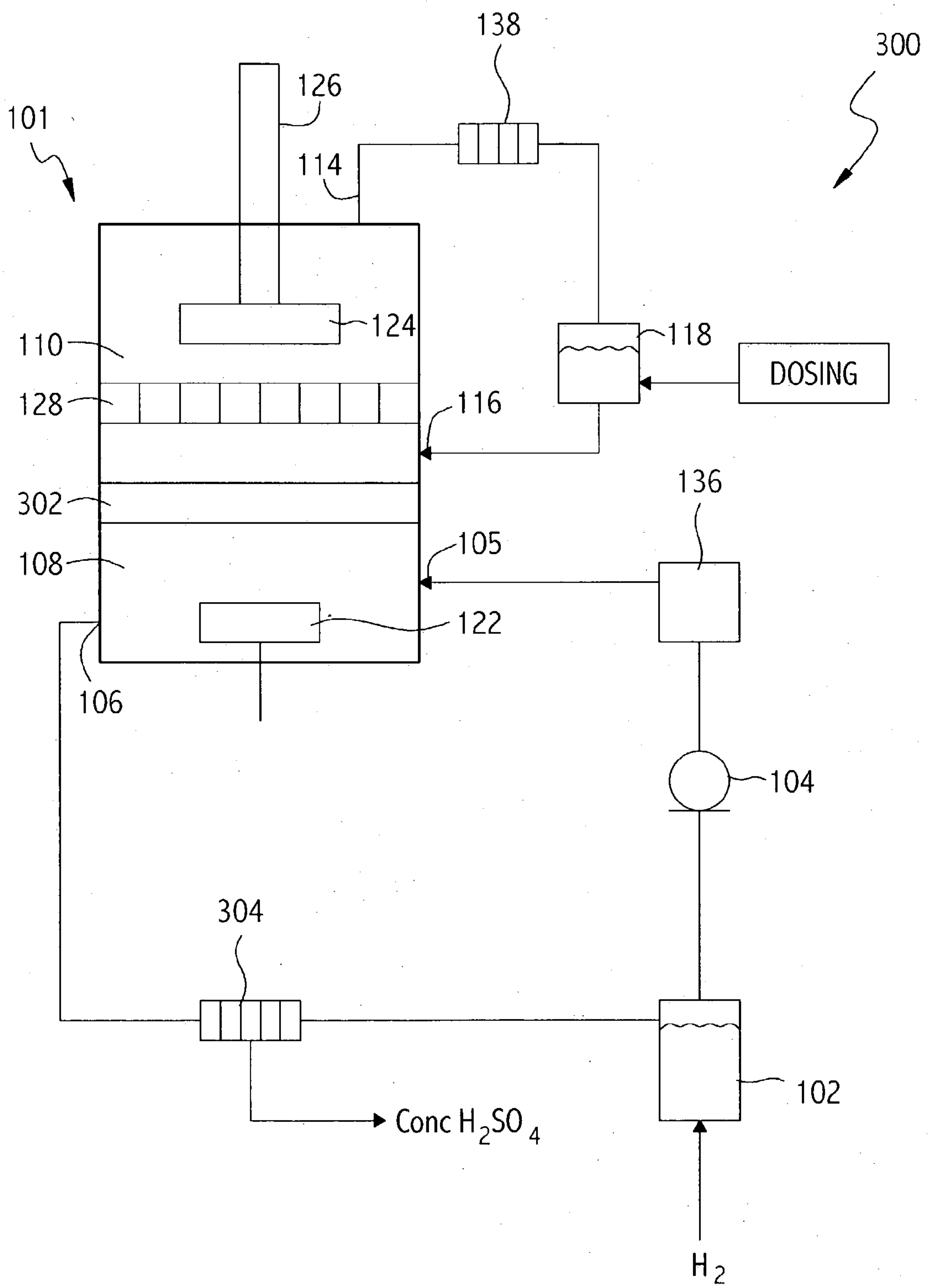

138
300
126
101
114
124
110
118
DOSING
128
116
302
136
105
108
122
106
104
304
102
Conc H_2SO_4
H_2

FIG. 3

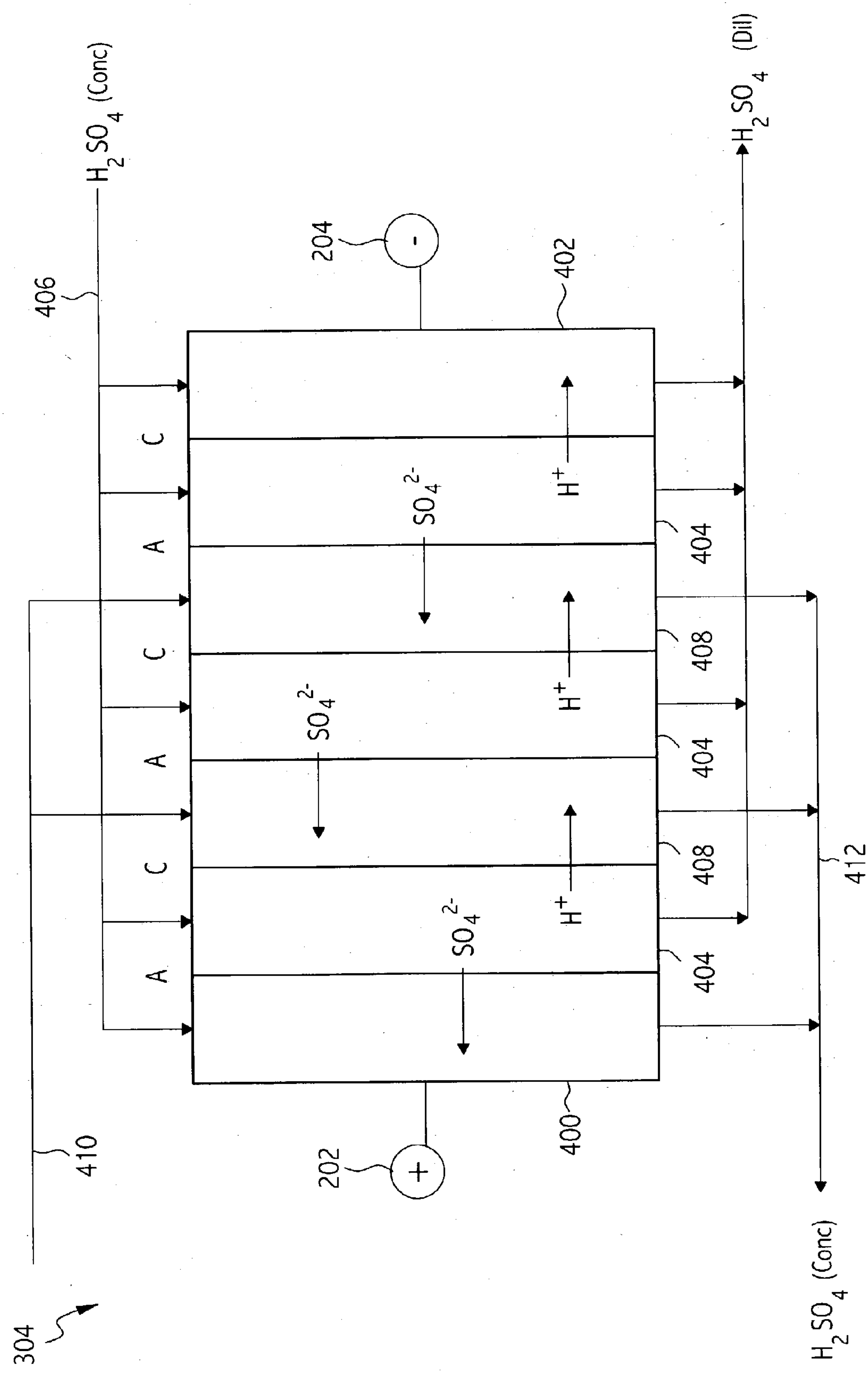

H_2SO_4 (Conc)
406
204
-
402
H_2SO_4 (Dil)
C
A
C
A
C
A
SO_4^{2-}
SO_4^{2-}
SO_4^{2-}
H^+
H^+
H^+
404
408
404
408
404
412
410
202
+
400
H_2SO_4 (Conc)
304

FIG. 4

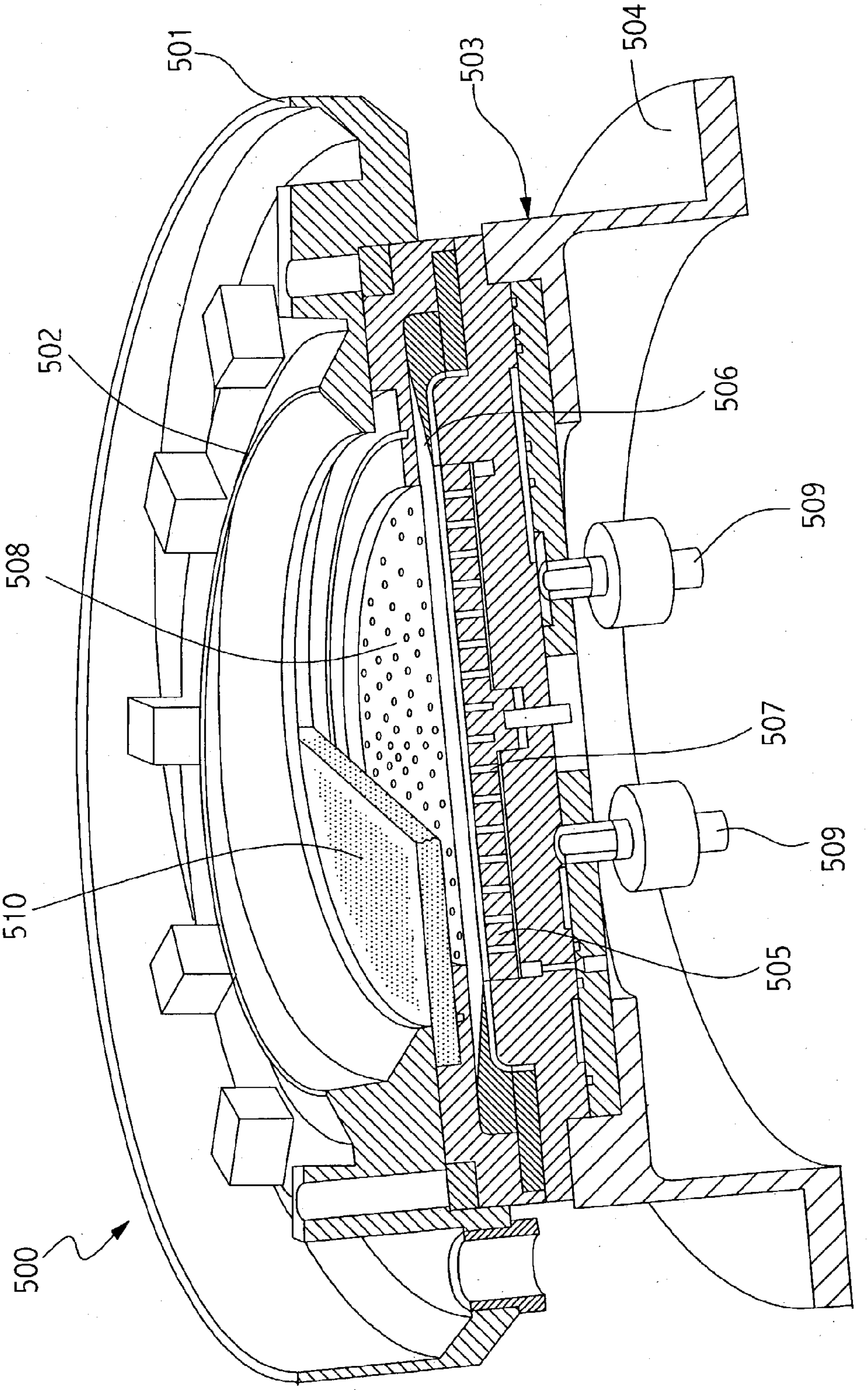


FIG. 5

INSOLUBLE ANODE LOOP IN COPPER ELECTRODEPOSITION CELL FOR INTERCONNECT FORMATION

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims benefit of U.S. provisional patent application No. ______ entitled Isoluble Anode Loop in Copper Electrodeposition Cell For Interconnect Formation, filed Aug. 6, 2002 which is herein incorporated by reference.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] Embodiments of the present invention generally relate to the removal and reduction of oxygen in an electrochemical plating system.

[0004] 2. Description of the Related Art

[0005] Metallization for sub-quarter micron sized features is a foundational technology for present and future generations of integrated circuit manufacturing processes. 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 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 interconnect sizes decrease and aspect ratios increase, void-free interconnect feature fill via conventional metallization techniques becomes increasingly difficult. As a result thereof, plating techniques, such as electrochemical plating (ECP) and electroless plating, for example, have emerged as viable processes for filling sub-quarter micron sized high aspect ratio interconnect features in integrated circuit manufacturing processes.

[0006] In an ECP process sub-quarter micron sized high aspect ratio features formed on a substrate surface 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 simultaneously applied between the substrate and an anode positioned within the electrolyte solution. The electrolyte solution is generally rich in ions to be plated onto the surface of the substrate. Therefore, the application of the electrical bias causes these ions to be urged out of the electrolyte solution and to be plated as a metal on the seed layer. The plated metal, which may be copper, for example, grows in thickness and forms a copper layer that fills the features formed on the substrate surface.

[0007] In order to facilitate and control this plating process, several additives may be utilized in the electrolyte plating solution. For example, a typical electrolyte solution used for copper electroplating may consist of copper sulfate solution, which provides the copper to be plated, having sulfuric acid and copper chloride added thereto. The sulfuric acid may generally operate to modify the acidity and conductivity of the solution. The electrolytic solutions also generally contain various organic molecules, which may be accelerators, suppressors, levelers, brighteners, etc. These organic molecules are generally added to the plating solution in order to facilitate void-free super-fill of high aspect ratio features and planarized copper deposition.

[0008] Furthermore, conventional systems may utilize a soluble metal anode to provide a continuous supply to metal ions for electrolyte replenishment. However, anode dissolution has disadvantages such as undesirable side products, e.g., sludge and copper ball formation, and undesirable side effects, e.g., anode passiviation, non-uniform anode dissolution, and consumption/breakdown of organic additives. Therefore, an insoluble anode may be utilized in electrochemical plating systems. However, the electrical bias applied to the anode may cause oxygen to form, thereby saturating the plating solution with oxygen and oxygen bubbles. Oxygen bubbles may cause undesirable side-effects, such as non-uniformity of the copper deposit distribution, formation of bubbles on the substrate, and blockage of the anode and membranes present in the plating cell. Therefore, there is a need for a method and apparatus that minimize the formation and effects of oxygen in semiconductor electroplating baths, wherein the method and apparatus addresses the deficiencies of conventional devices.

SUMMARY OF THE INVENTION

[0009] Embodiments of the present invention generally relate to an electrochemical plating system. The electrochemical plating system generally includes a plating cell having an anolyte compartment and a catholyte compartment, the anolyte compartment having an insoluble anode and an anolyte therein. The catholyte compartment generally includes a substrate support member and a catholyte therein. In addition, the plating cell generally includes an ion-exchange membrane disposed between the anolyte compartment and the catholyte compartment and a pump in fluid cocmunication with the anolyte compartment, the pump configured to provide an anolyte to the anolyte compartment having a linear velocity of between about 0.5 cm/sec to about 50 cm/sec.

[0010] Embodiments of the invention further include an electrochemical plating system including a cation exchange membrane disposed between the anolyte compartment and the catholyte compartment, the cation exchange membrane being selective to hydrogen ions and copper ions. The electrochemical plating system may further include a correction device in fluid communication with the anolyte compartment, the correction device including at least one of copper hydroxide, copper oxide, and combinations thereof configured to neutralize excess acid in the anolyte.

[0011] Embodiments of the invention further include a method for plating a metal on a substrate. The method generally includes supplying an anolyte solution to an electrochemical plating cell having an anolyte compartment and a catholyte compartment. The anolyte solution generally passes through the anolyte compartment at a linear velocity of between about 0.5 cm/sec to about 50 cm/sec. The method further includes plating a metal onto the substrate with a catholyte solution disposed in the catholyte compartment, the catholyte compartment and the anolyte compartment being separated by an ion-exchange membrane, removing used anolyte solution from the plating cell and passing at least a portion of the used anolyte solution through a correction device including at least one of copper oxide, copper hydroxide, and combinations thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

[**0012**] 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.

[**0013**] **FIG. 1** illustrates a plating system for use in embodiments of the present invention.

[**0014**] **FIG. 2** illustrates a schematic view of an exemplary catholyte EDC.

[**0015**] **FIG. 3** illustrates a plating system incorporating an anionic membrane.

[**0016**] **FIG. 4** illustrates an embodiment of an exemplary anolyte EDC.

[**0017**] **FIG. 5** illustrates a perspective and partial sectional view of an exemplary electrochemical plating cell.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[**0018**] **FIG. 1** illustrates a plating system **100** for use in embodiments of the present invention. The plating system **100** generally includes a plating cell **101**, which may be an electrochemical plating (ECP) cell for copper superfill plating or another electroplating cell configuration known in the semiconductor art. The ECP cell **101** is generally configured to fluidly isolate an anode **122** of the plating cell **101** from a cathode **124** or plating electrode of the plating cell **101** via a membrane **112** positioned between the substrate **123** being plated and the anode **122** of the plating cell **101**. Additionally, the plating cell **101** is generally configured to provide a first plating solution (anolyte) to an anolyte compartment **108**, i.e., the volume between the upper surface of the anode **122** and the lower surface of the membrane **112**, and a second fluid solution (catholyte) to a catholyte compartment **110**, i.e., the volume of fluid positioned above the upper membrane surface. In addition, the plating cell **101** further includes an anolyte inlet **105** configured to deliver the anolyte to the plating cell **101** and an anolyte outlet or drain **106** configured to remove anolyte from plating cell **101**.

[**0019**] A rotating head **126** configured to expose a substrate deposition surface to the plating solution generally supports the cathode electrode **124**. The anode **122** is generally insoluble and is not consumed in the plating process. The anode **122** may have a large surface area, thereby increasing contact with the plating solution. For example, the anode **122** may be a porous wire mesh, a sieve, or a metal grid formed of carbon fibers, carbon wool, sintered metal, or metallic titanium nitride fibers. The anode **122** may also be a thin disk or ring formed of titanium or a solid platinum foil. The anode **122** may further include a coating of platinized platinum, platinum iridium, platinum alloys or other noble metals stable in an acid medium under oxygen electroformation.

[**0020**] The membrane **112** is generally configured to prevent anode by-products from entering the catholyte compartment **110**, thereby increasing plating performance by decreasing the amount of defects present on the plated substrate. In addition, the membrane **112** generally prevents organic additive diffusion from the catholyte compartment **110** to the anolyte compartment **108**. Preventing additive migration to the anolyte compartment **108** prevents additive breakdown and contamination generally caused by additive contact with the anode **122**. The membrane **112** may include an ion exchange membrane, such as a cation exchange membrane or an anion exchange membrane.

[**0021**] These membranes may be one of many commercially available membranes. For example, Tokuyama Corporation manufactures and supplies various hydrocarbon membranes for electrodialysis and related applications under the trade name "Neosepta." Perfluorinated cation membranes, which are stable to oxidation and useful when it is necessary to separate an insoluble anode compartment by a cation membrane, are generally available from DuPont Co as Nafion membranes N-117, N-450, or from Asahi Glass Company (Japan) under the trade name Flemion as Fx-50, F738, and F893 model membranes. Asahi Glass Company also produces a wide range of polystyrene based ion-exchange membranes under the trade name Selemion, which can be very effective for concentration/desalination of electrolytes and organic removal (cation membranes CMV, CMD, and CMT and anion membranes AMV, AMT, and AMD). There are also companies that manufacture similar ion-exchange membranes (Solvay (France), Sybron Chemical Inc. (USA), lonics (USA), and FuMA-Tech (Germany) etc.). Further, in order to minimize the penetration of copper ions into cathode compartment, it may be helpful to separate this compartment by a bipolar ion-exchange membrane that is made from cation and anion membranes compiled together. Bipolar membranes, such as models AQ-BA-06 and AQ-BA-04, for example, are commercially available from Aqualitics (USA) and Asahi Glass Co.

[**0022**] In operation, the membrane **112** generally does not contact the anode **122**. Contact with the anode **122** generally affects plating performance and anode **122** operation. Therefore, the membrane **112** generally has a distance from the anode **122** of greater than about 0.1 mm. Preferably, the membrane **112** has a distance from the anode **122** of from about 0.5 mm to about 10 mm.

[**0023**] In certain embodiments, the plating cell **101** may further include a diffuser **128** disposed between a catholyte inlet **116** and the cathode **124**. The flow diffuser **128** provides a substantially uniform vertical velocity of plating solution across the width of the plating cell **101** above the flow diffuser **128**. The uniformity of plating conditions across the substrate **123** will therefore be enhanced due to the more uniform fluid flow conditions. The flow diffuser **128** is constructed to be substantially rigid. In this disclosure, the term "rigid" indicates sufficient structural rigidity of the diffuser to limit sufficient deformation or bending of the diffuser, under the normal operating conditions in the process cell, which would alter the electric resistance between the anode and a seed layer deposited on the substrate deposition surface. Such deformation would bend the diffuser **128** so the center of the diffuser **128** is nearer the nearest location on the substrate **123** than the periphery of the diffuser **128** is to its closest location on the substrate **123**. The flow diffuser **128** is preferably formed from microscopic, generally spherical, ceramic particles that are sintered to the adjacent spherical ceramic particles of the flow diffuser **128** at the points of spherical contact. Ceramic is a naturally hydrophilic material. Other suitable, substantially rigid, materials may also be utilized. Voids or spaces are formed between the adjacent ceramic particles. The diffuser **128** is designed with pores having dimensions of from about 0.1 microns to about 500 microns. Since the fluid flow resistance through a flow diffuser **128** is a function of the distance that the fluid travels through the flow diffuser **128**, the vertical height of the diffuser **128** can be altered to provide desired fluid flow characteristics. For example, a thicker flow diffuser **128** with the same pore dimensions will provide an increased resistance to fluid flow through the flow diffuser **128** to provide a more restricted fluid flow through the flow diffuser **128** having similar pore dimensions. Although a flow diffuser is described herein, any structure configured to provide uniform flow known to one skilled in the art may be used.

[**0024**] The exemplary **100** plating system illustrated in **FIG. 1** generally includes a cation exchange membrane **112**. The cation exchange membrane **112** generally is selective to positively charged ions, e.g., hydrogen ions (H^+) and copper ions (Cu^{2+}); therefore the H^+ and Cu^{2+} migrate from the anolyte compartment **108** to the catholyte compartment **110**. Generally, the ions migrating from the anolyte compartment **108** to the catholyte compartment **110** should include from about 95% to about 98% Cu^{2+} ions. The Cu^{2+} migration is generally necessary to compensate for copper losses in the catholyte solution due to copper plating. As a result of copper migration, the anolyte copper concentration decreases and becomes more acidic over time.

[**0025**] When utilizing a cation exchange membrane **112**, the anolyte generally includes from about 0.05 M to about 1 M copper sulfate and a minimal amount of acid, e.g., an amount sufficient to provide an anolyte pH of from about 2 to about 6, and more preferably to provide a pH of from about 2.5 to about 4. The acid may include sulfuric acid, phosphoric acid, and/or derivatives thereof. In addition to, copper sulfate, the plating solution may include other copper salts, such as copper fluoborate, copper gluconate, copper sulfamate, copper sulfonate, copper pyrophosphate, copper chloride, or copper cyanide, for example. However, embodiments of the invention are not limited to these parameters. The anolyte may further include salts, such as metal ligands or complexing agents, to prevent anode passivation or to reduce anode sludge formation.

[**0026**] The catholyte generally includes copper sulfate, sulfuric acid, and a small amount of copper chloride, e.g., from about 20 ppm to about 80 ppm. The plating solution may further include one or more additives. Additives, which may be, for example, levelers, inhibitors, suppressors, brighteners, accelerators, or other additives known in the art, typically adsorb onto the surface of the substrate **123** being plated. Useful suppressors generally include polyethers, such as polyethylene glycol, or other polymers, such as polyethylene-polypropylene oxides, which adsorb on the substrate surface, slowing down copper deposition in the adsorbed areas. Useful accelerators generally include sulfides or disulfides, such as bis(3-sulfopropyl) disulfide, which compete with suppressors for adsorption sites, accelerating copper deposition in adsorbed areas. Useful levelers generally include thiadiazole, imidazole, and other nitrogen containing organics. Useful inhibitors typically include sodium benzoate and sodium sulfite, which inhibit the rate of copper deposition on the substrate **123**. During plating, the additives are consumed at the substrate surface, but are being constantly replenished by the plating solution. However, differences in diffusion rates of the various additives result in different surface concentrations at the top and the bottom of features, thereby setting up different plating rates in features in the substrate **123**. Ideally, these plating rates should be higher at the bottom of the feature for bottom-up fill. Thus, an appropriate composition of additives in the plating solution is required to achieve a void-free fill of the features.

[**0027**] The anolyte is delivered to the plating cell **101** via anolyte inlet **105**, which is in fluid communication with an anolyte storage unit **102**. A fluid pump **104** is generally positioned between the anolyte storage unit **102** and the plating cell **101** and is configured to deliver the anolyte to plating cell **101** at a high linear flow rate. Generally, the anolyte enters the anolyte compartment **108** at a flow rate sufficient to prevent oxygen saturation of the anolyte by minimizing the anolyte residence time in the anolyte compartment **108**. For example, the flow rate of the anolyte may be between about 0.5 L/min and about 20 L/min, and more particularly is between about 1 L/min and about 10 L/min. The anolyte flow rate will generally depend upon the anolyte inlet **105** diameter. For example, the larger the inlet, the lower the required anolyte flow rate.

[**0028**] In addition, the anolyte flow rate generally results in a desired linear velocity of from about 0.5 cm/sec to about 50 cm/sec. The linear velocity at the anode **122** surface is a function of the anolyte flow rate, the anode diameter, and the distance between the anode **122** and the membrane **112**. Therefore, the anolyte flow rate generally varies as a function of the anode **122** cross-sectional area, i.e., the flow rate will be different for a 200 cm substrate versus a 300 cm substrate. A high anolyte flow rate generally operates to reduce oxygen bubble formation at the anode **122** and excessive acidification of the anolyte as a result of a shorter anolyte residence time near the anode **122**, e.g., the anolyte is passing through the plating cell **101** faster than the time needed for oxygen saturation. Furthermore, any oxygen formed in the anolyte is removed from the anolyte compartment **108** by the high flow of anolyte passing therethrough.

[**0029**] Although the high flow rate generally eliminates oxygen formation, systems utilizing lower anolyte flow rates may require additional treatment. Therefore, the anolyte outlet **106** may be generally in fluid communication with an input of a column **130**, that has an output thereof, which is in fluid communication with a filter **134**. Column **130** may include more than one column, wherein one column contains copper oxide (CuO) and another column contains copper hydroxide ($Cu(OH)_2$). When utilizing more than one column, valves may control the flow of anolyte so that the anolyte may flow through either column depending on the desired pH level of anolyte in the tank **102**. **FIG. 1** shows a single column, preferably including $Cu(OH)_2$, although any number of columns may be used depending on system requirements. Generally, the system **100** illustrated in **FIG. 1** includes passing the anolyte to a valve **132** disposed between the anolyte outlet **106** and the column **130**. The flow of anolyte to the column **130** may be split by the valve **132** and controlled by valves **132** and **140**, with the remaining flow of anolyte passing to the anolyte storage tank **102**. Determining the flow of anolyte through the column **130** may include monitoring the pH of the anolyte in the anolyte storage tank **102**. As the pH of the anolyte increases, with an anolyte pH of from about 2 to about 6 being preferable, a larger volume of anolyte may flow through the column **130**.

[**0030**] The column **130** generally includes a housing having either CuO or $Cu(OH)_2$, in powder or solid form, disposed therein. The powder may be in a cartridge, supported by a mesh support member, or supported by another means known to one skilled in the art.

[**0031**] In operation, passing the anolyte through a column **130** containing copper oxide or copper hydroxide results in the following reactions:

$$CuO+H_2SO_4=H_2O+CuSO_4 \quad (1)$$

$$Cu(OH)_2+H_2SO_4=2H_2O+CuSO_4 \quad (2)$$

[**0032**] The copper oxide or hydroxide dissolves upon contact with excess acid, thereby converting the excess acid present in the anolyte into copper sulfate. Although described in terms of a column, the excess acid in the anolyte may be neutralized by any means known to one skilled in the art. The anolyte may subsequently be passed through a filter **134** configured to remove copper oxide and copper hydroxide remaining in the anolyte solution. For example, the anolyte may be passed through a filter **134**. Upon treatment, the anolyte generally has a pH of from about 2.6 to about 3.6. The filter **134** is generally in fluid communication with the anolyte storage unit **102**. Furthermore, prior to passing the anolyte from the anolyte storage unit **102** to the plating cell **101**, the anolyte may be passed through a removal device, such as a degasser **136**. The degasser **136** is generally configured to remove at least of portion of dissolved gases, such as oxygen and nitrogen, from the anolyte prior to entry into the anolyte compartment **108**.

[**0033**] Additionally, a catholyte outlet **114** may be in fluid communication with an input of an electrodialysis cell (EDC) **138**, which may have an output thereof, which is in fluid communication with the catholyte storage unit **118**. The catholyte is recirculated to the catholyte compartment via a catholyte inlet **116**.

[**0034**] Generally, the EDC chamber **138** is configured to receive a portion of the used catholyte returning from plating cell **101** to catholyte storage unit **118**. The received portion of used catholyte is neutralized within the EDC **130** resulting in a restored catholyte, which may then be reintroduced into the catholyte storage unit **118** for subsequent use in plating operations. Although the exemplary EDC illustrated in **FIG. 1** receives the entire used catholyte passing through outlet **114**, it is contemplated that various configurations of EDCs may be implemented, which may receive only a portion of the used catholyte, e.g., via a slipstream type configuration.

[**0035**] **FIG. 2** illustrates a schematic view of an exemplary catholyte EDC **138**. The exemplary EDC **138**, for example, may be implemented into an ECP system configured to plate copper onto semiconductor substrates. The exemplary EDC **138** generally includes an outer housing **200** configured to hold or confine the essential elements of EDC **138**. A first end of housing **200** generally includes a copper anode source **202**, while a second end of housing **200** generally includes a cathode source **204**. The anode source **202** and cathode source **204** are generally positioned on opposite/opposing ends of the housing **200**. The volume between the cathode source **204** and anode source **202** within the housing **200** generally includes a plurality of chambers, wherein the chambers generally include an anode chamber **206** and a cathode chamber **208** corresponding to the anode **202** or cathode **204** positioned in the respective end of housing **200**. Used catholyte is supplied to EDC cell **138** via conduit **210**. Conduit **210** supplies the used catholyte into an input chamber **212** in the EDC cell **138**. Selectively permeable membranes individually separate the respective chambers.

[**0036**] An anion membrane **214**, which is selective and penetrable preferably to univalent anions, especially to $SO4^{2-}$, generally separates the anode chamber **206** and the input chamber **212**. A bipolar membrane **216** separates the input chamber **212** and the cathode chamber **208**. The cathode chamber **208** and anode chamber **206** may be supplied with a sulfuric acid solution via conduits **218** and **220**, which operate to circulate the acid solution through the respective chamber. The sulfuric acid generally is dilute. Therefore, an additional conduit (not shown) may supply deionized water to the respective chambers or to conduits **218** and **220**.

[**0037**] In operation, an electrical bias is applied across EDC cell **128** via anode **202** and cathode **204**. Generally the voltage drop between the cathode **204** and anode **202** is from about 0.4 volts to about 1.5 volts. The application of the electrical bias across EDC cell **128** operates to urge ions in the used catholyte solution towards the respective poles, i.e., positive ions will be urged in the direction of the cathode **204**, while negative ions will be urged in the direction of the anode **202**. Therefore, the disassociated sulfate ions from the used catholyte, which are generally illustrated as $SO4^{2-}$ in **FIG. 2**, are urged in the direction of anode **202** out of the used catholyte solution. Similarly, disassociated hydroxide ions, which are generally illustrated as OH^-, are urged in the direction of anode **202** and disassociated hydrogen ions, which are generally illustrated as H^+ ions are urged in the direction of the cathode **204**. Furthermore, although Cu^{2+} also penetrates the membrane **216**, the amount is negligible because the rate of H^+ migrating to the cathode chamber **208** is about 100 times greater than the copper ion migration. The hydroxide ions neutralize the excess acid present in the catholyte. In addition, the bipolar membrane **216** allows for removal of H^+ ions from the used catholyte to further neutralize the excess acid. The formed acidic copper sulfate solution may then be removed from input chamber **212** via conduit **222** and re-circulated into the plating system (or an electrolyte solution tank, etc.), as $CuSO_4/H_2SO_4$ are primary elements of an electrolyte solution for a copper electroplating system. Therefore, EDC **138** generally operates to receive used electrolyte from a plating system and separate viable components (copper sulfate and sulfuric acid) from the used catholyte for reuse in the plating system. Although the excess acid is neutralized upon treatment, the copper in the catholyte may remain depleted. Therefore, copper sulfate, along with additives may be added to the catholyte storage tank **118**. In addition, dry copper sulfate may be added to the catholyte either prior to dosing in the catholyte storage unit **118** or after storage. In addition, alternative embodiments of the EDC **138** may be implemented to further correct the copper concentration. The alternative EDC may utilize a cation membrane rather than an anion membrane and circulate a concentrated copper sulfate solution through anode chamber **206** to provide Cu^{2+} migration through the membrane and into the used catholyte.

[**0038**] **FIG. 3** illustrates a plating system **300** incorporating an anionic membrane **302**. The plating system **300** varies from that shown in **FIG. 1** in that the anolyte generally is a diluted acid solution, e.g., from about 0.05 M to about 0.1M. The acid generally is sulfuric acid. The anolyte may further include an organic or inorganic component reducer. For example, the anolyte may include dissolved gaseous hydrogen, hydroquinone, formic acid, Fe^{2+}, Kl, or Mn^{2+}, or combinations thereof. When gaseous hydrogen is included in the anolyte, the anolyte is generally saturated with hydrogen in the anolyte storage tank **102**. The component reducer generally reduces on the anode **122** through the following reaction, thereby limiting oxygen production:

$$H^+{=}H_2{+}2e^- \quad (3)$$

[**0039**] When utilizing an anionic membrane **302**, the excess acid in the anolyte is generally neutralized. Therefore, the system **300** can include an EDC **304** in fluid communication with the anolyte outlet **106**. **FIG. 4** illustrates an embodiment of an exemplary anolyte EDC **304**. EDC **304** is similarly constructed to EDC **138**, in that ELDC **304** includes an anode chamber **400** and a cathode chamber **402**. In similar fashion to ELDC **138**, inlet **404** communicates used or aged anolyte from a plating cell, such as a copper ECP cell, into the input chambers **406** of ELDC **304**. In this configuration, a diluted, e.g., from about 0.01 M to about 0.1 M, sulfuric acid solution may pass through isolation chambers **408** positioned in the anodic direction of the input chambers **404** via conduit **410**.

[**0040**] The membrane structure generally follows an alternating sequence, i.e., from left to right, an anionic membrane, then a cationic membrane, then an anionic membrane, then a cationic membrane, etc. In operation, ELDC **304** operates similarly to ELDC **138** illustrated in **FIG. 2**, as an electrical bias is applied between cathode **204** and anode **202**. The replenished anolyte may then be retrieved from the input chambers **404** via conduit **412** for replenishment. The application of the electrical bias causes positively charged ions in the used anolyte solution to migrate towards the cathode **204**, while negatively charged ions are urged to migrate towards the anode **202**. The configuration of cationic and anionic membranes operates to urge positive hydrogen ions, negative hydroxide ions, and negatively charged sulfate ions between the respective membranes and into the desired chambers as illustrated in **FIG. 4**. The positive hydrogen ions and the negative sulfate ions combine to neutralize excess acid and form a diluted sulfuric acid solution, which may then be extracted from ELDC **304** for reuse in a copper plating system.

[**0041**] **FIG. 5** illustrates a perspective and partial sectional view of an exemplary electrochemical plating cell **500** for use in the embodiments described above. Plating cell **500** generally includes an outer basin **501** and an inner basin **502** positioned within outer basin **501**. Inner basin **502** 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 **502** (at about 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 **502** and runs into outer basin **501**. The overflow plating solution is then collected by outer basin **501** and drained therefrom for recirculation into basin **502**. As illustrated in **FIG. 5**, plating cell **500** is generally positioned at a tilt angle, i.e., the frame portion **503** of plating cell **500** is generally elevated on one side such that the components of plating cell **500** are tilted between about 3° and about 30°. Therefore, in order to contain an adequate depth of plating solution within inner basin **502** during plating operations, the uppermost portion of basin **502** may be extended upward on one side of plating cell **500**, such that the uppermost point of inner basin **502** is generally horizontal and allows for contiguous overflow of the plating solution supplied thereto around the perimeter of basin **502**.

[**0042**] The frame member **503** of plating cell **500** generally includes an annular base member **504** secured to frame member **503**. Since frame member **503** is elevated on one side, the upper surface of base member **504** is generally tilted from the horizontal at an angle that corresponds to the angle of frame member **503** relative to a horizontal position. Base member **504** includes an annular or disk shaped recess formed therein, the annular recess being configured to receive a disk shaped anode member **505**. Base member **504** further includes a plurality of fluid inlets/drains **509** positioned on a lower surface thereof. Each of the fluid inlets/drains **509** are generally configured to individually supply or drain a fluid to or from either the anode compartment or the cathode compartment of plating cell **500**. Plating cell **500** further includes a membrane support assembly **506**. Membrane support assembly **506** is generally secured at an outer periphery thereof to base member **504**, and includes an interior region **508** 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 **506** to the other side of the membrane.

[**0043**] In operation, the plating cell **500** of the invention provides a small volume (electrolyte volume) processing cell that may be used for copper electrochemical plating processes, for example. Plating cell **500** 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 **FIG. 5**. If plating cell **505** 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.

[**0044**] Assuming a tilted implementation is utilized, a substrate is first immersed into a plating solution contained within inner basin **502**. 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 **505** positioned in a lower portion of plating cell **500**. 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 **502** is continually circulated through inner basin **502** via fluid inlet/outlets **509**. More particularly, the plating solution may be introduced in plating cell **500** via a fluid inlet **509**. The solution may travel across the lower surface of base member **504** 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 **500** that communicates with the cathode chamber at a point above membrane support **506**. Similarly, the plating solution may be removed from the cathode chamber via a fluid drain positioned above membrane support **506**, where the fluid drain is in fluid communication with one of fluid drains **509** positioned on the lower surface of base member **504**. For example, base member **504** 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 **504**.

[**0045**] Once the plating solution is introduced into the cathode chamber, the plating solution travels upward through diffusion plate **510**. Diffusion plate **510**, 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 **510** 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 **510** may be replaced by a hydrophilic plastic member, i.e., a treated PE member, an 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, is not permitted to travel downward through the membrane (not shown) positioned on the lower surface **404** of membrane support assembly **506** 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 **506** is not fluid permeable in either direction.

[**0046**] Additionally, the flow of the fluid solution (anolyte) 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 **509**. Fluid inlet **509** is in fluid communication with a fluid channel formed into a lower portion of base member **504** and the fluid channel communicates the anolyte to one of apertures **205**. Thereafter, the anolyte generally travels across the upper surface of the anode **505** towards the opposing side of base member **504**, which in a tilted configuration, is generally the higher side of plating cell **500**. The anolyte travels across the surface of the anode below the membrane positioned immediately above. Once the anolyte reaches the opposing side of anode **505**, it is received into a corresponding fluid channel **204** and drained from plating cell **504** for recirculation thereafter.

[**0047**] During plating operations, the application of the electrical plating bias between the anode and the cathode generally causes a chemical reaction on the anode, resulting in oxygen bubbles in the anolyte. However, the high anolyte flow rate operates to minimize the anolyte residence time at the anode, thereby preventing oxygen saturation. Furthermore, the removal device and the columns operate to remove any formed oxygen in the anolyte.

[**0048**] While the foregoing is directed to embodiments of the present invention, other and further embodiments of the invention may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

What is claimed is:

1. An electrochemical plating system, comprising:

a plating cell having an anolyte compartment and a catholyte compartment, the anolyte compartment having an insoluble anode and an anolyte solution therein, the catholyte compartment having a cathode substrate support member and a catholyte solution therein;

an ion-exchange membrane disposed between the anolyte compartment and the catholyte compartment; and

a pump in fluid communication with the anolyte inlet positioned in fluid communication with the anolyte compartment, the pump being configured to provide an anolyte solution to the anolyte compartment at a linear velocity sufficient to prevent saturation of the anolyte with oxygen.

2. The electrochemical plating system of claim 1, wherein the linear velocity is between about 0.5 cm/sec and about 50 cm/sec.

3. The electrochemical plating system of claim 1, further comprising an anolyte storage unit in fluid communication with the anolyte compartment.

4. The electrochemical plating system of claim 1, further comprising a catholyte storage unit in fluid communication with the catholyte compartment.

5. The electrochemical plating system of claim 1, wherein the anode comprises at least one of titanium, platinum, noble metals, and combinations thereof.

6. The electrochemical plating system of claim 1, wherein the ion-exchange membrane is positioned greater than about 0.1 cm above the insoluble anode.

7. The electrochemical plating system of claim 1, wherein the ion-exchange membrane is positioned between about 0.5 cm and about 10 cm above the insoluble anode.

8. The electrochemical plating system of claim 1, further comprising a ceramic diffuser disposed between the ion-exchange membrane and the cathode substrate support member.

9. The electrochemical plating system of claim 1, wherein the ion-exchange membrane comprises a cation membrane selective to hydrogen ions and copper ions.

10. The electrochemical plating system of claim 1, further comprising a correction device in fluid communication with the anolyte compartment, the correction device comprising at least one of copper hydroxide, copper oxide, and combinations thereof configured to neutralize excess acid in the anolyte.

11. The electrochemical plating system of claim 10, further comprising a selectively actuated valve disposed between an anolyte outlet and the correction device, the valve configured to adjust the flow of anolyte to the correction device.

12. The electrochemical plating system of claim 11, wherein the selectively actuated valve is configured to adjust the flow of anolyte to the correction device when the pH of the anolyte in an anolyte storage tank exceeds about 6.

13. The electrochemical plating system of claim 10, further comprising a filter in fluid communication with the correction device, the filter configured to remove excess copper hydroxide or copper oxide from the anolyte and form corrected anolyte.

14. The electrochemical plating system of claim 13, wherein the corrected anolyte has a pH of from about 2.6 to about 3.6.

15. The electrochemical plating system of claim 8, wherein the anolyte comprises copper sulfate in a concentration of from about 0.05 M to about 1.0 M and has a pH of from about 2 to about 6.

16. The electrochemical plating system of claim 8, wherein the anolyte comprises copper sulfate in a concentration of from about 0.05 M to about 1.0 M and has a pH of from about 2.5 to about 4.

17. The electrochemical plating system of claim 8, wherein the catholyte comprises copper sulfate, sulfuric acid, organic additives, and copper chloride in an amount of from about 20 ppm to about 80 ppm.

18. The electrochemical plating system of claim 1, further comprising a catholyte electrodialysis cell in fluid communication with the catholyte compartment, the catholyte electrodialysis cell being configured to correct a used catholyte concentration.

19. The electrochemical plating system of claim 18, wherein the catholyte electrodialysis device comprises:

a housing having a cathode electrode and an anode electrode;

an anode chamber positioned proximate the anode electrode and between the cathode electrode and the anode electrode, wherein the anode chamber is configured to receive a sulfuric acid solution;

a cathode chamber positioned proximate the cathode electrode and between the cathode electrode and the anode chamber, wherein the cathode chamber is configured to receive a sulfuric acid solution;

an input chamber positioned between the cathode chamber and the anode chamber, wherein the input chamber is configured to receive the used catholyte solution;

an anion membrane positioned between the anode chamber and the input chamber configured to remove sulfate ions from the used catholyte solution; and

a bipolar membrane positioned between the cathode chamber and the input chamber configured to remove hydrogen ions from the used catholyte solution and provide hydroxide ions to the used catholyte solution.

20. The electrochemical plating system of claim 1, further comprising a removal device in fluid communication with the anolyte compartment, the removal device configured to remove at least a portion of dissolved gases from the anolyte.

21. The electrochemical plating system of claim 20, wherein the dissolved gases comprise oxygen.

22. The electrochemical plating system of claim 1, wherein the ion-exchange membrane comprises an anion membrane selective to sulfate ions.

23. The electrochemical plating system of claim 22, further comprising an anolyte electrodialysis cell in fluid communication with the anolyte compartment, the anolyte electrodialysis cell being configured to correct a used anolyte concentration.

24. The electrochemical plating system of claim 23, wherein the anolyte electrodialysis device comprises:

a housing having a cathode electrode and an anode electrode;

an anode chamber positioned proximate the anode electrode and between the cathode electrode and the anode electrode, wherein the anode chamber is configured to receive the used anolyte solution;

a cathode chamber positioned proximate the cathode electrode and between the cathode electrode and the anode chamber, wherein the cathode chamber is configured to receive the used anolyte solution;

at least one input chamber positioned between the cathode chamber and the anode chamber, wherein the input chamber is configured to receive the used anolyte solution;

at least one isolation chamber positioned in the anodic direction of the at least one input chamber configured to receive a sulfuric acid solution;

an anion membrane positioned in the anodic direction of the input chamber configured to remove sulfate ions from the used catholyte solution; and

a cation membrane positioned in the cathodic direction of the at least one input chamber configured to remove hydrogen ions from the used catholyte solution.

25. The electrochemical plating system of claim 22, wherein the anolyte comprises sulfuric acid.

26. An electrochemical plating system, comprising:

a plating cell having an anolyte compartment and a catholyte compartment, the anolyte compartment having an insoluble anode and an anolyte solution therein, the catholyte compartment having a cathode substrate support member and a catholyte solution therein;

a cation exchange membrane disposed between the anolyte compartment and the catholyte compartment, the cation exchange membrane being selective to hydrogen ions and copper ions; and

a correction device in fluid communication with the anolyte compartment, the correction device comprising at least one of copper hydroxide, copper oxide, and combinations thereof configured to neutralize excess acid in the anolyte.

27. The electrochemical plating system of claim 25, further comprising a pump in fluid communication with an anolyte inlet positioned in fluid communication with the anolyte compartment, the pump being configured to provide an anolyte to the anolyte chamber having a linear velocity of between about 0.5 cm/sec to about 50 cm/sec.

28. The electrochemical plating system of claim 27, wherein the pump is configured to provide an anolyte having a flow rate of from less than about 6 L/min.

29. The electrochemical plating system of claim 25, further comprising a selectively actuated valve disposed between an anolyte outlet and the correction device, the valve configured to adjust the flow of anolyte to the correction device.

30. The electrochemical plating system of claim 25, wherein the selectively actuated valve is configured to adjust the flow of anolyte to the correction device when the pH of the anolyte in an anolyte storage tank exceeds about 6.

31. A method for plating a metal onto a substrate, comprising:

supplying an anolyte solution to a plating cell having an anolyte compartment and a catholyte compartment, the anolyte solution passing through the anolyte compartment at linear velocity of between about 0.5 cm/sec and about 50 cm/sec;

plating a metal onto a substrate in the plating cell with a catholyte solution disposed in the catholyte compartment, the catholyte compartment and the anolyte compartment separated by an ion-exchange membrane;

removing used anolyte solution from the plating cell; and

passing at least a portion of the used anolyte solution through a correction device comprising at least one of copper oxide, copper hydroxide, and combinations thereof.

32. The method of claim 31, further comprising the passing the used anolyte solution through a removal device configured to remove at least a portion of dissolved gases from the anolyte.

33. The method of claim 32, wherein the dissolved gases comprise oxygen.

34. The method of claim 31, further comprising monitoring a pH level of the anolyte contained in an anolyte storage tank, the anolyte storage tank being in fluid communication with the correction device.

35. The method of claim 34, further comprising increasing the flow of anolyte passing through the removal device when the pH of the anolyte contained in the anolyte storage tank is greater than about 6.

36. The method of claim 31, further comprising saturating the anolyte solution with hydrogen prior to passing the anolyte solution through the anolyte compartment.

37. The method of claim 31, further comprising an insoluble anode disposed in the anolyte compartment.

38. The method of claim 31, wherein the metal comprises copper.

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