

## (19) United States

## (12) Patent Application Publication (10) Pub. No.: US 2005/0092601 A1 Herchen

## May 5, 2005 (43) **Pub. Date:**

### (54) ELECTROCHEMICAL PLATING CELL HAVING A DIFFUSION MEMBER

(76) Inventor: Harald Herchen, Los Altos, CA (US)

Correspondence Address: MOSÉR, PATTERSON & SHERIDAN, LLP/ APPLIED MATERIALS, INC. 3040 POST OAK BOULEVARD, SUTIE 1500 HOUSTON, TX 77056 (US)

10/927,381 (21) Appl. No.:

(22) Filed: Aug. 26, 2004

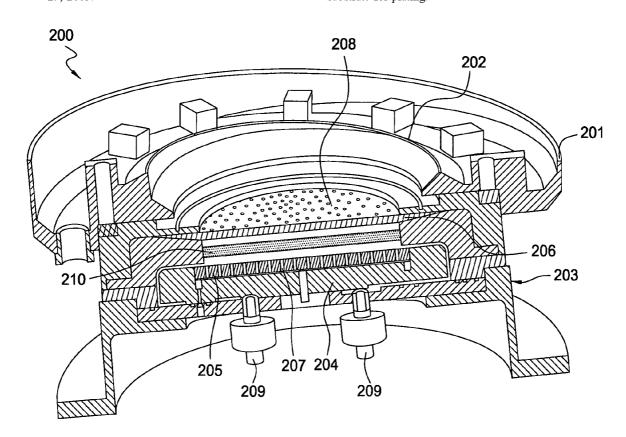
### Related U.S. Application Data

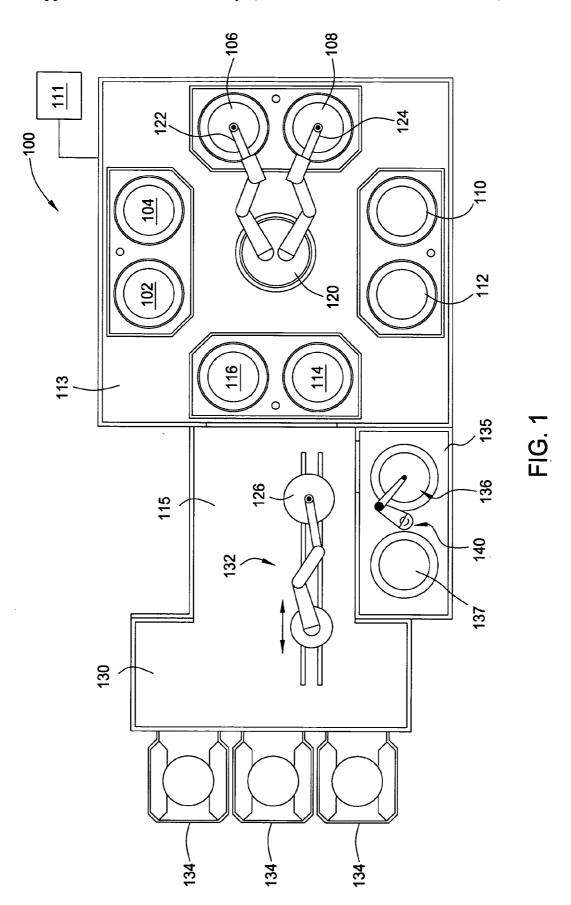
(60) Provisional application No. 60/515,465, filed on Oct. 29, 2003.

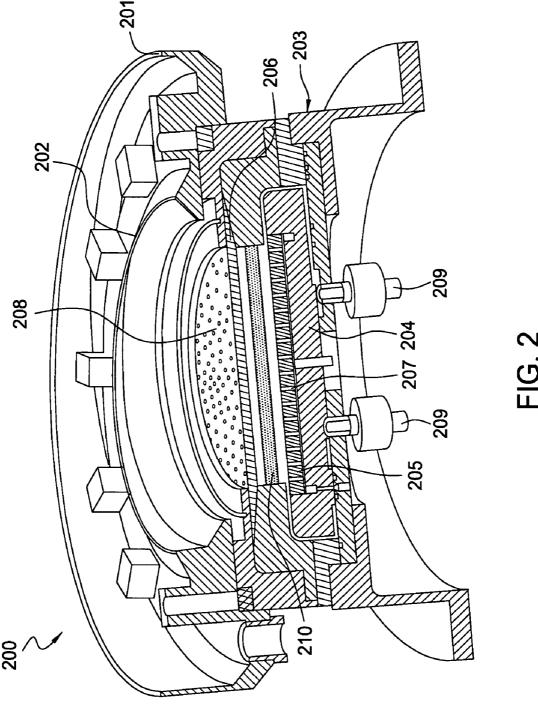
### **Publication Classification**

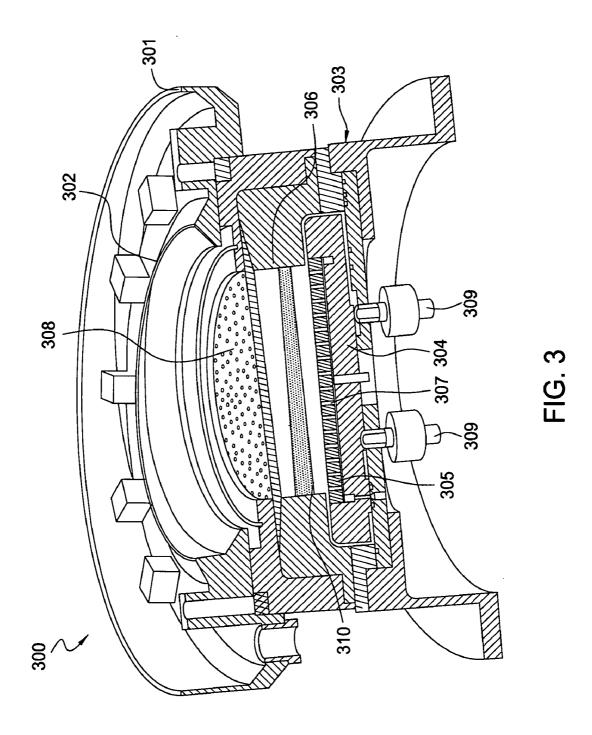
#### (57)**ABSTRACT**

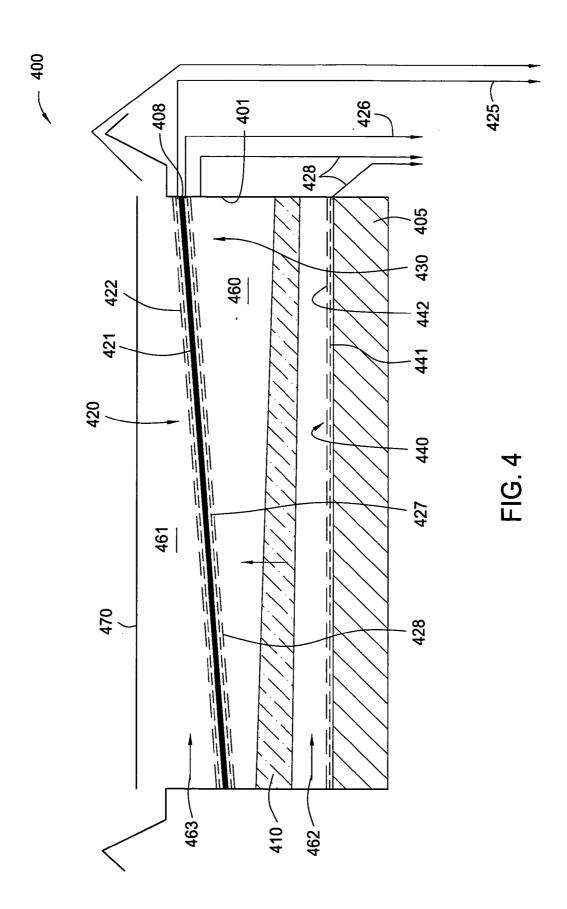
Embodiments of the invention provide an electrochemical plating cell that is divided by an ionic membrane into an anolyte volume and a catholyte volume. The anolyte volume of the plating cell includes an electrically resistive diffusion member and an anode positioned therein. The catholyte volume of the cell is generally configured to receive a substrate for plating.











# ELECTROCHEMICAL PLATING CELL HAVING A DIFFUSION MEMBER

# CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims benefit of U.S. provisional patent application Ser. No. 60/515,465, filed Oct. 29, 2003, 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 a flow control member for an electrochemical plating cell.

[0004] 2. Description of the Related Art

[0005] Metallization of sub 100 nanometer 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 15:1, interconnect features with a conductive material, such as copper. Conventional deposition techniques, such as chemical vapor deposition (CVD) and physical vapor deposition (PVD) have been unsuccessful in filling features of this size, and as such, plating techniques, i.e., electrochemical plating (ECP) and electroless plating, have emerged as promising processes for void free filling of sub 100 nanometer sized high aspect ratio interconnect features in integrated circuit manufacturing processes.

[0006] Conventional electrochemical plating cells contain an electrolyte bath that has an anode member positioned in a lower portion of the bath. A substrate to be plated is positioned in the electrolyte bath and an electrical bias is applied between the anode and the substrate surface to drive the plating process. Conventional plating cells may also include a membrane and/or a resistive diffusion member positioned across the fluid basin that holds the electrolyte solution. In recent plating cells, the cell basin has been divided into an anode compartment (also known as an anolyte compartment) and a cathode compartment (also known as a catholyte compartment) via use of a fluid isolation or ionic membrane. In these plating cells the diffusion member is positioned in the cathode compartment between the membrane and the substrate being plated and is used to control the electrolyte flow toward the substrate being plated.

[0007] However, positioning of the diffusion member in the catholyte compartment has been shown to contribute to defects in the plated copper layers. More particularly, positioning of the diffusion member in the catholyte solution has been shown to increase the likelihood of forming bubbles in the solution, which travel to the substrate surface and cause defects. Additionally, the diffusion members are generally manufactured from an electrically resistive material, and as such, the diffusion member presents challenges to plating a uniformly thick copper layer onto a thin seed layer that also has a substantially high resistivity. Further, the positioning

of the flow control member in the catholyte has been shown to contribute to undesirable terminal effect plating characteristics.

[0008] Therefore, there is a need for a plating cell configured to eliminate the challenges associated with positioning a diffusion member in the catholyte portion of a plating cell

#### SUMMARY OF THE INVENTION

[0009] Embodiments of the invention provide an electrochemical plating cell that is divided by an ionic membrane into an anolyte volume and a catholyte volume. The anolyte volume of the plating cell includes an electrically resistive diffusion member and an anode positioned therein. The catholyte volume of the cell is generally configured to receive a substrate for plating.

[0010] Embodiments of the invention further provide a plating cell having an anode compartment and a cathode compartment separated by an ionic membrane. An anode is positioned in a lower portion of the anode compartment and a flow control member is positioned above the anode in the anode compartment. The flow control member is generally a disk shaped member having a first thickness on a first side and a second thickness on a second opposing side, wherein the second thickness is different from the first, thus generating a wedge shaped member. The membrane is generally positioned at a tilt angle with respect to the upper surface of the anode, and further, the membrane tilt angle is generally opposite of a tilt angle of an upper surface of the flow control member.

[0011] Embodiments of the invention may further provide an electrochemical plating cell. The plating cell generally includes a fluid basin having a fluid outlet, a membrane positioned across the fluid basin, the membrane separating the fluid basin into a catholyte volume and an anolyte volume, an anode positioned in the anolyte volume, and a diffusion member positioned in the anolyte volume.

[0012] Embodiments of the invention may further provide an electrochemical plating cell. The plating cell generally includes a cell body defining a fluid processing volume and having an opening configured to receive a substrate for processing, a cationic membrane positioned across the fluid processing volume and separating the fluid processing volume into a catholyte volume and an anolyte volume, an anode positioned in the anolyte volume, and an electrically insulative fluid permeable diffusion member positioned across the fluid processing volume between the anode and the cationic membrane.

[0013] Embodiments of the invention may further provide a plating cell having a fluid basin having an opening configured to receive a substrate for processing, a copper anode positioned in a lower portion of the fluid basin, a porous electrically insulative diffusion member positioned across the fluid basin at a position between the anode and the opening, and a cationic membrane positioned across the fluid basin at a position between the diffusion member and the opening.

### BRIEF DESCRIPTION OF THE DRAWINGS

[0014] So that the manner in which the above recited features of the present invention can be understood in detail,

2

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.

[0015] FIG. 1 illustrates a plan view of an exemplary plating system of the invention.

[0016] FIG. 2 illustrates a sectional view of an exemplary plating cell of the invention.

[0017] FIG. 3 illustrates a sectional view of another embodiment of the exemplary plating cell of the invention.

[0018] FIG. 4 illustrates a sectional view of a third embodiment of the exemplary plating cell of the invention.

# DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0019] FIG. 1 illustrates a top plan view of an exemplary ECP system 100 of the invention. ECP system 100 includes a factory interface 130, which is also sometimes referred to as a substrate loading station. Factory interface 130 includes a plurality of cassette receiving stations configured to interface with substrate containing cassettes 134. A robot 132 is positioned in factory interface 130 and is configured to access substrates contained in the cassettes 134. Further, robot 132 also extends into a link tunnel 115 that connects factory interface 130 to processing mainframe or platform 113. The position of robot 132 allows the robot to access substrate cassettes 134 to retrieve substrates therefrom and then deliver the substrates to one of the processing cells 114,116 positioned on the mainframe 113, or alternatively, to an annealing station 135. Similarly, robot 132 may be used to retrieve substrates from the processing cells 114,116 or the annealing chamber 135 after a substrate processing sequence is complete. In this situation robot 132 may deliver the substrate back to one of the cassettes 134 for removal from system 100.

[0020] The processing mainframe 113 includes a substrate transfer robot 120 centrally positioned thereon. Robot 120 generally includes one or more arms/blades 122, 124 configured to support and transfer substrates thereon. Additionally, the robot 120 and the accompanying blades 122, 124 are generally configured to extend, rotate, and vertically move so that the robot 120 may insert and remove substrates to and from a plurality of processing locations 102, 104, 106, 108, 110, 112, 114, 116 positioned on the mainframe 113. Similarly, factory interface robot 132 also includes the ability to rotate, extend, and vertically move its substrate support blade(s), while also allowing for linear travel along the robot track that extends from the factory interface 130 to the mainframe 113. Generally, process locations 102, 104, 106, 108, 110,112,114, 116 may be any number of processing cells utilized in an electrochemical plating platform. More particularly, the process locations may be configured as electrochemical plating cells, rinsing cells, bevel clean cells, spin rinse dry cells, substrate surface cleaning cells (which collectively includes cleaning, rinsing, etching, and ozone treatment cells, etc.), electroless plating cells, metrology inspection stations, and/or other processing cells that may be beneficially used in conjunction with a plating platform. Each of the respective processing cells and robots are generally in communication with a process controller 111, which may be a microprocessor-based control system configured to receive inputs from both a user and/or various sensors positioned on the system 100 and appropriately control the operation of system 100 in accordance with the inputs.

[0021] In the exemplary plating system 100 illustrated in FIG. 1, the processing locations may be configured as follows. Processing locations 114 and 116 may be configured as an interface between the wet processing stations on the mainframe 113 and the dry processing regions in the link tunnel 115, annealing chamber 135, and the factory interface 130. The processing cells located at the interface locations may be spin rinse dry cells and/or substrate cleaning cells, for example. More particularly, each of locations 114 and 116 may include both a spin rinse dry cell and a substrate cleaning cell in a stacked configuration. Locations 102, 104, 110, and 112 may be configured as plating cells, either electrochemical plating cells or electroless plating cells, for example. Locations 106, 108 may be configured as substrate bevel cleaning cells. Additional configurations and implementations of an electrochemical processing system are illustrated in commonly assigned U.S. patent application Ser. No. 10/435,121 filed on Dec. 19, 2002 entitled "Multi-Chemistry Electrochemical Processing System", which is incorporated herein by reference in its entirety. Regardless of the configuration of the respective plating cells, ECP system 100 is generally configured to provide multiple plating cells on a single platform, wherein each of the multiple plating cells is capable of having a different chemistry therein from each of the other plating cells on the platform.

[0022] FIG. 2 illustrates a partial perspective and sectional view of an exemplary plating cell 200 that may be implemented in processing locations 102, 104, 110, and 112 (or other processing locations on system 100 as desired). The electrochemical plating cell 200 generally includes an outer basin 201 and an inner basin 202 positioned within outer basin 201. Inner basin 202 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 202, and therefore, the plating solution continually overflows the uppermost point (generally termed a "weir") of inner basin 202 and is collected by outer basin 201 and drained therefrom for chemical management and/or recirculation.

[0023] Plating cell 200 is generally positioned at a tilt angle, i.e., a frame portion 203 of plating cell 200 is generally elevated on one side such that the components of plating cell 200 are tilted between about 3° and about 30° from horizontal, or generally between about 4° and about 10°. The frame member 203 of plating cell 200 supports an annular base member 204 on an upper portion thereof, and since frame member 203 is elevated on one side, the upper surface of base member 204 is generally tilted from the horizontal at an angle that corresponds to the tilt angle of frame member 203 relative to a horizontal position. However, embodiments of the invention are not limited to tilted plating cells, as positioning the plating cell 200 at any angle with respect to horizontal, including 0°, for example, is contemplated within the scope of the invention.

[0024] Base member 204 generally includes an annular or disk shaped recess formed into a central portion thereof, the annular recess being configured to receive a disk shaped anode member 205 therein. Base member 204 further includes a plurality of fluid inlets/drains 209 extending from a lower surface thereof. Each of the fluid inlets/drains 209 are generally configured to individually supply or drain a fluid to or from either the anode compartment or the cathode compartment of plating cell 200 via conduits (not shown) formed through the base member 204. Anode member 205 generally includes a plurality of slots 207 formed therethrough, wherein the slots 207 are generally positioned in parallel orientation with each other across the surface of the anode 205. 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 207. However, embodiments of the invention are not limited to slotted-type anodes, as various other anodes, including solid disk-type anodes and other anodes conventionally used in electrochemical plating, are contemplated within the scope of the invention.

[0025] Plating cell 200 further includes a membrane support assembly 206. Membrane support assembly 206 is generally secured at an outer periphery thereof to base member 204, and includes an interior region configured to allow fluids to pass therethrough. A membrane 208 is stretched across the support 206 and generally operates to fluidly separate a catholyte chamber (positioned adjacent the substrate being plated) and anolyte chamber (positioned adjacent the anode electrode in the cell) of the plating cell. The membrane support assembly 206 may include an o-ring type seal positioned near a perimeter of the membrane 208, wherein the seal is configured to prevent fluids from traveling from one side of the membrane 208 secured on the membrane support 206 to the other side of the membrane 208. As such, membrane 208 generally provides fluid isolation between the anode and cathode portions of the plating cell 200, i.e., via use of a cationic membrane. Exemplary membranes that may be used to fluidly isolate an anolyte from a catholyte are illustrated in commonly assigned U.S. patent application Ser. No. 10/627,336 filed on Jul. 24, 2003 entitled "Electrochemical Processing Cell", which is hereby incorporated by reference in its entirety. Alternatively, membrane 208 may be a fluid permeable filter-type membrane that allows fluid to pass therethrough.

[0026] A diffusion plate 210, which is generally a porous ceramic disk member or other fluid permeable electrically resistive member is positioned in the cell between anode 205 and the membrane 208. The positioning of the diffusion member 210 below the membrane 208 is a departure from conventional plating cells where the diffusion member would generally be positioned above the membrane 208 adjacent the substrate being plated. When the diffusion member 210 is placed below the membrane 208, it does not generate substantially laminar flow of electrolyte toward the plating surface, as with conventional plating cells having the diffusion member above the membrane. The inventors have concluded that a substantially laminar flow may not be necessary, as the plating thickness or uniformity is predominantly controlled by the electric field and boundary layer thickness, and not the fluid flow at the plating surface, as previously thought. The boundary layer thickness at the substrate is driven mostly by the relative motion of the wafer and fluid induced by rotation of the substrate during the plating process. Put simply, the inventors profess that the uniformity of a plating process is affected by the electric field primarily, then the rotationally induced boundary layer, then the vertical flow induced boundary layer, in that order. As such, by the time variations in the vertical fluid flow are considered, the impact on the uniformity is a third or even fourth order effect.

[0027] However, there still is a benefit to a implementing a diffuser in a plating cell. That benefit is that it increases the cell electrical impedance, and in doing so, reduces the percentage increase in the cell voltage as the soluble anode erodes, and in effect, moves away from the substrate. To this end, if the diffuser thickness is doubled, the uniformity decreases with a single "standard" thickness, and if it is taken away, the uniformity, except at the very edge, improves. The edge effect is E-field driven, which is fixed by other techniques. In the case of this invention, the diffuser has the additional task of compensating for the difference in anolyte and catholyte conductivities, the path length for which is varying as a result of the tilt in the membrane relative to the workpiece. Further still, positioning the diffuser in the catholyte serves as a bubble trap, which has been shown to contribute to undesirable plating defects.

[0028] With the diffuser 210 positioned below the membrane 208, the diffusion member 210 is positioned in the anolyte solution, i.e., the solution flowing below the membrane 208 that does not include plating additives and that does not contact the plating surface of the substrate being plated. The diffusion member 210 is generally manufactured from an electrically insulating material, and as such, the diffusion member 210 also operates to control the electric field generated between the anode and the substrate. In conventional plating cells, and in some embodiments of the invention, the diffusion member 210 is a disk shaped member having a uniform thickness across the surface thereof.

[0029] However, in plating cell configurations wherein the upper surface of the anode 205 and the surface of the membrane 208 are not positioned in parallel relationship with each other, as will be further discussed herein, the diffusion member 210 may be configured to have a varying thickness across the surface thereof. More particularly, the thickness of the diffusion member 210 may be varied to compensate for variances in the resistance path between the anode 205 and the substrate being plated, such that the perpendicular line resistance between the anode 205 and the substrate being plated remains constant across all points on the surface of the substrate. Additionally, with regard to the type of the diffusion member 210 described above, embodiments of the invention are not intended to be limited to ceramic diffusion members, as other electrically insulative fluid permeable (porous) materials that are non-reactive with electrochemical processing fluids may also be used in embodiments of the invention without departing from the scope thereof. Additionally, embodiments of the invention further contemplate that electrically insulative materials that are not porous may also be used in embodiments of the invention, ie., as holes or bores may be formed through the electrically insulative material to allow fluid to flow therethrough in a manner similar to the fluid flow through the above noted porous diffusion member.

[0030] When a porous diffusion member is implemented in embodiments of the invention, then the porosity of the

diffusion member 210 may be between about 20% and about 60%, and more particularly, between about 30% and about 50%. These porosities have been shown to generate a resistivity when wet with electrolyte that is between about three and ten times greater or higher than the resistivity of the same shape of cell without the diffusion member 210 positioned therein. The thickness of the diffusion member 210 may be between about 1 mm and about 30 mm, for example, for a disk shaped or uniform thickness diffusion member 210, which has also shown improved plating characteristics when plating material onto thin seed layers, i.e., seed layers having a thickness of less than about 500 Å.

[0031] Further, positioning of the diffusion member 210 in the anolyte solution, e.g., below the membrane 208, assists with minimizing bubbles present at the substrate surface and removes the diffusion member as a possible source for surface defects on the substrate. Additional advantages of positioning the diffusion member 210 in the anolyte include improved terminal effect results and an improved ability to counteract the local variations in the resistivity of the membrane 208 and the anode 205. The positioning of the diffusion member 210 between the membrane 208 and the anode 205 also allows for the plating cell to be positioned vertically instead of tilted, which may mitigate immersion defects.

[0032] Additional embodiments of the exemplary plating cell illustrated in FIG. 2 are illustrated in commonly assigned U.S. patent application Ser. No. 10/268,284 which was filed on Oct. 9, 2002 under the title "Electrochemical Processing Cell", claiming priority to U.S. Provisional Application Ser. No. 60/398,345 which was filed on Jul. 24, 2002, both of which are incorporated herein by reference in their entireties. Additional embodiments of the plating cell are also illustrated in commonly assigned U.S. patent application Ser. No. 10/627,336 filed on Jul. 24, 2003 entitled "Electrochemical Processing Cell", which is also incorporated by reference herein in its entirety.

[0033] FIG. 3 illustrates another embodiment of the plating cell of the invention. In this embodiment the plating cell 300 may be positioned horizontally, at a tilt angle, or vertically. An anode 305 is positioned in a lower portion of the cell 300 and includes a generally planar upper surface. A diffusion member 310 is positioned above the anode 305 and a central plane of the diffusion member 310 plane (a central plane that is equidistant from both outer surfaces of the diffusion member), and further, the central plane is generally parallel to the upper surface of the anode 305. The thickness of the diffusion member 310 generally varies from one side to the other in one direction, which generally generates a wedge shaped disk member. A membrane support 306 and a membrane 308 are positioned above the diffusion member 310. The membrane 308 is generally positioned at a tilt angle, i.e., the membrane 308 is generally positioned at an angle with respect to horizontal or at an angle with respect to the upper surface of the anode. The tilt angle is generally between about 5° and about 30°, or more particularly, between about 5° and about 15°. The membrane 308 is generally an ionic membrane, and more particularly, a cationic membrane, for example. The remaining components of plating cell 300 are generally similar to the components of the plating cell illustrated in FIG. 2, i.e., frame 303, basins 301 and 302, fluid inlets 309, anode slots 307, and anode base 304.

[0034] In the embodiment of the invention illustrated in FIG. 3, the diffusion member 310 is generally positioned such that the thicker side of the diffusion member 310 is positioned on the same side of the plating cell as the lowermost portion of the membrane 308. More particularly, as illustrated in FIG. 3, the thicker side of the diffusion member 310 is positioned on the left side of the plating cell 300, which corresponds to the side of the plating cell 300 where the membrane 308 is positioned at its lowest point, e.g., at the point closest to the anode 305. Generally, the thickness of the diffusion member 310 at the thickest portion is between about 6 mm and about 37 mm, while the thickness at the thinnest portion is between about 1 mm and about 30 mm. As such, the diffusion member may be disk shaped, or wedge shaped with a surface angle that is between about 3° and about 15°, for example. Similarly, the tilt angle of the membrane 308 may be between about 3° and about 15°, for example, and more particularly, between about 6° and about 12°.

[0035] The embodiment of the invention illustrated in FIG. 3 is generally configured to generate an equal resistance path between the anode 305 and the substrate being plated at all locations across the plating cell, regardless of the thickness of the diffusion member 310 or the distance the membrane 308 is from the substrate or anode 305. Generally, this is accomplished by having the membrane 308 being positioned closer to the anode 305 at cell locations where the diffusion member 310 is thicker. Similarly, the membrane 308 is positioned closer to the substrate (farther away from the anode 305) at locations in the cell where the diffusion member 310 is thinner. Thus, the inventors have determined that the perpendicular line resistance between the anode 305 and the substrate being plated is proportional to the ratio of the thickness of the diffusion member 310 to the distance the membrane 308 is from the anode. As such, as the thickness of the diffusion member 310 increases, the distance of the membrane 308 from the anode 305 decreases in order to maintain an equal resistance path to the substrate from the anode 305. The proportion that determines the line resistance is generally based upon the concept that the analyte and catholyte solutions each have different resistances or conductances (the analyte is generally much more resistive than the catholyte), and as such, when the distance between the anode and the membrane is large, i.e., the anolyte is thick, then the diffusion member may be thin and the distance from the membrane to the substrate (the catholyte resistance) may be thin. The proportion balances the ratio of the anolyte thickness, catholyte thickness, and diffusion member thickness to generate an equal line resistance to the substrate at all points across the anode surface. Generally, the substrate is positioned in the plating cell in a manner such that the surface of the substrate being plated is parallel to the upper surface of the anode 305.

[0036] Further, embodiments of the invention, and in particular, the embodiments of the invention illustrated in FIGS. 2 and 3, are generally configured to use a diffuser having a porosity of about 40%, which is configured to generate a resistivity when wet with the electrolyte (anolyte) that is approximately five times higher than the same volume and shaped cell without the diffuser 210. Therefore, the plating cell can be positioned horizontally and the cationic membrane can be tilted by about 10° from the upper surface of the anode. As a result thereof, the diffusion member can be positioned in the anolyte (as opposed to the catholyte in

conventional plating cells) and cut or manufactured with a slope of about 10° (the tilt) divided by 5 (the difference in resistivity), which yields a cut or manufacture slope of approximately 2° relative to the slope of the opposing surface. Additionally, the thickness of the diffusion member may be increased, which facilitates thinner seed layers being plated in the same amount of time conventionally used to plate onto thicker seed layers, as the increased resistance anolyte used on conjunction with the thick diffuser therein has a much higher resistivity than provided by conventional plating cell configurations, and even those conventional plating cells having separated analyte and catholyte fluid regions or chambers. Further, positioning the diffuser in the anolyte increases the resistance for a given thickness, which increases uniformity for thin seed plating, counteracts the terminal effect, and counteracts local variations in resistivity present in the membranes of the cell and the anode.

[0037] In another embodiment of the invention, which is illustrated in the general sectional view of FIG. 4, a plating cell 400 includes a wedge shaped diffusion member 410 and a tilted ionic-type membrane 408 in similar fashion to FIG. 3. The ionic membrane 408 further includes a first membrane stack 420 positioned on or adjacent to an upper side thereof, i.e., the side positioned closest to the upper or open portion of plating cell 400 where a substrate is received for plating. The ionic membrane 408 also includes a second membrane stack 430 positioned on or adjacent to a lower side thereof, i.e., the side positioned closest to the lower portion of the plating cell 400 where the anode 405 is positioned. A third membrane stack 440 is positioned on or adjacent to the upper surface of the anode 405 below the ionic membrane 408.

[0038] The ionic membrane 408 is generally a cationic membrane configured to allow positively charged ions, such as Cu<sup>2+</sup> to travel upward through the membrane 408 from the anode 405 to the substrate being plated, while preventing plating solution additives and other constituents from traveling downward through the membrane from the catholyte solution into the anolyte solution where they may contact the anode 405 and breakdown. Exemplary ionic membranes that may be used in embodiments of the invention are described in commonly assigned U.S. patent application Ser. No. 10/616,044 filed on Jul. 8, 2003 entitled "Anolyte for Copper Plating", which is hereby incorporated by reference in its entirety.

[0039] The first membrane stack 420 generally includes a first membrane 421 positioned adjacent the ionic membrane 408 and a second membrane 422 positioned above the first membrane 421, such that the first membrane 421 is positioned between the second membrane 422 and the ionic membrane 408. The first membrane 421 is generally a hydrophilic fluid permeable membrane having a thickness of between about 50  $\mu$ m and about 150  $\mu$ m and having pores sized (diameter) between about 2  $\mu$ m and about 20  $\mu$ m, for example. The first membrane 421 is generally positioned immediately above the ionic membrane 408 with only a minimal fluid passage space positioned between the two membranes. The second membrane 422 is generally positioned immediately above the first membrane 421, again with a fluid passage space separating the membranes. The second membrane 422 generally has a thickness of between about 30  $\mu$ m and about 175  $\mu$ m and includes pores sized between about 1  $\mu$ m and about 15  $\mu$ m, for example. The outer perimeter of the first and second membranes 421, 422 is sealably attached to a sidewall 401 of the plating cell 400. The fluid space between the ionic membrane 408 and the first membrane 421 includes a catholyte fluid drain 425 positioned in communication therewith, while the fluid space positioned between the first and second membranes 421, 422 is sealably in communication with the sidewall 401 of the cell 400. The catholyte fluid drain 425 is also in fluid communication with a catholyte region 461 of the plating cell 400. Further, a corresponding catholyte supply 463 is in fluid communication with the catholyte region 461.

[0040] The second membrane stack 422 (positioned on the lower surface of the ionic membrane 408) also includes a two layer membrane stack. The membrane stack includes a first membrane 427 positioned adjacent the ionic membrane 408 and a second membrane 428 positioned adjacent the first membrane 427, such that the first membrane 427 is positioned between the second membrane 428 and the ionic membrane 408. Both the first and second membranes 427, 428 are sealably attached to the sidewall 401 of the plating cell 400. Further, first membrane 427 is positioned such that there is a fluid space positioned between the ionic membrane 408 and the first membrane 427. Similarly, the second membrane 428 is positioned such that there is a fluid space between the second membrane 428 and the first membrane 427. The fluid space between the ionic membrane 408 and the first membrane 427 is in fluid communication with an anolyte drain 426. The first membrane 427 is generally a hydrophilic fluid permeable membrane having a thickness of between about 50  $\mu$ m and about 150  $\mu$ m and having pores sized (diameter) between about 2  $\mu$ m and about 20  $\mu$ m, for example. The second membrane 427 generally has a thickness of between about 30  $\mu$ m and about 175  $\mu$ m and includes pores sized between about 1  $\mu$ m and about 15  $\mu$ m, for

[0041] The third membrane stack 440 is positioned on the upper surface of the anode 405. The third membrane stack generally includes a first membrane 441 and a second membrane 442. The first membrane 441 is generally positioned next to the upper surface of the anode 405, with a fluid space separating the anode 405 from the membrane 441. The second membrane 442 is positioned above the first membrane 441 and is separated from the first membrane 441 by a fluid space. Both the first and second membranes 441, 442 are generally sealably attached to the sidewall 401 of the plating cell 400, however, the fluid space between the first membrane 441 and the anode 405 includes an anolyte drain 428 positioned in fluid communication therewith. The anolyte drain 428 is also generally in fluid communication with an anolyte region 460 of the plating cell 400. Further, an anolyte supply line 462 is in fluid communication with the anolyte region 460.

[0042] In operation, the embodiment of the invention illustrated in FIG. 2 is configured to plate a metal, e.g., copper layer onto a semiconductor substrate having a thin seed layer, e.g., less than about 500 Å thereon. In this embodiment of the invention a substrate to be plated is positioned such that the plating surface, i.e., the seed layer, is in contact with a catholyte plating solution contained within the inner fluid basin 202. The catholyte plating solution is continually supplied to the inner fluid basin 202 via at least one fluid inlet 209 and at least one fluid conduit (not shown) formed through the base member 204 and

6

connecting the inlet 209 to the fluid volume above the membrane 208 within inner basin 202. Similarly, an anolyte solution is provided to the fluid volume within the inner basin 202 that is below the membrane 208 via at least one of the fluid inlets 209 and a fluid conduit 212. The anolyte solution generally flows over the upper surface of the anode 205 and is collected by a corresponding conduit 212 on the opposing side. Additionally, the fluid conduit 212 may also be positioned in fluid communication with the fluid volume above the diffusion member 210 and below the membrane 208

[0043] In this embodiment the copper ions in the anolyte solution are transferred through the diffusion member 210 and through the membrane 208 toward the substrate being plated during the electrolytic plating process. However, plating additives and contaminants that may accumulate in the catholyte solution are not permitted by virtue of the cationic membrane properties that do not allow these constituents to pass through the membrane 208 in the direction of the anode. The perpendicular line resistance between the anode 205 and the substrate being plated (which is generally positioned parallel to the anode during plating) is generally constant at all points across the anode 205, and further, as a result of the positioning of the diffusion member 210 in the anolyte, the resistance is substantially higher than in conventional plating cells.

[0044] In the embodiment of the invention illustrated in FIG. 3, the fluid flow pattern is similar to the fluid flow pattern for the embodiment illustrated in FIG. 2. Additionally, the perpendicular line resistance is again equal across all points on the anode surface, as the proportion of the diffusion member 310 thickness to the distance the membrane 308 is away from the anode remains constant for all points across the anode. As such, the diffusion member 310 may be wedge shaped and the membrane 308 may be positioned at a tilt angle. This configuration minimizes bubble formation at the surface of the substrate being plated, reduces the terminal effect, and allows for an electrolytic plating process to be conducted on thinner seed layers than possible in conventional plating cells where the diffusion member is positioned in the catholyte. In both of the embodiments illustrated in FIGS. 2 and 3, the analyte fluid conduits 212 may be configured to supply the analyte solution to the fluid volume both above the diffusion member 210, 310 and below the diffusion member 210, 310.

[0045] The operational characteristics of the embodiment of the invention illustrated in FIG. 4 are slightly different from previous embodiments as a result of the positioning of the respective membrane stacks 420, 430, 440. The respective membrane stacks 420, 430, 440 generally include a larger porous filter membrane positioned below a smaller porous filter membrane, wherein the larger porous membrane is generally positioned adjacent either the ionic membrane 408 or the anode 405, for example. Generally speaking, the positioning of the membrane stack 420 above the ionic membrane 408 allows copper ions coming out of the membrane 408 (ions transferring from the catholyte to the anolyte) to be moved away from the surface of the ionic membrane 408, thus reducing passiviation at the membrane 408 surface and increasing plating rates. More particularly, the catholyte fluid drain 425 positioned in fluid communication with the volume between the first membrane 421 and the cationic membrane 408 operates to generate a catholyte fluid flow exiting the fluid volume between the first membrane 421 and the ionic membrane 408. The exiting catholyte fluid flow generates a reduced pressure in the fluid volume between the first membrane 421 and the ionic membrane 408, and as a result thereof, replacement catholyte is pulled through the membrane stack 420 and into the fluid volume between the first membrane 421 and the ionic membrane 408. This fluid must travel through the second membrane 422 and the first membrane 421 in order to reach the fluid volume between the first membrane 421 and the ionic membrane 408.

[0046] The second membrane stack 430 operates in a similar manner to the first membrane stack 420. More particularly, a first large porous membrane 427 is positioned adjacent a lower surface of the ionic membrane 408 and a second smaller porous membrane 428 is positioned adjacent the first membrane 427. The analyte drain 428 operates to remove anolyte from the fluid volume between the lower surface of the ionic membrane 408 and the first membrane 427, which again generates a reduced pressure that pulls replacement fluid into the volume. The replacement fluid, i.e., anolyte, is pulled from through the second membrane 428 and first membrane 427 into the fluid volume between the first membrane 427 and the lower surface of the ionic membrane 408. This configuration generally operates to circulate the anolyte solution that is depleted of copper ions, i.e., the anolyte solution adjacent the ionic membrane surface, away from the surface of the ionic membrane 408. This provides a continual and sufficient supply of copper ions for transport through the ionic membrane 408, which in turn operates to prevent the cell voltage from rising as a result of a copper ion deficiency at the ionic membrane 408.

[0047] The third membrane stack 440 provides a similar function to the anode 405 as membrane stacks 420, 430 do for the ionic membrane 408. More particularly, the positioning of the larger porous first membrane 441 adjacent the anode and the smaller porous second membrane 442 adjacent the first porous membrane 441 operates to flush material away from the surface of the anode 405. Specifically, the anolyte conduit 426 is in fluid communication with the fluid volume between the first membrane 441 and the anode 405 and is configured to remove analyte therefrom. As such, a negative pressure is generated in the fluid volume between the first membrane 441 and the anode 405, which operates to pull anolyte into the fluid volume. The anolyte being pulled into the fluid volume travels through the second membrane 442 and the first membrane 441 to reach the fluid volume, and is then removed therefrom by the analyte conduit 426, thus generating an analyte circulation loop. The larger porous membrane 441 is similar in construction, thickness, and pore size to the first membrane 421 of first stack 420, and the second membrane 442 is similar in construction, thickness, and pore size to the second membrane 422 of the first membrane stack 420.

[0048] The third membrane stack 440 generally operates to pull sludge that forms on the surface of the anode away from the anode surface, which reduces the need to tilt the plating cell in order to urge the sludge to flow into the anode slots for removal from the anode surface. Additionally, this flow pattern also operates to pull the copper rich anolyte away from the anode surface and circulate the copper rich anolyte into the bulk anolyte solution volume, which allows higher plating rates that do not require increased fluid flow

in the plating cell. Additional benefits of the third membrane stack 440 positioned on or immediately above the anode 405 include reduced anode passiviation at current densities of less than about 80 mA/cm², reduced bowing of the ionic membrane 408 as a result of increased fluid pressure, which also minimizes center thin plating challenges, elimination of metallization of the ionic membrane 408, and increased anode life, as a slotted anode configuration, such as the anode 205 illustrated in FIG. 2, may be replaced with a solid disk shaped anode having a longer processing life.

[0049] 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, wherein the scope thereof is determined by the claims that follow.

- 1. An electrochemical plating cell, comprising:
- a fluid basin having a fluid inlet and a fluid outlet;
- a membrane positioned across the fluid basin, the membrane separating the fluid basin into a catholyte volume and an anolyte volume;
- an anode positioned in the anolyte volume; and
- an electrically resistive fluid permeable diffusion member positioned across the analyte volume.
- 2. The plating cell of claim 1, wherein the membrane comprises a cationic membrane.
- 3. The plating cell of claim 2, wherein the diffusion member comprises a varying thickness disk shaped member.
- **4**. The plating cell of claim 3, wherein the diffusion member comprises a porous ceramic disk.
- 5. The plating cell of claim 1, wherein the diffusion member comprises a disk shaped member having a substantially uniform thickness.
- 6. The plating cell of claim 3, wherein the diffusion member comprises a disk shaped member having a first thickness on a first edge of the disk shaped member and a second thickness on a second opposing edge of the disk shaped member, the first thickness being different from the second thickness.
- 7. The plating cell of claim 6, wherein a central plane of the diffusion member is positioned substantially parallel to an upper surface of the anode.
- 8. The plating cell of claim 7, wherein the membrane is positioned at an angle across the fluid basin with respect to the upper surface of the anode.
- 9. The plating cell of claim 8, wherein the membrane is positioned at a first distance from the anode surface on a thin side of the diffusion member and at a second distance from the anode surface on a thick side of the diffusion member, the first distance being greater than the second distance.
- 10. The plating cell of claim 3, wherein the diffusion member is positioned substantially parallel to an upper surface of the anode.
  - 11. An electrochemical plating cell, comprising:
  - a cell body defining a fluid processing volume and having an opening configured to receive a substrate for processing;
  - a cationic membrane positioned across the fluid processing volume and separating the fluid processing volume into a catholyte volume and an anolyte volume;

- an anode positioned in the anolyte volume; and
- an electrically insulative fluid permeable diffusion member positioned across the fluid processing volume between the anode and the cationic membrane.
- 12. The plating cell of claim 11, wherein the cationic membrane is positioned parallel to an upper surface of the anode.
- 13. The plating cell of claim 11, wherein the cationic membrane is positioned at an angle with respect to an upper surface of the anode.
- 14. The plating cell of claim 11, wherein the diffusion member comprises a disk shaped member having a substantially uniform thickness.
- 15. The plating cell of claim 13, wherein the diffusion member comprises a disk shaped member having a first thickness on a first edge and a second thickness on a second edge, the first thickness being greater than the second thickness.
- 16. The plating cell of claim 15, wherein the cationic membrane is positioned a first distance from the anode at a position in the fluid processing volume adjacent the first side and a second distance from the anode at a position in the fluid processing volume adjacent the second side, wherein the first distance is less than the second distance.
- 17. The plating cell of claim 13, wherein the angle is between about 5° and about 15°.
- 18. The plating cell of claim 11, further comprising an anolyte fluid inlet and an anolyte fluid outlet in fluid communication with the anolyte volume, and a catholyte fluid inlet and a catholyte fluid outlet in fluid communication with the catholyte volume.
- 19. The plating cell of claim 18, wherein the anolyte fluid inlet is positioned to deliver an anolyte solution to a volume below the diffusion member and to a volume above the diffusion member.
  - 20. An electrochemical plating cell, comprising:
  - a fluid basin having an opening configured to receive a substrate for processing;
  - a copper anode positioned in a lower portion of the fluid
  - a porous electrically insulative diffusion member positioned across the fluid basin at a position between the anode and the opening;
  - a cationic membrane positioned across the fluid basin at a position between the diffusion member and the opening.
- 21. The plating cell of claim 20, wherein the diffusion member is wedge shaped and has a central plane that is substantially parallel to an upper surface of the anode.
- 22. The plating cell of claim 21, wherein the cationic membrane is positioned at a tilt angle with respect to the upper surface of the anode.
- 23. The plating cell of claim 22, wherein the tilt angle is proportional to a slope of the diffusion member.
- 24. The plating cell of claim 20, wherein the diffusion member is disk shaped member having a substantially uniform thickness.
- **25**. The plating cell of claim 24, wherein the cationic membrane is positioned parallel to the diffusion member.

\* \* \* \* \*