INERT ANODE REACTION CHAMBER

INCORPORATION BY REFERENCE

[0001] A PCT Request Form is filed concurrently with this specification as part of the present application. Each application that the present application claim benefit of or priority to as identified in the concurrently filed PCT Request Form is incorporated by reference herein in its entirety and for all purposes.

BACKGROUND

[0002] An active anode, such a solid copper anode, in electrochemical plating consumes a physical copper anode quickly resulting in repetitive, time-consuming operations to replace the anode. Thicker plating exacerbates this problem by more rapidly depleting the copper anode.

[0003] Background and contextual descriptions contained herein are provided solely for the purpose of generally presenting the context of the disclosure. Much of this disclosure presents work of the inventors, and simply because such work is described in the background section or presented as context elsewhere herein does not mean that such work is admitted prior art.

SUMMARY

[0004] Aspects of this disclosure pertain to electroplating apparatus that may be characterized by the following elements:

(a) an anode chamber;

(b) an anolyte flow system configured to deliver anolyte to at least one inlet and receive the anolyte from at least one outlet; and

(c) a cathode chamber comprising a cathode support for holding a cathode during electroplating.

[0005] The anode chamber may comprise the following elements: an inert anode; an anode support in contact with the inert anode; an ionically conductive membrane, wherein the ionically conductive membrane is separated from the inert anode by a gap in the anode chamber; a membrane clamp configured to hold the ionically conductive membrane; at least one inlet configured to flow anolyte into the gap at a first position; and at least one outlet configured to receive the anolyte flowing out of the gap at a second position;

[0006] The cathode chamber may be configured to attach to the anode chamber in a manner that permits, during operation, ionic communication between a catholyte in the cathode chamber and the anolyte in the anode chamber.

[0007] In certain embodiments, the inert anode comprises a metal and/or a metal oxide that does not substantially dissolve or corrode when exposed to an anodic current and the anolyte during electroplating. In certain embodiments, the inert anode comprises titanium, platinum and/or a mixed metal oxide.

[0008] In certain embodiments, the inert anode comprises a sheet of inert anode material. In certain embodiments, the inert anode comprises a three-dimensional structure configured to have the anolyte flow in three dimensions through the inert anode.

[0009] In certain embodiments, during electroplating, the anolyte has a minimum flow rate in the gap of at least about 1 mm/s. In certain embodiments, during electroplating, the anolyte has a minimum flow rate in the gap of at least about 30 mm/s. In certain embodiments, the minimum flow rate in the gap is achieved when current flowing through the inert anode has a current density of about 50 to 100 mA/cm^2.

[0010] In certain embodiments, the gap has a separation distance between the inert anode and the ionically conductive membrane, which separation distance is, on average, at most about 130 mm. In certain embodiments, the gap has a separation distance between the inert anode and the ionically conductive membrane, which separation distance is, on average, at most about 50 mm. In certain embodiments, the gap has a separation distance between the inert anode and the ionically conductive membrane, which separation distance is, on average, at most about 10 mm.

[0011] In certain embodiments, the gap has a separation distance between the inert anode and the ionically conductive membrane, which separation distance is substantially constant within the anode chamber. In certain embodiments, the gap has a separation distance between the inert anode and the ionically conductive membrane, wherein the gap separation distance decreases from the first position to the second position.

[0012] In certain embodiments, the inert anode has a substantially planar surface in contact with the gap. In some cases, the inert anode's surface is substantially horizontally oriented. In certain embodiments, the inert anode's surface slopes upwards from the first position to the second position. In certain embodiments, the membrane is substantially horizontally oriented. In certain embodiments, the membrane slopes upwards from the first position to the second position.

[0013] In certain embodiments, the first position is at a center position of the inert anode. In certain embodiments, the first position is located proximate at least a portion of a circumference of the inert anode.

[0014] In certain embodiments, the anode chamber further comprises one or more second inlets

configured to flow anolyte into the gap at an intermediate position between the first position and the second position. In certain embodiments, the first position is at a center position of the inert anode, wherein the intermediate position is at position radially intermediate between the center position and a circumference of the inert anode, and wherein the second position is located at a circumference of the inert anode. In certain embodiments, the first position is proximate one edge of the inert anode and the second position is proximate an opposite edge of the inert anode.

[0015] In certain embodiments, the membrane clamp is configured to hold the membrane in tension over the gap. In certain embodiments, the membrane clamp comprises a substantially rigid membrane frame that holds the membrane in a substantially fixed position during electroplating. In some cases, the membrane frame comprises a spoke arrangement. In some cases, the membrane frame comprises a plurality of channels configured to provide, during operation, a substantially uniform ionic current distribution over an active surface of the cathode in the cathode chamber.

[0016] In certain embodiments, the anode chamber further comprises a flow diverter configured to receive upward flowing anolyte and divert the flowing anolyte into the gap in a generally horizontal flow direction. In certain embodiments, the anode chamber further comprises an electrical bus for applying, during electroplating, an anodic electrical potential to the inert anode.

[0017] In certain embodiments, the ionically conductive membrane comprises an anionically conductive polymer.

[0018] Any combination of the features mentioned for these aspects may be implemented together in an electroplating apparatus in accordance with this disclosure.

[0019] Aspects of this disclosure pertain to anode assemblies that may be characterized by the following elements:

an inert anode;

an anode support in contact with the inert anode;

an ionically conductive membrane, wherein the ionically conductive membrane is separated from the inert anode by a gap in the anode chamber;

a membrane clamp configured to hold the ionically conductive membrane;

at least one inlet configured to flow anolyte into the gap at a first position; and

at least one outlet configured to receive the anolyte flowing out of the gap at a second position.

[0020] In certain embodiments, the inert anode comprises a metal and/or a metal oxide that does not substantially dissolve or corrode when exposed to an anodic current and the anolyte

during electroplating.

[0021] In certain embodiments, during electroplating, the anolyte has a minimum flow rate in the gap of at least about 30 mm/s. In certain embodiments, the gap has a separation distance between the inert anode and the ionically conductive membrane, which separation distance is, on average, at most about 10 mm.

[0022] In certain embodiments, the gap has a separation distance between the inert anode and the ionically conductive membrane, which separation distance is substantially constant within the anode chamber. In certain embodiments, the gap has a separation distance between the inert anode and the ionically conductive membrane, wherein the gap separation distance decreases from the first position to the second position. In some cases, the inert anode's surface is substantially horizontally oriented.

[0023] In certain embodiments, the inert anode's surface slopes upwards from the first position to the second position. In certain embodiments, the membrane is substantially horizontally oriented. In certain embodiments, the membrane slopes upwards from the first position to the second position.

[0024] In certain embodiments, the first position is at a center position of the inert anode. In certain embodiments, the first position is located at least a portion of a circumference of the inert anode. In certain embodiments, the first position is proximate one edge of the inert anode and the second position is proximate an opposite edge of the inert anode.

[0025] In certain embodiments, the anode chamber further comprises one or more second inlets configured to flow anolyte into the gap at an intermediate position between the first position and the second position.

[0026] In certain embodiments, the membrane clamp is configured to hold the membrane in tension over the gap. In certain embodiments, the membrane clamp comprises a substantially rigid membrane frame that holds the membrane in a substantially fixed position during electroplating. In some cases, the membrane frame comprises a plurality of channels configured to provide, during operation, a substantially uniform ionic current distribution over an active surface of the cathode in the cathode chamber.

[0027] In certain embodiments, the anode chamber further comprises a flow diverter configured to receive upward flowing anolyte and divert the flowing anolyte into the gap in a generally horizontal flow direction.

[0028] Any combination of the features mentioned for these aspects may be implemented together in an anode assembly in accordance with this disclosure.

[0029] Certain aspects of this disclosure pertain to methods of electroplating onto an electronic

device using an anode assembly comprising an inert anode. Such methods may be characterized by the following operations:

applying a cathodic current and/or potential the electronic device and applying an anodic current and/or potential to the inert anode;

flowing anolyte through a gap between the inert anode and an ionically conductive membrane in the anode chamber, wherein the gap has an average separation distance of at most about 50 mm between the inert anode and the membrane, and wherein the flowing is accompanied by delivering the anolyte to at least one inlet in the anode chamber and receiving the anolyte from at least one outlet in the anode chamber; and

passing ions through the membrane to provide ionic communication between a catholyte and the anolyte.

[0030] In certain embodiments, the electronic device is a partially fabricated integrated circuit.

[0031] In certain embodiments, the inert anode comprises a metal and/or a metal oxide that does not substantially dissolve or corrode when exposed to an anodic current and the anolyte during the electroplating.

[0032] In certain embodiments, the inert anode comprises titanium, platinum and/or a mixed metal oxide.

[0033] In certain embodiments, the inert anode comprises a three-dimensional structure and the anolyte flowing through the gap flows through three dimensions of the inert anode.

[0034] In certain embodiments, the anolyte flowing through the gap has a minimum flow rate of at least about 1 mm/s.

[0035] In certain embodiments, the anolyte flowing through the gap has a minimum flow rate at least about 30 mm/s. In some cases, the minimum flow rate in the gap is achieved when the anodic current applied to the inert anode has a current density of about 50 to 100 mA/cm^2.

[0036] In certain embodiments, the average separation distance of the gap between the inert anode and the membrane is, on average, at most about 10 mm.

[0037] In certain embodiments, the separation distance of the gap between the inert anode and the ionically conductive membrane is substantially constant between a first position of the at least one inlet to a second position of the at least one outlet.

[0038] In certain embodiments, the separation distance of the gap between the inert anode and the ionically conductive membrane decreases from a first position of the at least one inlet to a second position of the at least one outlet.

[0039] In certain embodiments, the inert anode's surface slopes upwards from a first position of the at least one inlet to a second position of the at least one outlet.

[0040] In certain embodiments, the membrane slopes upwards from a first position of the at least one inlet to a second position of the at least one outlet.

[0041] In certain embodiments, the first position is at a center position of the inert anode. In certain embodiments, the first position is located proximate at least a portion of a circumference of the inert anode. In certain embodiments, the first position is proximate one edge of the inert anode and the second position is proximate an opposite edge of the inert anode.

[0042] In certain embodiments, the flowing is further accompanied by delivering the anolyte to the gap via one or more second inlets at an intermediate position between the first position and the second position. In some cases, the first position is at a center position of the inert anode, wherein the intermediate position is at position radially intermediate between the center position and a circumference of the inert anode, and wherein the second position is located at a circumference of the inert anode.

[0043] In certain embodiments, a membrane frame holds the ionically conductive membrane, and wherein the membrane frame comprises a plurality of channels that provide a substantially uniform ionic current distribution over an active surface of the electronic device.

[0044] Any combination of the features mentioned for these aspects may be implemented together in a method in accordance with this disclosure.

[0045] These and other features of the disclosure will be discussed in further detail below, sometimes with reference to the figures.

BRIEF DESCRIPTION OF THE DRAWINGS

[0046] Figure 1 presents a schematic depiction of certain components of an anode chamber.

[0047] Figures 2A-2D present four embodiments of anolyte chambers, each with a different anolyte flow pattern. Each of the four figures includes a top view of an inert anode (upper depiction) and a cross-sectional view of the corresponding anode chamber gap. Arrows depict the direction of anolyte flow in the gap.

[0048] Figure 2A shows an anode chamber utilizing a radially outward flow pattern.

[0049] Figure 2B shows another embodiment utilizing a radially outward flow pattern.

[0050] Figure 2C shows an embodiment in which an anode chamber has a radially inward flow pattern.

[0051] Figure 2D shows embodiment utilizing a crossflow pattern, in which anolyte enters the chamber from one azimuthal position and exits through a different azimuthal position.

[0052] Figure 3 depicts five non-limiting embodiments of gap geometry having different slopes and cross-sectional height variations.

[0053] Figure 4 presents an example of one of many different design configurations and component groups of an anode chamber.

[0054] Figures 5A and 5B show and example inert anode configured as a metal or metal oxide plate or strip having a generally continuous surface, optionally with one or more holes for introducing and/or removing flowing anolyte.

[0055] Figures 5C and 5D show and example inert anode having a complex three-dimensional surface structure.

[0056] Figure 6A schematically illustrates an anode chamber having a membrane with a peripheral membrane clamp.

[0057] Figure 6B illustrates details of a peripheral membrane clamp.

[0058] Figure 7A illustrates an anode chamber comprising an anode support, an inert anode, a gap, a membrane, and a membrane frame, which contacts the interior regions of membrane.

[0059] Figures 7B-7D illustrate three different versions a membrane frame that contacts the interior region of a membrane. Each version is illustrated as top view of the membrane and membrane frame.

[0060] Figures 8A and 8B present experimental results generated using an anode chamber in accordance with embodiments of this disclosure. In the experiments, an inert anode was operated at a current density of 85 mA/cm2, with average gap height of 4 mm, and a flow velocity of approximately 0.05 m/s in the gap.

DETAILED DESCRIPTION

Context and Overview

[0061] This disclosure pertains to anode chambers that maintain an environment specific to the anode of an electroplating cell that is used for electroplating a material onto a cathode comprising an electronic device such as a partially fabricated integrated circuit or a package for one or more integrated circuits. Partially fabricated integrated circuits are often provided on silicon or other semiconductor wafers. In some embodiments, electroplating deposits metal in a via or trench on an active surface of the cathode. In some embodiments, electroplating deposits metal over a wide, continuous area on the active surface of the cathode.

[0062] An anode chamber may comprise features that isolate an electrolyte's composition and flow pattern from the cathode. The electrolyte in the anode chamber is sometimes referred to as an anolyte to distinguish it from the electrolyte that contacts the cathode, which electrolyte is sometimes referred to as a catholyte. The cathode and catholyte may be provided in a separate chamber referred to as cathode chamber. The cathode and anode chambers may be

separated by an ionically conductive membrane that permits ions to pass between the anolyte in the anode chamber and the catholyte in the cathode chamber. Otherwise, the ionically conductive membrane may isolate the two chambers so that the compositions and flow patterns of the anolyte and catholyte are different.

[0063] Certain embodiments herein enable incorporation of an inert anode into the electrochemical deposition process. Inert anodes address many of the challenges created by active anodes, which may be large blocks of metal (often copper or other metal to be electroplated) that is placed in anode chambers. The metal or other anode material is rapidly consumed during high thickness plating operations and requires extensive system downtime to replenish. An inert anode eliminates the need to replenish this source metal, greatly increasing tool uptime regardless of the thickness of the material being deposited.

[0064] Previous inert anode designs have had limited success. This was partially due to the excessive impedance in the plating circuit which was a result of gas generated as a byproduct of the anodic reaction, e.g.:

$$2H_2O \rightarrow 2H^+ + O_2(g) + 2e^-$$

[0065] If the oxygen gas bubbles are not efficiently cleared off of the anode surface, they can greatly increase the electroplating cell's impedance, locally at their positions on the inert anode or in the vicinity thereof.

[0066] The longer the bubble stays, the more likely it is to create localized deposition or exclusion from deposition in certain areas of the wafer or other cathodic workpiece.

[0067] Some previous designs employing inert anodes employed trenches above the inert anode, which facilitated gas removal but also provided a lower available surface area of anode, thus making it more difficult to electroplate at high current densities.

[0068] Certain embodiments herein employ a conformal anode design, optionally employing a thin, tapered anode chamber geometry. In such designs, the flow pattern within an anode chamber optimizes both fluid flow and bubble removal. As an example, the flow pattern may be radially directed; e.g., center to edge over the face of the inert anode.

[0069] The anode chamber may be defined by its internal geometry and/or top-plate contours. The design may facilitate a high velocity anolyte flow across the anode surface, which allows for efficient clearance of gas bubbles that are generated during electrolysis. In embodiments herein, the overall cell impedance is reduced due to optimal bubble clearance conditions.

[0070] An anode chamber geometry can be implemented in several different configurations by modifying the fluid flow direction, anode shape, reaction chamber geometry, and fluid flow velocities. The overall concept however remains essentially the same: Anolyte solution flows

over the anode at high velocity though a narrow anode chamber, thus carrying away the generated gas from the anode surface that would otherwise impede the passage of current. Additionally, the chamber geometry maximizes the potential anode surface area, further reducing overall circuit impedance.

Anode Chamber

[0071] Figure 1 presents a schematic depiction of certain components of an anode chamber. The anode chamber comprises an inert anode 103, which is shown in top view to the left and in cross-section to the right. In addition to inert anode 103, the anode chamber includes an anode support 105, a membrane 107, and a gap characterized by a distance "dx" between the anode 103 and the membrane 107. Anode support 105 holds inert anode 103 in place, typically in a fixed position, within the anode chamber during electroplating. Membrane 107 may be an ion exchange membrane such as an anion exchange membrane. It defines a top of the anode chamber, or at least the top of a gap in the anode chamber.

[0072] The anode chamber gap defines a flow path of anolyte in the anode chamber. For example, anolyte may enter the anode chamber by flowing upward through an opening in the center of inert anode 103. Upon reaching the anode chamber, the anolyte flow changes direction and flows horizontally or substantially horizontally through the gap and along the face surface of inert anode 103. For example, the anolyte may flow radially outward along the face of inert anode 103. By choosing the dimensions of the gap to be sufficiently thin, anolyte flowing through the gap may have a sufficiently high flow velocity to effectively remove gas bubbles formed on the inert anode during electroplating.

Flow Paths

[0073] Figures 2A-2D present four embodiments of anolyte chambers, each with a different anolyte flow pattern. Each of the four figures includes a top view of an inert anode (upper depiction) and a cross-sectional view of the corresponding anode chamber gap. Arrows depict the direction of anolyte flow in the gap.

[0074] Figure 2A shows an anode chamber utilizing a radially outward flow pattern. The anode chamber includes an inert anode 203a, an anode support 205a and a membrane 207. Inert anode 203a has a central inlet 209a through which anolyte flows in an upward direction and into a gap 211a. Upon entering gap 211a, the anolyte flows radially outward, and while doing so, it pushes away gas bubbles 213.

[0075] Figure 2B shows another embodiment utilizing a radially outward flow pattern. This embodiment is similar to that of Figure 2A except that it includes additional anolyte inlet ports beyond a central port of the inert anode (209a in Figure 2A, and 209b in Figure 2B). The anode

chamber of Figure 2B includes an inert anode 203b, an anode support 205b and a membrane 207. Anode support 205b includes a plurality of channels 217b that provide passages for anolyte to flow upward and enter a gap 211b via inlets i in inert anode 203b, including a central inlet 209b and a plurality of radially offset intermediate inlets 215b. Anolyte flows upwardly through each of these inlets and into gap 211b. Upon entering gap 211b through each of the ports, the anolyte flows radially outward, and as in the embodiment of Figure 2A, it pushes away gas bubbles 213.

[0076] Figure 2C shows a different embodiment in which an anode chamber has a radially inward flow pattern. The anode chamber includes an inert anode 203c, an anode support 205c and a membrane 207. The anode chamber includes one or more anolyte inlets (not shown) proximate the periphery of inert anode 203c. Anolyte enters a gap 211c flowing horizontally or substantially horizontally from the peripheral inlet(s). While flowing radially inward through the gap 211c, the anolyte pushes away gas bubbles 213 formed on the surface of inert anode 203c. The anolyte exits gap 211c via a central outlet 209c in inert anode 203c and then an outlet channel 217c in anode support 205c. In some embodiments, inert anode 203c and anode support 205c have one or more inlet ports at, e.g., intermediate radial positions, where additional anolyte flows into the gap 211c and thereafter in a radially inward direction.

[0077] Figure 2D shows embodiment utilizing a crossflow pattern, in which anolyte enters the chamber from one azimuthal position and exits through a different azimuthal position. The anode chamber of Figure 2D includes an inert anode 203d, an anode support 205d and a membrane 207. The anode chamber includes one or more anolyte inlets (not shown) proximate a right side on the periphery of inert anode 203d. Anolyte enters a gap 211d flowing horizontally or substantially horizontally from the peripheral inlet(s). The anolyte flows over the face of inert anode 203d in parallel or substantially parallel streamlines and exits gap 211d via one or more anolyte outlets (not shown) proximate a left side on the periphery of inert anode 203d. While flowing crosswise through the gap 211d, the anolyte pushes away gas bubbles 213 formed on the surface of inert anode 203d. Note that neither inert anode 203d nor anode support 205d need have any inlet ports for anolyte.

[0078] While Figures 2A-2D depict various flow patterns within an anode chamber, many other patterns may be employed. These may be defined different combinations of horizontal and vertical inlets and outlets to the gap in the anode chamber. And the inlets and/or outlets to not need to be exactly horizontally or vertically oriented. They have any of various angles. In certain embodiments, anolyte flow within the gap is unobstructed by trenches, baffles, or other any other blocking structure.

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Gap Uniformity and Slope

[0079] The gap in an inert anode chamber may be defined by various parameters, some of which influence the chamber's ability to quickly remove gas bubbles. Among the parameters are the gap's height or thickness (sometimes illustrated as "dx" herein), any change in dx along the flow path, and the slope or angle of incline of the gap or its boundaries (the inert anode and the membrane). As an example, a gap that slopes upward in the direction of flow may utilize buoyancy to facilitate bubble removal. Further, a gap that decreases in dx in the direction of radially outward flow may promote a more uniform flow velocity over the radius of the inert anode.

[0080] More generally, changing dx as a function of flow position (upstream or downstream) allows control of the fluid flow velocity in the anode chamber gap. One control objective may be to promote a uniform flow velocity over the face of the inert anode. For example, in some cases, the gap of the anode chamber starts to pinch off toward the perimeter of the of the inert anode. Decreasing the value of dx in the downstream, radially outward direction squeezes more fluid through a thinner gap, which increases the magnitude of the fluid's flow velocity, which would otherwise be decreasing as the fluid moves toward the perimeter of the anode chamber.

[0081] Figure 3 depicts five non-limiting embodiments of gap geometry.

[0082] In an "Embodiment A" (the topmost embodiment of Figure 3), an anode chamber gap 311a has a substantially horizontal and uniform thickness. As shown, the anode chamber has an anode support 305a, an inert anode 303a disposed on anode support 305a, and a membrane 307a. Inert anode 303a and membrane 307a are separated from each other by anode chamber gap 311a, characterized by a gap thickness dx. As shown, inert anode 303a and membrane 307a have substantially parallel facing surfaces. Therefore, the value of dx is substantially uniform over the anolyte flow path defined by gap 311a. Further, as shown, inert anode 303a and membrane 307a are substantially horizontal. Therefore, gap 311a is substantially horizontally oriented.

[0083] In an "Embodiment B" of Figure 3, an anode chamber gap 311b has a substantially uniform thickness but a generally upward sloping orientation in the direction the inert anode perimeter. As shown, the anode chamber has an anode support 305b, an inert anode 303b disposed on anode support 305b, and a membrane 307b. It may be assumed that the left side of the depicted anode chamber is toward the center of inert anode 303b and the right side is toward the perimeter of inert anode 303b. Also, it may be assumed that the anolyte flow is generally from the center to the perimeter of inert anode 303b. As shown, inert anode 303b and membrane 307b have substantially parallel facing surfaces. Therefore, the value of dx is

substantially uniform over the anolyte flow path defined by gap 311b. However, as shown, inert anode 303b and membrane 307b both slope generally upward toward in the direction of anolyte flow. Therefore, gap 311b is oriented in upward sloping direction, which may take advantage of the buoyancy of gas bubbles and thereby facilitate removal of the gas bubbles.

[0084] In an "Embodiment C" of Figure 3, an anode chamber gap 311c has a non-uniform thickness with a partially upward sloping orientation in the direction the inert anode perimeter. Similar to the other depicted embodiments, the anode chamber has an anode support 305c, an inert anode 303c disposed on anode support 305c, and a membrane 307c. The anolyte flow direction may be assumed to go left to right in gap 311c. In Embodiment C, membrane 307c is oriented substantially horizontally, while inert anode 303c slopes upward in the direction of anolyte flow. This causes the value of dx to decrease in the direction of flow, thereby controlling the anolyte flow velocity within gap 311c. This decrease in thickness causes the flow velocity to increase, compared to a uniform thickness gap, in downstream positions. In the case of radially outward flow (left to right in the figure), the decrease in thickness tends to cause a more uniform flow velocity as a function of radial position. The upward slope of inert anode 303c may utilize the buoyancy of gas bubbles to facilitate their movement in the radial direction.

[0085] In an "Embodiment D" of Figure 3, an anode chamber gap 311d has a non-uniform thickness and an upward sloping orientation in the direction the inert anode perimeter. As with the other depicted embodiments, the anode chamber has an anode support 305d, an inert anode 303d disposed on anode support 305d, and a membrane 307d. The anolyte flow direction may be assumed to go left to right in gap 311d.

[0086] In Embodiment D, both membrane 307d and inert anode 303d slope upward in the direction of anolyte flow. This may further, in comparison with previously described embodiments, utilize buoyancy in bubble removal. Of course, the overall degree to which buoyance assists is a function of the magnitude of the gap slope and other parameters.

[0087] While both inert anode 303d and membrane 307d slope upward, they do so at different magnitudes, with the slope of inert anode 303d being greater than that of membrane 307d. As a consequence, the value of dx decreases in the direction of flow. In a radial flow embodiment, this decrease increases the downstream anolyte flow velocity within gap 311d in comparison to similar design with a constant value of dx.

[0088] In an "Embodiment E" of Figure 3, an anode chamber gap 311e has a non-uniform thickness and an upward sloping orientation in the direction the inert anode center. As with the other depicted embodiments, the anode chamber has an anode support 305e, an inert anode

303e disposed on anode support 305e, and a membrane 307e. The anolyte flow direction may be assumed to go right to left in gap 311e. In many regards Embodiment E is similar to Embodiment D, but the flow is in the opposite direction. In some versions of Embodiment E, the outlet for the anolyte flow is at or proximate the center of inert anode 303e. While the slopes of membrane 307e and inert anode 303e are shown to cause the value of dx to decrease in a downstream direction, in other embodiments, the slopes may be set so that dx remains constant or even increases in the downstream direction.

Example Anode Chamber Design

[0089] An anode chamber of this disclosure may be implemented in many different design configurations and using many different components. Figure 4 presents one example. The figure presents a perspective view of a portion of an anode chamber 401. The portion is a one-quarter slice cut in the radial direction.

[0090] Anode chamber 401 includes a chamber wall 402 that may serve as an outer containment structure for the anode chamber or, in some embodiments, for the entire electroplating cell, which may include a cathode chamber as well as an anode chamber.

[0091] Within anode chamber 401 is a membrane clamp 406 and that's the structure that holds a membrane in place. The membrane itself is not shown in Figure 4. In some embodiments, it is located on the bottom surface of membrane clamp 406.

[0092] Below membrane clamp 406 is an inert anode 403, which may be a disk-shaped component. Between the membrane held by membrane clamp 406 and inert anode 403 is an anode chamber gap 411. During operation, anolyte flows through gap 411.

[0093] An anode support 405 (e.g., a base plate) supports and optionally holds inert anode 403 in place during electroplating. Anode support 405 optionally includes one or more channels or slots for delivering anolyte into and/or removing anolyte from gap 411.

[0094] In some embodiments, the membrane clamp 406 and the anode support 405 together define the geometry of gap 411. This is particularly the case when inert anode 403 is not rigid.

[0095] Anode chamber 401 also includes a charge carrying plate 425 that is electrically coupled inert anode 403 so as to provide anodic voltage and/or current to the anode.

[0096] Anolyte may be introduced into and removed from gap 411 by any of various fluidic elements. In the depicted embodiment, anolyte flows into anode chamber 401 from an inlet port 421 and then flows upward through a central channel in charge carrying plate 425. There it encounters a flow diverter 423, which diverts anolyte in a radially outward direction and into gap 411. Flow diverter 423 may be configured to minimize drag at the entry to gap 411. In some embodiments, diverter 423 minimizes turbulence in the flow path by laminarizing the

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anolyte flow.

[0097] At a fluid exit of gap 411 is an outlet 427, which may be a continuous outlet channel around the entire circumference of the of the anode or a segmented set of outlet channels.

[0098] Other configurations for introducing and removing anolyte from gap 411 are contemplated. Some of these involve anode support 405. In one example, anode support 405 has a central channel from transferring anolyte from inlet port 421 into gap 411. In some embodiments, anode support includes one or more mid-radius channels for directing anolyte into gap 411. Any inlet and/or outlet channels in anode chamber 401 may have any of various diameters, cross-sectional shapes, fluid path directions, etc. In some embodiments, such as crossflow embodiments, anode support 405 need not have channels.

Inert Anode Design

[0099] The inert anode may take many different forms. It may have any of various materials, shapes, surface textures, etc.

[0100] In certain embodiments, it is a metal or metal oxide plate or strip having a generally continuous surface, optionally with one or more holes for introducing and/or removing flowing anolyte. See solid anode 503a in Figure 5A.

[0101] If an inert anode such as solid anode 503a is not sufficiently rigid to retain its shape during anolyte flow, the anode support may define a contour of the gap. In other words, the anode support may be used to give shape to the anode. For example, in the dual slope design (e.g., Embodiment C of Figure 3), a designer can set the anode's profile using the shape of the anode support.

[0102] In some embodiments, an inert anode has a mesh structure, optionally with one or more holes through the mesh for introducing and/or removing flowing anolyte. See solid anode 503b in Figure 5B. A mesh may provide a high surface area compared to a solid structure. The mesh structure may also allow intimate contact with flowing anolyte and thereby further facilitate gas bubble removal. In some embodiments, an inert anode is made of a metal foam.

[0103] In some cases, an inert anode has a complex surface structure such as the depicted 3D anode structures 503c and 503d depicted in Figures 5C and 5D, respectively. Such 3D structure may be made by additive manufacture. The large surface area allowed by such designs may create its own flow channels for intimately contacting the flowing anolyte. In addition to the anode's top surface, there also be flow in between the channels to remove gas bubbles. In one example, a 3D inert anode may comprise a titanium base with a coating of mixed metal oxide.

[0104] Examples of materials from which an inert anode may be fabricated include platinum, titanium, and mixed metal oxides such as oxides of platinum, titanium, ruthenium, iridium, and

the like.

[0105] In various embodiments, an inert anode has a generally circular shape. For example, it may be shaped and sized to fit in a generally circular anode chamber wall. However, the inert anode need not be circular in shape. As examples, it may be polygonal (e.g., triangular, rectangular, trapezoidal, elliptical, star shaped, etc.

Membrane Design

[0106] A membrane of an inert anode chamber may have any one of many different shapes, sizes, compositions, mechanical properties, electrical properties, etc. In certain embodiments, the membrane is ionically conductive. For example, the membrane may be an ionically conductive polymer.

[0107] In some cases, the membrane is an anionically conductive material such as a material that is conductive to sulfate ions. In some implementations, sulfate ions come from the cathode chamber to the anode chamber and address a charge imbalance that would otherwise be created by the hydrogen ions that are generated at the inert anode. In some cases, the membrane is a cationically conductive material such as a material that is conductive to protons and/or copper cations. In one such scenario, protons generated at anode surface are separated from gas and transferred to other side of the cationically conductive membrane.

Membrane Clamp Design

[0108] A membrane clamp 406 of anode chamber 401, may serve multiple purposes. Because a membrane may be a flexible material the membrane clamp may provide a rigid structure for defining the position and shape of the membrane. For example, the membrane clamp may define an upper boundary of a gap for flowing anolyte. Also, a membrane frame may ensure that membrane is held taught or in tension so that it does not contain dimples, crinkles, or other surface shape variations where gas bubbles could collect and be difficult to remove. In addition to holding the membrane in place, the membrane clamp may provide an interface with a cathode chamber, which holds the wafer on which electroplating occurs. For example, during operation, the channels of one membrane clamp design serve as ionically conducting channels for the catholyte.

[0109] Figure 6A schematically illustrates an anode chamber 601 having a membrane 607 with a membrane clamp 606. The structure illustrated on the left is a cross-sectional view of anode chamber 601, the structure illustrated on the right is a top of membrane 607 and membrane claim 606. Also illustrated in Figure 6A is an inert anode 603 and an anode support 605, both of which may have characteristics of the types presented elsewhere herein.

[0110] In the depicted embodiment, membrane clamp 606 may serve to hold membrane 607

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in tension, like a snare drum, so the membrane maintains a flat profile or otherwise contours the profile of the membrane clamp. Membrane clamp 606 may contact membrane 607 only at the membrane's periphery or perimeter.

[0111] Figure 6B illustrates an example of a membrane clamp 606 in the context of a cross-sectional view of the radial edge of an anode chamber 601. As illustrated, rings 621 and 623 sandwich the membrane (not shown). This assembly then is attached to membrane clamp (606). In doing so, the membrane is stretched over the membrane clamp edge geometry. Like features from Figures 4 and 6A are illustrated with similar call out numbers in Figure 6B. For example, anode chamber 601 includes an inert anode 603, an anode support 605, and a gap 611.

[0112] In other embodiments, a membrane clamp contacts the membrane not just at the membrane's perimeter (or at the edge of the anode chamber) but contact interior regions of the membrane. Examples of such embodiments are depicted in Figures 7A, 7B, 7C, and 7D.

[0113] Figure 7A illustrates an anode chamber 701 comprising an anode support 705, an inert anode 703, a gap 711, a membrane 707, and a membrane clamp 706. As illustrated, in contrast to the design of anode chamber 601, membrane clamp 706 contacts the interior regions of membrane 707.

[0114] Figures 7B-D illustrate three different versions a membrane clamp or frame that contacts the interior region of a membrane. Each version is illustrated as top view of the membrane and membrane frame.

[0115] In version 1, a membrane frame comprises a plurality of vertical holes. In certain embodiments, the holes are arranged in aa honeycomb pattern. The diameter of the holes in the membrane frame may be sufficiently small to prevent bulging of the membrane within the holes. Such bulges might allow gas bubbles to collect and remain fixed against the membrane. In certain examples, the holes of the membrane clamp have a diameter of about 0.2 to 13mm. In certain embodiments, the number of channels in the membrane clamp is about 1 to 10,000, or at least about 10 or at least about 100, or at least about 1000.

[0116] In addition to holding the membrane in place, the membrane clamp may provide an interface with a cathode chamber, which holds the wafer on which electroplating occurs. For example, during operation, the channels of one membrane clamp design serve as ionically conducting channels for the catholyte.

[0117] In version 2, a membrane frame comprises radially directed spokes, and in version 3, the membrane frame comprises a checkerboard grid.

Gap Height

[0118] As indicated, the gap height is a parameter describing the distance between the top of

the inert anode and the and the surface of the membrane. It is sometimes referred to as dx herein. In certain embodiments, the gap height (dx) is, on average, about 130 mm or less. In certain embodiments, the gap height (dx) is, on average, about 100 mm or less, or about 50 mm or less, or about 10 mm or less, or about 3 mm or less. As indicated above, the gap height may be constant over the direction of anolyte flow within the gap, or the gap height may be tapered over the direction of flow. The average values recited here do not assume that the gap height is constant or uniform within the anode chamber.

Flow velocity

[0119] As indicated, an anode chamber may be designed and operated in a manner that rapidly clears gas bubbles from an inert anode surface and/or associated gap. Ideally, as soon as a bubble is generated, flowing fluid removes it from the anode surface. Gas bubbles should be removed rapidly enough to avoid negatively impact electroplating. If the gas bubbles reside in the gap too long, they will locally increase impedance and deposit non-uniform films on the cathode surface.

[0120] To this end, the anode chamber may be operated in a manner that produces a rapidly flowing anolyte within the gap between inert anode and membrane.

[0121] In certain embodiments, anolyte flows in the gap at velocity of at least 1mm/s. This value may be viewed as a *minimum* flow velocity over the face of the inert anode. In some embodiments, the minimum flow velocity over the face of the inert anode is at least about 10 mm/s, or at least about 20 mm/s, or at least about 50 mm/s. In some embodiments, the minimum flow velocity over the face of the inert anode is about 20-100 mm/s.

[0122] An anolyte's minimum flow velocity within a gap is a function of various parameters. Of course, the total volumetric flow rate has an impact, as well as the gap dimensions and the arrangement of inlets and outlets to the gap. And the current density at the inert anode surface is another variable. In some embodiments, at minimum flow velocities in the range of 10-100 mm/s, the average current density may be about 50 to 85 mA/cm^2.

Examples

[0123] Figures 8A and 8B present experimental results generated using an anode chamber in accordance with embodiments of this disclosure. In the experiments, an inert anode was operated at a current density of 85 mA/cm2, an average gap height of 4 mm, and a flow velocity of approximately 0.05 m/s in the gap.

[0124] As illustrated in the plot on the top, copper was electroplated onto six different 300 mm test wafers, and in each case the deposit thickness was highly uniform across the wafer's diameter. The bar chart in Figure 8B presents values of the copper deposits' non-uniformity

for the six wafers. The non-uniformity values were calculated using three different edge exclusions.

Conclusion

[0125] The foregoing description is merely illustrative in nature and is in no way intended to limit the disclosure, its application, or uses. The broad teachings of the disclosure may be implemented in a variety of forms. Therefore, while this disclosure includes particular examples, the true scope of the disclosure should not be so limited since other modifications will become apparent upon a study of the drawings, the specification, and the following claims. For purposes of clarity, the same reference numbers will be used in the drawings to identify similar elements. As used herein, the phrase at least one of A, B, and C should be construed to mean a logical (A, B, or C), using a non-exclusive logical OR. It should be understood that one or more steps within a method may be executed in different order (or concurrently) without altering the principles of the present disclosure.

CLAIMS

What is claimed is:

1. An electroplating apparatus comprising:

(a) an anode chamber comprising:

an inert anode;

an anode support in contact with the inert anode;

an ionically conductive membrane, wherein the ionically conductive membrane is separated from the inert anode by a gap in the anode chamber;

a membrane clamp configured to hold the ionically conductive membrane;

at least one inlet configured to flow anolyte into the gap at a first position; and

at least one outlet configured to receive the anolyte flowing out of the gap at a second position;

(b) an anolyte flow system configured to deliver the anolyte to the at least one inlet and receive the anolyte from the at least one outlet; and

(c) a cathode chamber comprising a cathode support for holding a cathode during electroplating, wherein the cathode chamber is configured to attach to the anode chamber in a manner that permits, during operation, ionic communication between a catholyte in the cathode chamber and the anolyte in the anode chamber.

2. The electroplating apparatus of claim 1, wherein the inert anode comprises a metal and/or a metal oxide that does not substantially dissolve or corrode when exposed to an anodic current and the anolyte during electroplating.

3. The electroplating apparatus of claim 1, wherein the inert anode comprises titanium, platinum and/or a mixed metal oxide.

4. The electroplating apparatus of claim 1, wherein the inert anode comprises a sheet of inert anode material.

5. The electroplating apparatus of claim 1, wherein the inert anode comprises a three-dimensional structure configured to have the anolyte flow in three dimensions through the inert anode.

6. The electroplating apparatus of claim 1, wherein, during electroplating, the anolyte has a minimum flow rate in the gap of at least about 1 mm/s.

7. The electroplating apparatus of claim 1, wherein, during electroplating, the anolyte has a minimum flow rate in the gap of at least about 30 mm/s.

8. The electroplating apparatus of claim 7, wherein the minimum flow rate in the gap is achieved when current flowing through the inert anode has a current density of about 50 to 100 mA/cm^2.

9. The electroplating apparatus of claim 1, wherein the gap has a separation distance between the inert anode and the ionically conductive membrane, which separation distance is, on average, at most about 130 mm.

10. The electroplating apparatus of claim 1, wherein the gap has a separation distance between the inert anode and the ionically conductive membrane, which separation distance is, on average, at most about 50 mm.

11. The electroplating apparatus of claim 1, wherein the gap has a separation distance between the inert anode and the ionically conductive membrane, which separation distance is, on average, at most about 10 mm.

12. The electroplating apparatus of claim 1, wherein the gap has a separation distance between the inert anode and the ionically conductive membrane, which separation distance is substantially constant within the anode chamber.

13. The electroplating apparatus of claim 1, wherein the gap has a separation distance between the inert anode and the ionically conductive membrane, wherein the gap separation distance decreases from the first position to the second position.

14. The electroplating apparatus of claim 1, wherein the inert anode has a substantially planar surface in contact with the gap.

15. The electroplating apparatus of claim 14, wherein the inert anode's surface is substantially horizontally oriented.

16. The electroplating apparatus of claim 1, wherein the inert anode's surface slopes upwards from the first position to the second position.

17. The electroplating apparatus of claim 1, wherein the membrane is substantially horizontally oriented.

18. The electroplating apparatus of claim 1, wherein the membrane slopes upwards from the first position to the second position.

19. The electroplating apparatus of claim 1, wherein the first position is at a center position of the inert anode.

20. The electroplating apparatus of claim 1, wherein the first position is located proximate at least a portion of a circumference of the inert anode.

21. The electroplating apparatus of claim 1, wherein the anode chamber further comprises one or more second inlets configured to flow anolyte into the gap at an intermediate position between the first position and the second position.

22. The electroplating apparatus of claim 21, wherein the first position is at a center position of the inert anode, wherein the intermediate position is at position radially intermediate between the center position and a circumference of the inert anode, and wherein the second position is located at a circumference of the inert anode.

23. The electroplating apparatus of claim 1, wherein the first position is proximate one edge of the inert anode and the second position is proximate an opposite edge of the inert anode.

24. The electroplating apparatus of claim 1, wherein the membrane clamp is configured to hold the membrane in tension over the gap.

25. The electroplating apparatus of claim 1, wherein the membrane clamp comprises a substantially rigid membrane frame that holds the membrane in a substantially fixed position during electroplating.

26. The electroplating apparatus of claim 25, wherein the membrane frame comprises a spoke arrangement.

27. The electroplating apparatus of claim 25, wherein the membrane frame comprises a plurality of channels configured to provide, during operation, a substantially uniform ionic current distribution over an active surface of the cathode in the cathode chamber.

28. The electroplating apparatus of claim 1, wherein the anode chamber further comprises a flow diverter configured to receive upward flowing anolyte and divert the flowing anolyte into the gap in a generally horizontal flow direction.

29. The electroplating apparatus of claim 1, wherein the ionically conductive membrane comprises an anionically conductive polymer.

30. An anode assembly comprising:

an inert anode;

an anode support in contact with the inert anode;

an ionically conductive membrane, wherein the ionically conductive membrane is separated from the inert anode by a gap in the anode chamber;

a membrane clamp configured to hold the ionically conductive membrane;

at least one inlet configured to flow anolyte into the gap at a first position; and

at least one outlet configured to receive the anolyte flowing out of the gap at a second position.

31. The anode assembly of claim 30, wherein the inert anode comprises a metal and/or a metal oxide that does not substantially dissolve or corrode when exposed to an anodic current and the anolyte during electroplating.

32. The anode assembly of claim 30, wherein, during electroplating, the anolyte has a minimum flow rate in the gap of at least about 30 mm/s.

33. The anode assembly of claim 30, wherein the gap has a separation distance between the inert anode and the ionically conductive membrane, which separation distance is, on average, at most about 10 mm.

34. The anode assembly of claim 30, wherein the gap has a separation distance between the inert anode and the ionically conductive membrane, which separation distance is substantially constant within the anode chamber.

35. The anode assembly of claim 30, wherein the gap has a separation distance between the inert anode and the ionically conductive membrane, wherein the gap separation distance decreases from the first position to the second position.

36. The anode assembly of claim 35, wherein the inert anode's surface is substantially horizontally oriented.

37. The anode assembly of claim 30, wherein the inert anode's surface slopes upwards from the first position to the second position.

38. The anode assembly of claim 30, wherein the membrane is substantially horizontally oriented.

39. The anode assembly of claim 30, wherein the membrane slopes upwards from the first position to the second position.

40. The anode assembly of claim 30, wherein the first position is at a center position of the inert anode.

41. The anode assembly of claim 30, wherein the first position is located at least a portion of a circumference of the inert anode.

42. The anode assembly of claim 30, wherein the anode chamber further comprises one or more second inlets configured to flow anolyte into the gap at an intermediate position between the first position and the second position.

43. The anode assembly of claim 30, wherein the first position is proximate one edge of the inert anode and the second position is proximate an opposite edge of the inert anode.

44. The anode assembly of claim 30, wherein the membrane clamp is configured to hold the membrane in tension over the gap.

45. The anode assembly of claim 30, wherein the membrane clamp comprises a substantially rigid membrane frame that holds the membrane in a substantially fixed position during electroplating.

46. The anode assembly of claim 45, wherein the membrane frame comprises a plurality of channels configured to provide, during operation, a substantially uniform ionic current distribution over an active surface of the cathode in the cathode chamber.

47. The anode assembly of claim 30, wherein the anode chamber further comprises a flow diverter configured to receive upward flowing anolyte and divert the flowing anolyte into the gap in a generally horizontal flow direction.

48. A method of electroplating onto an electronic device using an anode assembly comprising an inert anode, the method comprising:

applying a cathodic current and/or potential the electronic device and applying an anodic current and/or potential to the inert anode;

flowing anolyte through a gap between the inert anode and an ionically conductive membrane in the anode chamber, wherein the gap has an average separation distance of at most about 50 mm between the inert anode and the membrane, and wherein the flowing is accompanied by delivering the anolyte to at least one inlet in the anode chamber and receiving the anolyte from at least one outlet in the anode chamber; and

passing ions through the membrane to provide ionic communication between a catholyte and the anolyte.

49. The method of claim 48, wherein the electronic device is a partially fabricated integrated circuit.

50. The method of claim 48, wherein the inert anode comprises a metal and/or a metal oxide that does not substantially dissolve or corrode when exposed to an anodic current and the anolyte during the electroplating.

51. The electroplating apparatus of claim 48, wherein the inert anode comprises titanium, platinum and/or a mixed metal oxide.

52. The method of claim 48, wherein the inert anode comprises a three-dimensional structure and the anolyte flowing through the gap flows through three dimensions of the inert anode.

53. The method of claim 48, wherein the anolyte flowing through the gap has a minimum flow rate of at least about 1 mm/s.

54. The method of claim 48, wherein the anolyte flowing through the gap has a minimum flow rate at least about 30 mm/s.

55. The method of claim 54, wherein the minimum flow rate in the gap is achieved when the anodic current applied to the inert anode has a current density of about 50 to 100 mA/cm^2.

56. The method of claim 48, wherein the average separation distance of the gap between the inert anode and the membrane is, on average, at most about 10 mm.

57. The method of claim 48, wherein the separation distance of the gap between the inert anode and the ionically conductive membrane is substantially constant between a first position of the at least one inlet to a second position of the at least one outlet.

58. The method of claim 48, wherein the separation distance of the gap between the inert anode and the ionically conductive membrane decreases from a first position of the at least one inlet to a second position of the at least one outlet.

59. The method of claim 48, wherein the inert anode's surface slopes upwards from a first position of the at least one inlet to a second position of the at least one outlet.

60. The method of claim 48, wherein the membrane slopes upwards from a first position of the at least one inlet to a second position of the at least one outlet.

61. The method of any of claims 57-60, wherein the first position is at a center position of the inert anode.

62. The method of any of claims 57-60, wherein the first position is located proximate at least a portion of a circumference of the inert anode.

63. The method of any of claims 57-62, wherein the flowing is further accompanied by delivering the anolyte to the gap via one or more second inlets at an intermediate position between the first position and the second position.

64. The method of claim 63, wherein the first position is at a center position of the inert anode, wherein the intermediate position is at position radially intermediate between the center position and a circumference of the inert anode, and wherein the second position is located at a circumference of the inert anode.

65. The method of any of claims 57-62, wherein the first position is proximate one edge of the inert anode and the second position is proximate an opposite edge of the inert anode.

66. The method of claim 48, wherein a membrane frame holds the ionically conductive membrane, and wherein the membrane frame comprises a plurality of channels that provide a substantially uniform ionic current distribution over an active surface of the electronic device.